HYDROPHOBIC INTERACTIONS IN MODEL SYSTEMS

BY

DOGAN EMIN GUVELI

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PREFACE.

This dissertation, which is being submitted for the degree of Doctor of Philosophy of the University of Aston in Birmingham, is an account of the work carried out under the supervision of Dr.J.B.Kayes in the Department of Pharmacy of the University of Aston in Birmingham, from October, 1972 to June 1976.

Except where acknowledged by reference in the text, the work described herein is claimed to be original and has not been submitted for any other award.

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SUMMARY

Hydrophobic interactions in model systems have been studied. Cationic and non-ionic aqueous surfactant systems were used as model systems. The physico-chemical properties of surfactant solutions studied, in order to evaluate hydrophobic interaction, were critical micelle concentrations, hydrodynamics, conductance, partial molal volumes, light scattering and the thermodynamic data of micellization.

The observed hydrodynamic micellar properties of cationic surfactants indicate that the intrinsic viscosity of micelles is affected by hydration, the electroviscous effect and the micellar shape by means of hydrophobic interactions. The micellar properties are changed when aliphatic alcohol is added to the system. The intrinsic viscosity of the micelles does not increase significantly, although the relative viscosity of the solution is higher compared with the aqueous surfactant solution.

The increase in viscosity has been discussed in terms of hydrophobic interactions and the change in micellar shape. The observed decrement in intrinsic viscosity shows that the hydration and electroviscous effect decreases with increasing concentration of alcohol.

The critical micelle concentrations of cationic surfactant solutions containing alcohols were discussed considering the structure promoting effect of alcohols at low concentration, the reverse effect at higher concentration; solubility; hydrophobic interactions between possible orientated configurations, and their effect on the surface charge of the micelles.

The positive B coefficients of alkylammonium bromides confirm the structure maker effect of the nonpolar groups of the surfactants. This behaviour is considerably influenced by the addition of alcohol to the system. At low concentration of alcohol the B coefficient is positive, but as the concentration of alcohol is increased it shifts to a negative value. This is due to destruction of water clusters around the nonpolar groups, and the breaking of structured water molecules in the bulk liquid.

The volumetric properties of cationic surfactants below the critical micelle concentration, and above the critical micelle concentration show that the partial molal volume of the surfactant increases with increasing alkylchain length. The micelle formation is accompanied by an increase in volume. When aliphatic alcohol is added to the system, it contributes to the volume change and increases the partial molal volume of the micelles.

The effect of aromatic alcohols, ureas and urethane on micellar properties of cationic systems has been examined by measuring the conductance of the micelles. The observed conductance of the micelles indicate that the critical micelle concentration increases, when 0.01M alcohol is added to the system. As the concentration of alcohol is increased the critical micelle concentration value shifts to lower values. The increment in critical micelle concentration has been discussed in terms of hydrophobic interactions between alcohol, surfactant and water molecules, taking into account the solubility of alcohols and their structure promoting behaviour at low concentration.

However the decrement in critical micelle concentration has been attributed to the structure breaking behaviour of alcohol at high concentration. On the addition of urea and urethane the critical micelle concentration increases. The increment in specific conductance at the critical micelle concentration has been attributed to the cooperative effect of the solutes on water structure. It is believed that ureas and urethane behave as structure promoting, since they take an active part in mixed cluster formation, which are big enough to accommodate nonpolar groups.

Light scattering data on micelles of cationic surfactants indicates that the micellar molecular weight increases as the chain length increases. The addition of aliphatic alcohol to the system, first increased the apparent molecular weight, then it decreased with increasing concentration. The aliphatic alcohols decreased the scattering intensity, and the turbidity of the solution in terms of the density, and concentration fluctuations in refractive index of the solution near the surfactant molecule. The effective charge on the micelles increased, then decreased with increasing concentration of the alcohol.

Hydrophobic interactions in non-ionic surfactant systems of the polyoxyethylene n-alkanol type were also studied in terms of the hydrodynamic, volumetric, light scattering and thermodyanmic data of micellar properties. The intrinsic viscosity of the micelles increases as the ethylene oxide chain length increases. The increment in relative viscosity, and in intrinsic viscosity of the micelles is due to the hydration of micelles, micellar size and shape.

The observed critical micelle concentrations indicate that the critical micelle concentration decreases as the ethylene oxide chain length increases. This behaviour has been discussed by means of the decrement in solubility of non-ionics in aqueous solution, when the ethylene oxide chain length is increased, and the increment in degree of coiling as the hydrophilic chain length increases. It is likely that the hydrophilic chain coils tightly at the end of the hydrocarbon chain, this is entropically favourable allowing hydrogen bonded water molecules to be released, this type of configuration will increase the hydrophobic surface area of the molecule. Consequently the critical micelle concentration decreases with increasing hydrophobic character of the non-ionic surfactant. The volumetric properties of micelles show that a volume change occurs during the micelle formation. The partial molal volume change decreases with increasing hydrophilic chain length.

The addition of aromatic alcohols to the system shows similar behaviour to that observed with cationic systems. The critical micelle concentration is increased when 0.01M aromatic alcohol is added to the system, then the effect of additive on critical micelle concentration tends to the reverse direction as the concentration increases.

The observed phenomen is due to the selective adsorption of additive on the surfactant molecule, the change in density, and concentration fluctuations in the refractive index of the solution near the surfactant molecule, and a complex type of association of surfactant with alcohol through hydrophobic interactions. The scattering intensity, and turbidity of the solution containing alcohol is higher compared with the aqueous surfactant solution.

The change in micellar properties of non-ionics in aqueous urea, and urethane, show that the critical micelle concentration increases. The increases arise from the active participation of urea, and urethane in mixed cluster formation in terms of hydrophobic interactions. The increment in scattering intensity and turbidity of the solution also supports the idea that these substances behave as structure makers inaqeuous surfactant solution.

The thermodynamic investigation of cationic and non-ionic micellization shows that micelle formation is an entropy directed process. The free energy of micellization decreases as the chain length, and ethylene oxide chain length increases. This decrement is due to the reduction of structural order of water molecules, which arises from the minimization of hydrocarbon water interface, this causes the transference of monomers to the nonpolar environments.

The decrement in enthalpy (cationics) is caused by the change in the translational energy of monomers, in water structure and the effect of hydrated head groups. The observed entropy change is governed by hydrophobic interactions between nonpolar, polar and structural water molecules.

The enthalpy and entropy of micellization of non-ionic surfactants is always positive showing that micelle formation is governed by the gain in entropy. Entropy increases during the micelle formation, which contributes largely to the free energy.

The increase in entropy is due to the hydrophobic interactions between nonpolar groups, and structured water molecules which is accompanied by a release of energy, due to the structural melting of water molecules, when the nonpolar groups move to the nonpolar environment. The reorientation of the solvent molecules contributes also to an increase in entropy.

CHAPTER I Theory

I.Ia - Role of Hydrophobic Interactions

I.Ib - Theories of Hydrophobic Interactions

I.Ic - Structural Models of liquid water

I.Id - Models for the Study of Hydrophobic Interactions

I.Ia - Role of Hydrophobic Interactions

The features of various molecules in aqueous solutions, have been studied for some 50 years. The nature of such solutions have been introduced in terms of conceptual models. Various solute-solvent interactions have been observed in aqueous solutions, in order to evaluate physio-chemical parameters of solution behaviour.

Among solute-solvent interactions, one special type of interaction, so called Hydrophobic interactions, have been paid much attention, and it is necessary to understand its role, in different aqueous systems.

The term Hydrophobic Interactions is simply long range interactions of apolar groups, causing association in aqueous environment, decreasing the degree of nonpolar-polar (water) contact.

This tendency is derived from a favourable Entropy effect, since the structural order of liquid water decreases due to removal of apolar solutes, from aqueous solution to nonpolar regions. Hydrophobic interactions play a unique role in Biological systems, aqueous, non-aqueous solutions of low molecular weight substances and macromolecules.

The features of molecular interactions in different systems such as:

Binding of biologically interesting molecules to each other, the binding of some pharmacologically active molecules to their substrates, binding of drugs to the receptors of such biological macromolecules as proteins and polypeptides, stabilization of double helical form of DNA and certain conformations of proteins and protein aggregation, formation of micelle-like structures in aqueous and non-aqueous systems, conformational changes of enzymes, related to the effects of subtrates, activators or inhibitors, stacking processes in polynucleotides and in nucleic acids, small-molecule binding to polymers in vitro and in vivo, specific aggregation of polymers to form supra molecular structures, enzyme catalytic processes, lipid bilayers. Cell membranes, local and general anasthesii have been discussed in terms of Hydrophobic Interactions.

I.Ib - Theories of hydrophobic interactions.

To understand the role of hydrophobic interactions, extensive theoretical and experimental investigations have been made(1,2,3) with hydrocarbon-aqueous sytems, in order to evaluate thermodynamic parameters of intermolecular interactions of hydrocarbons and liquid water structure.

In the study(3) of solubility of some hydrocarbons, unitary entropy has been found, with a decrease of the order of 20 e.u. The reason for this has been attributed to the structural restrictions involved on the water structure(4) surrounding the apolar solute, when transferring a mole of solute from nonpolar environment to aqueous region. Hydrophobic interactions in this approach are introduced by this structural restriction effect of the water molecules around the nonpolar moiety.

This attention towards molecular interactions of hydrocarbon moieties in aqueous solutions, has been centred by another theory(5) on the theoretical derivation of the thermodynamic parameters of liquid water and the thermodynamic behaviour of aqueous hydrocarbon solutions.

This theory is based on the flickering cluster model for liquid water(6). A derived partition function(7) for liquid water in the first layer of water around solute, has been used to obtain the contribution of structural changes of water to the total free energy of solution.

The contribution of the solute to the free energy is observed by means of changes of configurations of molecules, and Van der Waals interactions when solute transfers to the aqueous state.

Since aliphatic hydrocarbons exothermally dissolve in water by negative enthalpy counter balanced by a large entropy effect, hydrophobic interactions have been considered, as the partial or complete reversal of the solution process for hydrocarbons in water.

This theory has been developed by calculating hydrophobic interactions between nonpolar side chains of amino acid residues in polypeptides(8). This treatment has been constructed on the quantity of free energy observed, per water molecule in the first layer of solvation shell, around the side chains and the energy involved with the exclusion of water molecules from this solvation shell, when the side chains transfer to the nonpolar region.

Also the entropy change is introduced as a main driving force, for the hydrophobic interactions. But with the aqueous aromatic hydrocarbon solutions, positive enthalpy and negative entropy effect is obtained due to the stronger association of the water molecules with the π electron orbitals of benzene ring than with aliphatic groups.

The total free energy $\Delta F_H{}^{\circ}$ of hydrophobic interactions is given by

$$\Delta F_H{}^{\circ} = \Delta F_W{}^{\circ} + \Delta F_S{}^{\circ} \qquad \text{I-1}$$

$\Delta F_W{}^{\circ}$ = contributions from the change of the water structure to the $\Delta F_H{}^{\circ}$

$\Delta F_S{}^{\circ}$ contributions from the change in the states of the side chains themselves.

(9,10,11,12) A different view of hydrophobic interactions, has been given by considering the ordering of water in a lattice around nonpolar groups as a stabilizing effect, in analogy with gas hydrates.

The magnitude of hydrophobic interaction has also been examined within the framework of classical statistical mechanics, by considering a system consisting of N solvent molecules and two solute particles at fixed positions R_1 and R_2 in aqueous solution(13).

Various solute-solute distances and related strength of hydrophobic interactions are discussed in this approach. Helmholtz free energy is given by three terms for such a system as follows:

$$A_{N+2}(R_1,R_2) = A^\circ + U_{12}(R_1,R_2) + A_{H1}(R_1,R_2) \qquad \text{I-2}$$

and the hydrophobic interaction has been defined as a indirect part of the work by the equation:

$$A_{H1}(R_{12}=\infty) - A_{H1}(R_{12}) \qquad \text{I-3}$$

when two solute particles are brought from infinity to the distance R_{12}. This statistical approach has been extended by taking into account a system, consisting of a number of identical, spherical nonpolar particles and number of solvent molecules(14).

Solute particles tend to adhere each other, and the process involves bringing the solute particles from infinity to close configuration has been examined in various solutions(14).

A different view(15), involving the degree of overlap of solvation cospheres about solutes, has also been given for evaluation of some features of hydrophobic interactions.

Hydrophobic interactions, based on the solubility parameters of hydrocarbons in water, have also been discussed(16) in terms of the structure theory of the liquids(17,18,19). This theory successfully applied to water(20). The obtained free energy, entropy and internal energy, except low heat capacity values(16) which agree well with the values given in literature.

This approach has been extended, by taking into account, the solvent cavity surface area(21), considering the water molecules in the first layer of water, used as being a factor(5) for the hydrocarbon solubility in aqueous environment.

The above approaches(16,21) have been developed by application of the first-order liquid state pertubation theory(22). In order to apply the usual form of liquid pertubation theory(23,24) to the gaseous hydrocarbon water interactions, the energy of the non-spherical cavity, that accommodates the solute molecule, has been assumed to be equal to the energy of the spherical cavity of equal area.

The Lennard-Jones potential has been used(22) to derive the hydrophobic interaction energy which has been given as the difference between the sum of cavity energy and solute-solvent interaction energy when hydrocarbon molecules come close to each other and when they are apart.

Some of well known theories of hydrophobic interactions in different systems have been summarized to introduce some information about their nature.

I.Ic - Structural Models of liquid water.

From the earliest theories(25), water has been recognized as an associated liquid. However these theories were not able to explain many observed properties.Bernal and Fowler(26) and later Morgan and Warren(27) showed by X-Ray diffraction measurements on liquid water that it is to be characteristic of tetrahedral water coordination, and suggested that the observed structure of liquid water should be similar to that of ice.

A number of theories of water structure have emerged from the above observations, these can be classified into two groups, in terms of obtained characteristics(28).

I.Ic1 - continuum models

I.Ic2 - mixture models

<u>I.Ic1 - Continuum Models</u>, treat water in terms of a continuous distribution of interactions of an uninterrupted,three dimensional lattice of tetrahedrally coordinated hydrogen bonded molecules. Bernaland Fowler(26) proposed a model for liquid water, on the basis of a broken-down ice structure, with most of the hydrogen bonding still in existence. The existence of highly hydrogen bonded regions and the gradual breakdown of hydrogen bonding, with increasing temperature appear as main features of the model. Pople(29) used a statistical mechanical approach to get the average degree of hydrogen bond bending, taking into account the harmonic restoring force constant. With this view, the obtained radial distribution function for relative positions of molecules, agreed well with the results introduced by Morgan-Warren(27) from X-Ray scattering. Also it is assumed that each bond bends independently of all others.

Bernal(30) developed a picture of water, considering the liquid water, as an intrinsically irregular structure. Rahman-Stillinger(31) employed molecular dynamics to obtain the dynamic properties of the molecular assembly of liquid water. Barker-Watts(32) used Monte-Carlo procedure to calculate the radial distribution function of water structure.

The small number of water molecules included in the sample and the nature of the pair potential function chosen resulted in only moderate agreement, with X-Ray radial distribution function.

Stevenson(33) suggested that the monomeric water molecules in liquid water, should be small at ordinary temperature. He introduced his concept of water structure, using IR and UV spectra data of liquid water.

I.Ic2 - Mixture models in which the water is considered as a collection of differently hydrogen bonding species where each water molecule can fluctuate through the states where the molecules are involved in hydrogen bending.

By Raman spectrum analysis, Cross(34) concluded that the liquid has considerable amounts of molecules, with four, three and two hydrogen bonds as seen in a broken-down ice-lattice. Eucken(35) introduced a model that has two four and eight molecules in the liquid state.

Adjusting the mole fractions of the aggregates he obtained the values that agree well with experimental values of compressibility and thermal expansion. Grjotheim-Krogh-Moe(36) gave a different view assuming that liquid water consists of an ice like species of density identical to that of ice and of a non-hydrogen bonded close-packed species.

Haggis-Hasted-Buchanan(37) considered the dielectric properties of aqueous solutions and they derived simultaneous equations, for the probability of transition between the systems that have been treated as reacting species which consist of different hydrogen bonded molecules. Frank-Wen(6,38) have centred their attention on the partially covalent character of the hydrogen bond. They postulated that the formation of the hydrogen bonds in the liquid is a cooperative phenomenon and involves a contribution from delocalization energy, due to electron overlap. This approach assumes that the formation and dissolution of flickering clusters that are short-lived highly hydrogen bonded molecules is governed by local energy fluctuations.

Pauling(39) has taken the structure of solid gas hydrates, formed by small size tetrahedrally hydrogen bonded water molecules and nonpolar substances, as a basis of his qualitative model for liquid water. He suggested similar type of structure for pure water considering the structure of gas hydrates.

Forslind(40) represented a lattice-point model, treating liquid water as an extended crystalline system, similar to ice and assumed this crystalline system has sufficient size cavities to accept the monomeric water molecules.

Nemethy-Scheraga(7) constructed a structure partition function, taking into account the treatment of (0.1.2.3.4) hydrogen bonded water molecules and derived a number of model details, such as cluster sizes and relative numbers of molecules of different bondedness.

Walrafen(41) in his model of liquid water structure, deals with Raman scattering spectra in the valency-stretching region and the analyses of these into bands of related to bonded and unbonded O-H and O-D motions.

As it can be seen these are a number of competing models each of which gives useful details of some of the features of water but not for the others.

I.Id - Models for the Study of Hydrophobic Interactions.

Amphiphilic substances are very suitable materials, as they have strong molecular interactions, with solvent molecules in solutions. These interactions are operated between nonpolar, polar sides of amphiphile and water structure in aqueous solutions. Also they have distinctive features, such as molecular dispersion, depression of surface and interfacial tension due to the absorption and orientation of molecules at interface, micelle formation above a certain concentration due to free energy decrease of system.

Hence amphiphilic systems can be used as model systems, to investigate hydrophobic interactions which can be assessed relatively easily through measurements of critical micelle concentration and mentioned properties.

To examine the physico-chemical properties of hydrophobic interactions in aqueous solutions, two types of model systems have been employed. These systems can be divided into two categories, in terms of their physico-chemical nature, which are:

A. Ionic systems (Cationic)

B. Non-Ionic " (Polymeric)

These two kind of systems will be used, to obtain some information about the unique role of the phenomenon, which is known as hydrophobic interactions.

CHAPTER II Hydrodynamic Properties of Alkylammonium Bromides in water and alcohol solutions.

- II.Ia - Electroviscous Effect
- II.Ib - Hydration
- II.Ic - Dielectric Effect
- II.Id - Thermodynamics of Solute-Solvent Interactions
- II.Ie - Effect of Aliphatic alcohols
- II.If - Relative, Reduced and Intrinsic Viscosities of Aqueous solutions of Alkyltrimethyl ammonium bromides
- II.Ig - Experimental Procedure
- II.Ih - Micellar Properties from Hydrodynamic Data
- II.Ii - Conclusions

II.Ia - Electroviscous Effect.

It has been observed that the viscosity of a colloidal system increases, when the dispersed particle is charged. This increase in viscosity, is due to the charge of the particle and is called the "Electroviscous Effect", which is connected with the existence of an electrical double layer around the particle.

Hence, the electrokinetic phenomenon known as the electroviscous effect occurs, when the outer part of the electrical double layer is drawn away from the particle in a laminar field flow. Consequently the electrical double layer tends to restore itself by conduction. The dissipation energy in the process of conduction effect, is the cause of the increase in viscosity.

The micelles of surface active agents carry an electric charge in aqueous solution, and an electroviscous effect is always included, as a part of the measured intrinsic viscosity $[\eta]$(42).

The intrinsic viscosity and the electroviscous effect can be obtained theoretically from the Booth modification(43,44) of the Einstein's theory, taking into account the size and electrophoretic mobility of the micelle.

$$[\eta] = 2.5\left[1 + \pi\,\bar{\rho}\,\bar{\mu}\,b^2(1+b)^2\,Z\,\gamma\,\zeta\,B^2\right] \qquad \text{II-1}$$

where

$$\bar{\rho} = \sum_i c_i z_i^2\,\mu_i^{-1} \Big/ \sum_i c_i z_i^2 \qquad \text{II-2}$$

$$\bar{\mu} = \sum_i c_i z_i^2\,\mu_i \Big/ \sum_i c_i z_i^2 \qquad \text{II-3}$$

$$\gamma = D^2/4\pi^2\sigma\eta a^2 \qquad \text{II-4}$$

Smoluchowski(45,46), Krasny-Ergen(47) and Finkelstein-Cursin(48) also have introduced similar equations for the spherical particle, considering the intrinsic viscosity, size and electrophoretic mobility of the dispersed particle in aqueous sytems. In the evaluation of the following three equations, the thickness of the double layer has been assumed smaller than the radius of the particle.

$$\eta = 2.5 \left[1 + \gamma\zeta^2\right] \qquad \text{(Smoluchowski)} \qquad \text{II-5}$$

$$\eta = 2.5 \left[1 + \frac{3}{2}\gamma\zeta^2\right] \qquad \text{(Kransny-Ergen)} \qquad \text{II-6}$$

$$\eta = 2.5 \left[1 + \frac{77}{25}\,\bar{\rho}\;\bar{\mu}\;\gamma\zeta^2\right] \qquad \text{(Finkelstein-Cursin)} \qquad \text{II-7}$$

The increase in the intrinsic viscosity values of the micelles of n-alkylbromides in aqueous solutions, and in aqueous solutions containing added solutes, is due to one of the operating phenomena , which is the dissipation energy effect in the conduction, which restores the electrical double layer situation of the particle, that has been disturbed in the laminar field flow, because of the internal friction of the particle with the solvent molecules.

II.Ib - Hydration.

An ionic solution has three components, solvent, cations and anions, in which the interactions between the ions and solvent molecules, can be termed as solvation, and in the case of water, hydration(49,50).

In the ionic solution, water molecules become attached to the ion, with loss of their own translational freedom but remain in activated exchange equilibrium with the rest of the solvent.

Ionic hydrations have been extensively studied, by using model systems. A simple model has been given by Born(51). In his model, the ions are introduced as charged hard spheres, and the solvent is considered as a fluid, which has a uniform dielectric constant, even in the presence of the ionic fields. The concept that the major part of the hydration free energy is related to the respective ionic charge and size, has met with great acceptance.

Another approach(52,53) is concerned with the spherical distribution of rigid spherical ions of radius r_i, and charge $z_i e$, in the solution, where the dielectric constant of the medium varies in the neighbourhood of the ion. It has been proposed that the accurate view of the electrostatic part of the ionic hydration, can be derived by taking into account the contributions of the discharge ions.

The ionic hydration free energy, is given(50) by an equation such as

$$\Delta G_H^\theta = \Delta G_{iel}^\theta + \Delta G_{inel}^\theta \qquad \text{II-8}$$

Noyes(54,55) applied a model to investigate the ionic hydration, and he has extended it for studying the thermodynamic coefficients of the hydration. Booth(56) has employed Kirkwood's(57) theory of the dielectric constant of an assembly of polar and polarisable molecules to the highfield state, and found that the theoretical results for water compared with the values given in the literature(58,59).

A further model which uses the Hamiltonian function(50), describing the interactions between nonpolar solutes, and water molecules and distribution of water molecules around an ion is given by:

$$H_{N+1}(\rho_1,\ldots,\rho_{N+1}, r_1, \ldots r_{N+1}) = \sum_{i=1}^{N+1} (\rho_i^2/m_i) + U_{N+1}(r_1,\ldots,r_{N+1}) \qquad \text{II-9}$$

In order to investigate the ionic hydration in view of this approach, a definite functional form for the Hamiltonian is derived, in terms of the exact statistical approximations. In the light of this treatment, an analytical solution has been used(60) to observe the ion-solvent iterations in an assembly of hard spheres with the electric multipoles of the various orders, and this study has been extended(61,62,63) by using the pertubation methods of statistical mechanics, in order to obtain the thermodynamic coefficients of the hydration.

The process which involves the calculation of the interaction of an ion with its first nearest neighbour solvent molecules, in terms of the intermolecular forces, is known as the Hybird type model.

A modal particle which has the same dipole moment, as an isolated real water molecule, has been used(64) as a water molecule, in order to obtain the complex $(X.n\ H_2O)^z$.

The observed ΔG_H^θ is the summation of the three terms such as, (1) the interaction of the charge on X^z with the charges on n water molecules, (2) the London dispersion force acting between an ion and each of the n-water molecules, including nearest neighbour water molecules, and (3) the repulsive force operating between an ion and each of the n-water molecules in the complex.

This view has been subjected to several investigations, in order to evaluate the binding energies and force constants of the complexes, which relate to the $(X.n\ H_2O)^z$, that were formed with X^z or other ions.

Burton and Daly(65,66) applied a quantum mechanical treatment to a system, in which the water-ion distance varies. The calculations have been constructed, on the basis of fixed relative configurations of the nuclei of water molecules, and a series of configurations of fixed symmetries.

On the relation of the thermodynamic properties of the molecules, the additive contributions of the chemical bonds to the energies, has been also introduced to describe the chemical models of the ion-solvent interactions(50). In view of a chemical model, it is assumed that each solute particle X^z has a region around it, and it is called cosphere which has the thickness of one solvent molecule, in which the solvent property is affected by the presence of the neighbour molecules, and it has been characterized by an equation, such as

$$n\left[\text{Solvent(pure bulk liquid)}\right] \rightarrow n\left[\text{Solvent(in cosphere state next to } X^z\text{)}\right] \qquad \text{II-10}$$

Robinson and Stokes(67,68) studied the excess free energies of aqueous solutions of the strong electrolytes, in terms of the complexes of the solute species, which have fixed numbers of the solvent molecules. The solvation models have been introduced by Gurney(69) and Samilov(70) for examining the ion-solvent interactions.

Frank and Evans(4) proposed a chemical model for the investigation of the hydration phenomena, which has introduced very successful information , and they showed that there is something like a double cosphere around each ion.

The Barclay-Butler rule(71), its applicability to the solvation phenomena, and the basis of the rule have been extensively studied, in terms of the molecular interactions(72,73). The chemical approach has been developed(4,74), on the basis of the configurational treatments of the interactions, between hydrogen-bonded assemblies of water molecules and the cospheres of the ions.

II.Ic - Dielectric Effect.

When two parallel conducting plates have on their surface electric charges of densities $+\sigma$, $-\sigma$ respectively, in a parallel plate condenser(68), the field intensity between the plates in vacuo is given by an equation

$$E_v = 4\pi\sigma \qquad \text{II-11}$$

The field intensity of the condenser is altered with the displacement of the medium by another insulating medium, and consequently the field strength drops to a value:

$$E = 4\pi\sigma/\varepsilon_s \qquad \text{II-12}$$

where ε_s is called the static dielectric constant of the medium. The static dielectric constant of a polar liquid arises from the electrical distorsion of the molecules, and the orientations of the permanent electric dipoles (μ) in the static electric field(28). Both effects can be expressed by an equation:

$$\rho = (N_o/V)\bar{\mu}_o \qquad \text{II-13}$$

In a steady uniform electric field, the orientated permanent dipole is distributed according to a Boltzmann distribution. The populations in different energy states are governed by thermal fluctuations, which are originally different orientations. The permanent dipole orientation polarizibility, in such distribution is given by

$$A_{or} = \mu_o^2/3kT \qquad \text{II-14}$$

The average orientation polarization has been calculated by Debye(75,76), in terms of the molecular electric dipole moment effect, on the assumption that the energy of the orientated dipole is distributed according to Boltzmann distribution.

Onsager(77) has interpreted the local field effect on a molecule in a liquid, by considering a model molecule, which has polarizibility α and a point dipole at the centre cavity of radius a_1 in continuous dielectric constant field. He proposed that only the cavity field orientates the dipoles, and the remaining part of the electric field has been termed a 'Reaction field'. According to Onsager's theory, this field should be parallel to the dipole moments of the dipoles.

Oster and Kirkwood(78) examined the directions of the neighbour molecules of a given molecule, in terms of the direction of the central molecule. The number of nearest neighbour molecules, has been calculated by taking into account Morgan-Worren's(27) X-Ray diffraction distribution function. The dielectric of the homogeneous static electric field, in the vicinity of the molecule, has been discussed by Kirkwood(57) in terms of the hindering of rotations of the neighbouring molecules. He proposed that the average dipole moment of an H_2O molecule, surrounded by the neighbouring molecules is the vector sum of the dipoles moments of all the neighbours, which are at fixed orientations for a given molecule.

The liquids which are completely miscible with water are polar in nature, and they possess correlation parameters, which are the measure of the mutual hindering rotations of the neighbouring dipoles, and the orientational correlations. Consequently he concluded that the mixtures of the polar liquids with water, can be examined along the same lines.

Pople(29,79) employed Kirkwood's Theory to his own hydrogen bond bending model. Haggis(37) investigated the static dielectric constant, in terms of the statistical analysis of hydrogen bond breaking, neglecting the bond bending.

The orientational(80) correlation is governed by the molecular dipole, and the location of the permanent charge distribution, in the interior of a polar molecule, which has been interpreted by means of the energy of the hydrogen bonding.

The dipole is affected by the static electric field of the continuous medium, and it relaxes to its equilibrium state of random orientation by taking a finite time. The lag between the motion of the dipoles, and the static electric fields introduces a dielectric loss. The contribution energy arising from the field is dissipated as heat in the medium.

The principal(28) relaxation time of pure water is often interpreted, in terms of the breakage of a hydrogen bond. The water molecule is supposed to reorient with rotational Brownian motion, and a water molecule bonded with one bond to one neighbour, can rotate without involving an activation energy. But a molecule bonded to two neighbours needs for reorientation an activation energy.

The relaxation process of the alcohol-water mixture, has been studied by Cole(81) in terms of breakage of the hydrogen bonds, and he obtained an activation energy for the relaxation process in the monohydroxylic alcohol system, which is of the order of the hydrogen bond energy.

This result has been attributed to the reorientation of a molecular OH moment, by breaking of its hydrogen bond, and subsequently forming a bond to the oxygen of another molecule. In view of this approach, the relaxation is supposed as a cooperative process in the entire medium.

Hassion and Colo(82) discussed the small quantities of water in various alcohols. They observed that the relaxation time is affected by the addition of water. Pottel-Kaatze(83) investigated cospheres of the ions, in a static electric field. They concluded that water molecules in each hydration sheath, have different relaxation times to that of the pure water in the solution, and they contribute a certain fraction of entire static permittivity of the solution.

The static dielectric constant, and dielectric relaxation time, decreases as the concentration of electrolyte is increased. The reason for the changing of the dielectric properties of the medium, has been attributed to the structure breaking effect of the solute(80).

The electric field of an ion polarizes the neighbouring solvent molecules. The electric field near an ion is quite intense enough to cause a marked dielectric saturation in surrounding water molecules.

At the water-ion interface, a water molecule carries bound charge(50), (i.e. a polarization charge) which is opposite to that of the ion charge. This polarization charge becomes assymetric with respect to the ion, due to the orientational relaxation of water, in the applied electric field(84).

The ion-pairs have smaller reorientational times than water molecules. They reduce the principal dielectric relaxation time, in terms of their contributions to the total orientational polarization. Only the small cations such as $Li^{(+)}$ and $Na^{(+)}$, are saturated dielectrically towards their inner hydration layers by the strong ionic electric field. The small cations have the highest number of moles of water, without orientational polarizability per mole of electrolyte, which is smaller for the large cations.

Ritson and Hasted(85) calculated the dielectric constant of water as a function of the distance from a point electronic charge, and concluded that the difference between dielectrically saturated positive and negative ions, is due to the ionic size.

Macroscopic electrical property of a disperse system, can be characterized(86) by the static dielectric constant of the dispersed medium. The dielectric increment effects of the particles arise from their polarizibility, the orientational relaxations, and their correlation parameters.

The static dielectric constant of a colloidal solution is different from that of the pure dispersion medium. In the colloidal system, the molecules of the dispersion phase are replaced by the particles, which have lower dielectric effects. Consequently the dielectric constant of the medium is lowered.

The orientations of permanent dipole moments of hydrophilic colloids by the electric field change the polarization, and the dielectric constant of the medium(87). The electrical double layer influences the static dielectric constant of the disperse system. The particles possess dipole moment which are directed opposite to the field, due to having electrical double layers. This process changes the orientations of the particles, their polarizibilities, and the dielectric constant of the dispersion medium.

The solute which dissolved in dispersion medium lowers or increases the correlation parameter, which governs the static dielectric constant, and it raises or decreases the relaxation time.

The correlation factor is lowered by the added solute, due to 'structure breaking' effect, and is increased by the iceberg formation (i.e. structure-making), which contributes the largest contribution to the correlation factor.

II.Id - Thermodynamics of Solute -Solvent Interactions.

Various thermodynamic quantities have been employed, in order to obtain thermodynamic properties of the systems. Some of them are most important, and the commonly evaluated properties of the systems, are the Enthalphy(H), Entropy(S), and Free energy(G)(88). These are related by the equation

$$\Delta G = \Delta H - T\Delta S \qquad \text{II-15}$$

The other quantities which are frequently measured are the change in heat capacity ΔC_p, where

$$\Delta C_p = \left[\partial\ (\Delta H)/\partial T\right]_P \qquad \text{II-16}$$

and the partial molal volume, a quantity used to observe solute-solvent interactions.

$$\bar{V} = \left(\frac{\partial v}{\partial n_1}\right)_{T,P,n,n_2} \qquad \text{II-17}$$

The solutes can be classified(80) into two groups, in terms of their thermodynamic magnitudes of ΔH and TΔS. The solutes where $T/\Delta S > \Delta H$ are called aqueous in nature, whereas those for which $T/\Delta S < \Delta H$ are the nonaqueous. In other words, the characteristic of an aqueous nature solute is entropy control of the solution thermodynamics. The series of apolar solutes have been examined. It has been postulated that the hydrocarbons have low solubility in water, hence have a positive ΔG soln. The ΔH_{soln} is negative for the lower hydrocarbons. The low solubility is due to the negative ΔS_{soln}.

Butler(1) calculated the entropy of nonelectrolytes in dilute solution, and showed that ΔS_h plays a unique role in determining the free energy of hydration of the alcohols. In addition to this view Barclay-Butler(71) introduced a plot of ΔH_h against Δh, for the rare gases in the nonaqueous solvents, which is a straight line.

Frank -Evans(4) explained that the negative ΔS_h is due to the formation of hydrogen bonded clusters around the apolar solute, in terms of hydrophobic interactions. The structural effect of the liquid water has been examined by Nemethy-Scheraga(5). They employed the Frank-Wen(6) model for water of the flickering cluster, and based their calculations with statistical mechanical basis, on the assumption that a water molecule possessing four hydrogen bonded water neighbours,could accommodate neighbour solute molecule by lowering the energy of the water molecule. According to the Aranow-Witten(89) model the chain mobility is restricted when a hydrocarbon molecule or the chain length of the alcohol or amine transfer from vapour state to the aqueous environment. As a result, the internal entropy is reduced. This behaviour has been attributed to the loss in entropy rather than any formation of hydrogen bonded configurations.

Miller-Hildebrand(90) proposed a different view for the behaviour of the apolar solutes in aqueous solution considering the bent hydrogen bond.

Krishnan-Friedman(91) studied the thermodynamic transfer properties of hydrocarbons from water to dimethylsulfoxide (DMSO), and to propylene carbonate (PC) environments. They have observed that there is no structural increase of water, which gives a positive entropy change for the transfer as pointed out by Frank-Evans(4).

The view which is related to the structural properties of the water in the presence of apolar solutes, has been extensively studied in order to evaluate the thermodynamic properties of the hydration of apolar solutes in aqueous systems(92,93,94,95).

In recent years, new results concerning the heats of the solutions of the alcohols at various temperature, ranging from methanol to the butanol have been introduced.

Butler(96) was able to evaluate enthalpy, entropy and the free energy of the hydration, in terms of the heat of vaporization of the alcohol. In this process it is apparent that the apolar region of the alcohol behaves the same as an apolar solute.

Arnett-Kover-Carter(97) have determined the heat capacities of the solutions of lower alcohols. They also found large positive values of ΔC_p. This observaton indicates that the apolar part of the alcohol molecule controls the solution behaviour, and the lower ΔC_p value being due to the branching of the chain. The heat capacity of the solution from the vapour phase was compared with the entropy of hydration. This treatment supported the idea that the heat capacity reflects also the solvent structuring character of the apolar side of the alcohol molecule.

The solvent-structuring concept has been extended for measuring the ΔH_{soln} of the alcohols in water and the other solvents. The enthalpies of transfer of the molecules from one state to another, has been calculated(91) by taking into account the contributions of the groups to the solvation enthalpies. This approach has enabled the evaluation of group contributions, and the magnitude of the solvent structuring in water. It is reasonable to consider that ΔH_h and ΔS_h of the apolar group hydration of the alcohol up to C_6 is not affected by the presence of the C-OH(4,71,80) group.

Another study has been carried out by Konicek-Wadsö(98). The most interesting conclusion arising from their results, is the independent nature of the polar group in the increment of vapour heat capacity per $-CH_2-$ group. In this process it appears that the water structure around the apolar group is only slightly affected by the polar group.

Similar behaviour has been observed in the solution of the tetraalkylammonium ions(6,99). The obtained heat capacities are large and positive, due to effects of the apolar groups on water structure, and depend on the nature and size of the alkyl groups of the ions, (i.e. Bu_4N^+ ion has more positive heat capacity $\Delta C_p{}^\circ$ than the Pr_4N^+ ion). It can be concluded that the apolar groups govern the interactions of the ions, in terms of the electrostrictive structure making and breaking effects.

Considering the solvation enthalpies, Krishnan-Friedman suggested(91,100) that Me_4N^+ is a net structure breaker, while Pr_4N^+, Bu_4N^+ and AmN^+ ions are net structure makers. This conclusion has been confirmed by other investigators(101,102). The volumetric properties of ions are also interesting. In the case of simple ions there is a volume decrease on solution, and it decreases with increasing ion size, due to the apolar group of the ion(103).

Hepler(104) studied the relationship between the structure-making and structure-breaking solutes, and the thermal expansion of the aqueous solutions.

He introduced the relationship:

$$\left(\partial \bar{C}_p{}^\circ \big/ \partial P\right)_T = -T\left(\partial^2 V \big/ \partial T^2\right)_P \qquad \text{II-18}$$

and concluded that structure-breaking solutes should have negative $\partial \bar{a}_2/\partial T$ and structure-making solutes positive $\partial \bar{a}_2/\partial T$.

The ultrasonic velocity measurement method has been employed by Conway-Verrall(105) for the investigation of solution properties of a series of tetraalkyl ammonium salts. They obtained negative values of the apparent molal adiabatic compressibilities of the ions, which decreased as the apolar groups increased.

Frank-Wen(6) introduced the idea that the partial molal heat capacity of the solution, in the presence of the ionic solute is negative, due to "freezing out" of a degree of freedom in the region of immobilization of water molecules, and destroying the ice-likeness region around the ion. They have also studied the apparent molal heat capacity of the solute $(n\text{-}C_4H_9)_4N\,Br$ in aqueous solution.

The observed large value of ϕ_{cp} which is about 270 Cal/deg.mole, has been interpreted in terms of the increased ordering of the water molecules around the apolar side of the alkylhalide ion, and according to their postulation the hydrogen bonded water configurations around the solute decrease with increasing temperature, consequently it melts due to the adsorbed extra heat.

The activity and osmotic coefficients of the tetraalkylammonium salts, have been investigated by Lindenbaum-Boyd(106). They have shown that at low concentration the coefficients of the chloride salts increase with the size of cations,

$$Me_4N^+ < Et_4N^+ < Pr_4N^+ < Bu_4N^+ \qquad \text{II-i.1}$$

bromides and iodides show the reverse order. At high concentration the osmotic coefficient of the salt decreases with increasing ion size. This behaviour has been attributed to the structure making ability of the chlorides, and the enforcement of the bromides, and iodides for ion-pairing.

Lindenbaum has extended(107,108,109) his investigation by examining the apparent molal heat contents of one molar aqueous solutions of the sodium salts of butyric and valeric acides. The results follow a similar pattern to those of cationics, except inorganic cationics which decrease with increasing cation size. On the other hand, the exothermic heats of tetrabutylammonium carboxylates, have been discussed in terms of hydrophobic interactions, under the influence of both cationic and anionic hydrophobic groups.

The effect of apolar groups on the entropies and enthalpies of theaqueous salt solutions, have been also examined in order to explain the solvent-solute interactions.

The order of decreased heat of the solution of a given halide can be defined such as,

$$Bu_4N^+ > Pr_4N^+ > Et_4N^+ > Me_4N^+ \qquad \text{II-i.2}$$

Timasheff-Fasman(110) have introduced the partial molal unitary entropy of the solution, in order to characterize the effects of a given solute on the solution property.

The entropy related to the solute, and its cosphere in the solution, has been termed the cratic portion of the conventional partial molal entropy of the solution. He has shown that the partial molal unitary entropy of the solution is related to $\overline{\Delta S}$ as,

$$\Delta S_{unitary} = \overline{\Delta S} - 2R \ In \ M \qquad \text{II-19}$$

Wen-Hung(111) measured the solubilities of lower hydrocarbons in water containing 0,1 to 1.0M solutions of ammonium bromides $(HOC_2H_4)_4NBr$ and R_4NBr at four temperatures. They explained that ammonium bromide salted out all the gases, while the large tetraalkylammonium ion had a salting-in effect. Both $(CH_3)_4NBr$ and $(HOC_2H_4)_4Br$ salted in the larger gas molecule, while salting out the smaller molecule. Their explanations have been based on two fundamental effects, a) indirect interactions between R_4NBr and RH, due to changes in the structure of the solvent molecules. b) direct hydrophobic interactions between two solutes. The salting out efficiency between 5° and 35° is,

$Bu_4N^+ > Pr_4N^+ > Et_4N^+$ 5°

$Et_4N^+ > Pr_4N^+ > Bu_4N^+$ 35°

The thermodynamics of electrolytes of aqueous binary mixtures have shown that ΔH_t and ΔS_t contain the structural contributions. It has been shown(112,113) that ΔH_t is positive, increases with the dilution of the solution. But ΔH_t becomes negative when the organic solvent concentration is increased. This behaviour has been examined by means of the solvent-organic solute interactions. Feakins(114) suggested that at low concentrations, organic solutes behave as structure making (i.e. increase solvent structure).

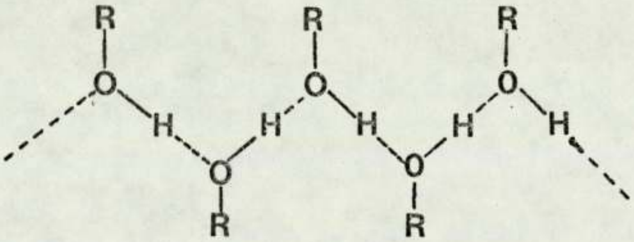
The standard partial molal heat capacities of sodium tetraphenylborons in the aqueous solutions from 0° to 90°, have been examined(115) in terms of the variations of the integral heats of the solutions with temperature. The relationship between heat and temperature shows two discontinuities, which corresponds to a minimum around 50°, and maximum around 70°. The minimum has been interpreted in terms of hydrophobic interactions, and the maximum is attributed to a reduction in structure makers capacity of the solute above 70°.

The thermodynamics of the mixed solutes in water at infinite concentrations provide valuable information about the solute-solvent interactions. In order to evaluate the solution properties, one must experimentally determine the thermodynamic parameters of the solution. No doubt, the obtained features will be the thermodynamic description of a system.

II.Ie - Effect of Aliphatic Alcohols.

The interactions between water and the alcohols are rather complex. An alcohol molecule has one oxygen atom which carries one proton, and two lone pairs of electrons. Therefore it acts as a proton donor, and as a proton accepter. It has been shown(116) that only two bonds are formed in the liquid state, due to the average coordination number of a molecule being two.

It has therefore been suggested(117,118,78) that the molecules are arranged in chains, in terms of hydrogen bonds as linear polymers or cyclic aggregates (most probably linear polymers as shown below)



II.i.4

The water behaves as a host to the molecules, which have a certain affinity for water. Since the alcohols possess both hydrophilic and hydrophobic functions, the alcohol-water-mixture reflects the strength of the intercomponent attractions.

In the alcohol-water mixture, the hydrogen bonded water molecules are endothermically destructed with the alcohol molecules, which interact with water by hydrogen bonding(116). Consequently this could be attributed to the bond breaking, and loss of order involved in the pseudo crystalline structure of water(26). Such breakdown increases with increasing concentration of the alcohol.

On the other hand, the water molecules depolymerise the cyclic or linear polymeric aggregates of the alcohol molecules in the mixture, by intercomponent hydrogen bonding, and preferential hydrogen bonding occurs between dissimilar species(119).

The molecule of the alcohol is able to 'build in' to the water structure. This is quite certain for the methanol-water mixture(120). It has been observed that, the alcohols have more 'basic character' than that of water in the alcohol-water mixtures, and they behave more as protons acceptors than donors(116). This interaction can be shown by a simple acid-base proton transfer of the kind(119).

$$H_3O^+ + RO^- = H_2O + ROH = OH^- + ROH_2^+ \qquad \text{II.i.5}$$

The order of increasing proton accepting facility has been given by Gerrad-Macklen(121);

$$\text{Me-OH} < \text{Et-OH} < \text{Pr-OH} < \text{t.Bu-OH} \qquad \text{II.i.6}$$

Eley observed(2) that a mole of water can accommodate nonpolar molecules, since it has 9 cm^3 of empty space provided by its ice like structure. So it is reasonable to assume that nonpolar parts of the lower alcohol molecules, could fit well into such cavities.

The lowering of the transition temperature in aqueous protein solutions containing aliphatic alcohols, has been interpreted(122) in terms of the binding of the nonpolar portions of the alcohol molecules, to the nonpolar sides of the denaturated proteins. This binding has been explained, by means of the formation of hydrophobic bonds between nonpolar sides of the molecules.

The polar end of the alcohol is considered to retain its hydrogen bonding to water. Herskowits et al.(123) introduced a similar type of interaction, in an aqueous solution of a protein containing the alcohol, taking into account the interactions between the water cluster and the alcohol molecule(123,124,125).

The addition of aliphatic alcohols to the aqueous solution of alkylammonium bromides, have increased the relative viscosities of the systems. (1.2148 and 1.3210 for 0.1M aqueous solution of C_{10} containing 1M and 2M, CH_3OH respectively. Table II.I.2). The observed viscosity is much higher than that of aqueous solution (1.0761. Table II.I.1). The intrinsic viscosity of micelles increases also nonlinearly with the increasing alcohol chain length (0.0415 $g.dl^{-1}$, 0.056 $g.dl^{-1}$ and 0.058 $g.dl^{-1}$ for C_{10} in addition to 1.M. CH_3OH, C_2H_5OH, and C_3H_7OH respectively (Fig.II.12 and Tables II.I.2, II.I.2,A,C).

It is reasonable to consider that the interactions of water molecules with the OH groups of the alcohols, hydrophobic interactions between nonpolar parts of the alcohol molecules and the aggregated alkyl groups, and the interactions mentioned in this chapter contribute to the viscosity increment of the aqueous solutions of n-alkylbromides containing alcohols.

II.If - Relative, Reduced and Intrinsic viscosities of Aqueous Solutions of n-Alkyltrimethyammonium Bromides.

The viscosity increases in aqueous solution which occurs with the addition of solute particles, has been explained by Einstein. When a particle is dispersed in a liquid, this disturbs the flow of the liquid. Consequently the internal friction of the system is higher than that of the pure liquid.

This disturbance was calculated by Einstein(126,127) by investigating how the energy dissipation of the system was changed by the presence of the spherical particle which carries no electrical charge.

The liquid was treated as a viscous continuum, with rigid spherical obstructions at the surface of which the liquid is at rest. He obtained a well known expression,

$$\eta = \eta_0(1+2.5\phi) \qquad \text{II-20}$$

which is valid at low concentrations. The equation is strictly applicable only to systems in which the particles are perfect spheres, which do not interact with one another.

In order to derive the relative viscosity, which is the ratio of the viscosity of the dispersion to that of the solvent the Einstein equation (II-20) can be written as,

$$\eta_{rel} = \frac{\eta}{\eta_o} = 1+2.5\phi \qquad \text{II-21}$$

The relative increase in the viscosity of the dispersion, over that of the solvent alone, is defined as specific viscosity, which is given as,

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \frac{\eta}{\eta_o} - 1 \qquad \text{II-22}$$

and the Einstein equation becomes,

$$\eta_{sp} = \frac{\eta}{\eta_o} - 1 = 2.5\phi \qquad \text{II-23}$$

The reduced viscosity is obtained from equation (II-23), dividing by the volume fraction ϕ,

$$\frac{\eta_{sp}}{\phi} = 2.5 \qquad \text{II-24}$$

Since the volume fraction ϕ is directly proportional to the concentration, the determined reduced viscosities of various concentrations are plotted versus concentrations in $g.dl^{-1}$. The extrapolation of the obtained curve to c = o gives the intercept α, which is known as the intrinsic viscosity $[\eta]$ (Fig.II.5, Fig.II.10, II.10.A).

The relative viscosity which is relative to the solvent viscosity increases as the hydrocarbon chain length increases. The absolute viscosity of water at 25°C is 0,8949 cP(139). The lowest concentrationsused for the determination of viscosities of alkylammonium bromides are 1×10^{-2} $m.dm^{-3}$, 4×10^{-3} $m.dm^{-3}$ and

1×10^{-3} m.dm^{-3} for C_{10}, C_{12} and C_{14} respectively. (Tables II.I.1, II.I.1.A). The corresponding viscosities are 1.0027, 1.0035 and 1.003 respectively. This increase in relative viscosity as can be seen (Fig.II.1), is independent of the concentration, and molecular weight of the surface active agent.

The viscosity increases nonlinearly as the chain length and concentration increases. The obtained relative viscosities are larger than unity. This increase is mainly due to the solute-solvent interactions in the aqueous solution. In aqueous solutions of alkylammonium bromides, the structural order of liquid water increases near the nonpolar solutes, and forms hydrogen bonded water networks or clusters around the nonpolar groups(4).

The increased volume of liquid water, stronger associations of the polar head groups, and the ions with water can be given as possible reasons for the increased viscosities of the system.

An abrupt change occurs at a critical concentration on the viscosity-concentration curve (Fig.II.2). The viscosity gradually increases with the concentration. However at a critical concentration (6.5×10^{-2} m.dm^{-3} and 1.68×10^{-2} m.dm^{-3} for C_{10} and C_{12} respectively) the slopes of the curves change.

This is due to the release of ordered water molecules around the nonpolar groups(128), and transferring of nonpolar groups from the aqueous environment to nonpolar region. As a result of this process the free energy of the system decreases(129,130).

The hydrodynamic result of the distortion of stream lines by the particles in aqueous solution, and the electrical forces between the ions in adjacent layers of an electrolyte solution, could be also considered as possible effects, which play a unique role, for increasing the viscosities of systems(131).

In order to isolate the effect of solute, we can compute the value of the specific viscosity. This is found to be small compared with the relative viscosities. As it can be seen, the specific viscosity of particular concentration such as 0.06 $m.dm^{-3}$ and 0.01 $m.dm^{-3}$ for C_{12} are 0.09386 and 0.0081 respectively. (Table II.I.1). These values are very small compared with the respective relative viscosities (1.0938 and 1.0081). However the respective reduced viscosities 0.0507 $g.dl^{-1}$ and 0.0262 $g.dl^{-1}$ are relatively large. The reduced viscosity does not change much in the dilute solution. It would not change at all, if the specific viscosity was proportional to the concentration.

The reduced viscosity is an indication of the increase in viscosity due to the mentioned effects,for per unity concentration in the solution concentration, the intrinsic viscosity of micelles increases with the increasing chain length, (0.06 $g.dl^{-1}$ and 0.069 $g.dl^{-1}$ for C_{10} and C_{12} respectively Fig.II.6).

It is precisely the desired quantity needed, in order to measure the solute- solvent interactions, in terms of the hydrodyanmic properties of micelles.

II-Ig - Experimental Procedure.

II-Ig1 - Materials.

Methanol, n-propanol and n-butanol were BDH A.R. material. Absolute ethanol was obtained from Fisons(132) as absolute grade material. The alcohols were dried by standing over anhdrous sodium sulphate for 24h, and then distilled from all Pyrex glass apparatus. n-decyl, n-dodecyl and myristyl bromide were Kochlight(133) purus grade and cetyltrimethylammonium bromide, trimethylamine (anhydrous) were BDH(134) grade. The distilled water used was doubly distilled from all Pyrex glass apparatus. It had a surface tension of 71.5 dyn cm^{-1}, and a conductance (Λw) of the order of $< 1 \times 10^{-6}$ $ohm^{-1}cm^{-1}$ at 25°C.

II-Ig2 - Preparation of n-Alkyltrimethyammonium bromides.

An homologous series of alkyltrimethylammonium bromides with 10 to 14 carbon atoms was prepared with trimethylamine (anhydrous);(135) the alkylbromide was added slowly to a cold solution of excess (anhydrous) trimethylamine in absolute ethanol, and the mixture stirred at 0° for one hour, then the mixture was heated under a reflux condenser, cooled and the solvent evaporated. The obtained salts were filtered and dried. These salts and the commercial cetyltrimethylammonium bromide were recrystallized several times from benzene-ethanol (20:1) mixture.

The purity of the compounds was checked by using Du Nouy tensiometer(136). The alkylammonium bromides were recrystallized until a fine intersection on the surface tension-concentration curve was obtained. The C_0 values for alkylammonium bromides (6×10^{-2} mol.dm^{-3} and 1.9×10^{-2} mol.dm^{-3} for C_{10} and C_{12} respectively. Table II.I.1, II.I.1A and Fig.II3) are very close to the C_0 values obtained by viscosity method (6.5×10^{-2} mol.dm^{-3} and 1.68×10^{-2} mol.dim^{-3} respectively. Fig.II.2). These reported C_0 values were in good agreement with the values given in literature(137) (6×10^{-5} mol.dim^{-3} and 1.5×10^{-2} mol.dm^{-3} for C_{10} and C_{12} respectively). The bromide content 28.50%, and 25.90% for C_{10} and C_{12} was found very close to the theoretical values (28.51% and 25.91% for C_{10} and C_{12} respectively).

II.Ig3 - Measurement and Instrumentation.

II.Ig3.A - Viscosity Measurement.

For the viscosity measurements a U-tube capillary viscometer (Size A Serial No.4857 B.S. U.S.A.Volac Fisons)(132) with a flow time of ca.291s. for double distilled water ($\Lambda w < 1 \times 10^{-6}$ ohm^{-1}cm^{-1}) at 25° was employed. The viscometer was calibrated by using double distilled water, and 20% sucrose solution according to BS.188.1957(138).

The viscometer was carefully cleaned, rinsed with distilled water, and dried before filling with the calibration solution, then immersed in a thermostat, and 15 minutes allowed for equilibrium with the temperature 25°C ± 0.005 deg C, then the flow times of the reference liquids were measured by using an electric stop clock (cap. $^1/_{50}$th sec). The procedure was repeated three times, then the average time was used as flow time of the liquid. (291 sec. and 513.22 sec. for double distilled water and 20% sucrose solution at 25°C respectively).

The values of B and C constants for the viscometer used were calculated by following equations, taking into account the viscosities (absolute) of the reference liquids (0.8949 cp and 1.701 cp for distilled water(139) and 20% sucrose solution(140) respectively)

$$B = \frac{t_1 . t_2 (\eta_2 t_1 - \eta_1 t_2)}{t_2^2 - t_1^2} \qquad \text{II-25}$$

$$C = \frac{\eta_2 t_2 - \eta_1 t_1}{t_2^2 - t_1^2} \qquad \text{II-26}$$

The obtained values of B and C constants are 30 and 0.00342 respectively. The kinematic viscosity of the double distilled water was calculated by using an equation(138) at 25°C

$$\eta_k = C . t_1 - \frac{B}{t_1} \qquad \text{II-27}$$

The obtained kinematic viscosity of the double distilled water is 0.8921 cp, which is in good agreement with the value (0.8975 cp) given in literature)(139).

After the calibration, the absolute viscosity of the solutions were calculated using an equation(87) taking into account the density, and viscosity of the reference liquid (distilled water).

$$\frac{\eta_a}{\eta_1} = \frac{t_a \times d_a}{t_1 \times dw} \qquad \text{II-28}$$

II.Ig3.B - Density of the solutions.

The density of solutions were measured with a 10 ml pycnometer at 25°C ± 0.005 deg.C(141). In order to obtain the density of a solution, the weight of the dry pycnometer was determined (Wd), and was filled with double distilled water, then was thermostated at 25°C for about 10 to 15 minutes. After the equilibrium with temperature the stopper of the pycnometer was inserted. It was made certain that the outside of the pycnometer was completely dry, then the weight of the pycnometer filled with water was determined (Ww).

From the density of water at 25°C (dw = 0.9971 g/ml) the volume of the pycnometer was determined by the equation,

$$V = \frac{Ww - Wd}{dw} \qquad \text{II-29}$$

then the density of solutions were measured in the same way by using calibrated pycnometer at 25°C (1.0002 g/ml for C_{10} of 0.1 mol.dm^{-3} Table II.I.1.).

II-Ig3.C - Density of Solids.

A weighed amount of substance was introduced into a calibrated pycnometer, (known volume) then a suitable liquid (paraffin liquid B.P.) was added to the reference mark. The weights of the empty and filled pycnometer was used to calculate the density of the alkyl-ammonium bromides at 25°C, in terms of the following equation(142)

$$D_s = \frac{D_L \quad W_s}{V_p \; D_L + W_d + W_s - W_T} \qquad \text{II-30}$$

II.Ig3.D - Surface Tension measurement.

The surface tension measurements of the solutions were made using the Du Nouy Tensiometer according to the instrument manual(136).

II.Ig3.D.1 - Zero adjustment.

First the tension of the torsion wire was checked. After this procedure the pointer on the torsion head was set to zero on the scale by means of the knurled knob, then the other head at the other end of the wire was turned to adjust the boom until the line on the mirror appeared to be halfway between the boom and its image (zero point).

II.Ig3.D.2 - Calibration.

Calibration was made using a liquid (double distilled water) of known surface tension, and a weight. A piece of tissue paper was put on the ring, and the boom was adjusted to zero. After that a 0.5g weight put on the paper, then the pointer was adjusted until the boom was again at zero. Since the ring has a total contact of length of 8 cm, the corresponding surface tension is 61.3 dyne cm^{-1}. The obtained reading (61.2 dyne cm^{-1}) was very close to the above value.

On the other hand, double distilled water was used to calibrate the instrument. The obtained surface tension of water at 25°C (71.5 dyne cm^{-1}) is very close to the value given in literature (71.9 dyne cm^{-1})(139).

II.Ig3.D.3 - Measurement of Surface Tension by the Ring Method.

The ring was cleaned by heating in a bunsen flame before taking the measurement. The clock glass containing the solution was placed on the circular table, and the height was adjusted so that the liquid level was about 1 cm below the ring. The pointer, and the boom both were set to zero (as described), then the liquid was raised until it touched the ring. The torsion head was turned until the boom was again on zero.

After this procedure, the liquid was lowered slowly at the same time, turning the torsion head so that the boom remains on zero. The detachment of the ring from the surface of liquid corresponds to the pointer reading, which gives the surface tension.

The C_0 of surfactants with an alkyl chain from 10 to 16 carbon atoms in aqueous solutions, and solutions containing additives was determined by means of the viscosity, and surface tension methods, plotting $^1/\eta_{red}$ viscosity versus concentration (surfactant), and the surface tension against the concentration. (3.4×10^{-3} mol.dm^{-3}, and 3.7×10^{-3} mol.dm^{-3} for C_{14} by surface tension, and viscosity methods respectively. Figs.II.3, II.2, II.8, II.8.A and Tables II.I.1, II.I.1.A). The partial specific volume at C_0 in aqueous solution and solution containing additives was calculated from corresponding partial molal volume of the micelles(88).

II.Ih - Micellar Properties from Hydrodynamic Data.

II.Ih1 - The aqueous solutions of n-Alkylammonium bromides.

The viscosities of surfactant solutions have been widely investigated for the determination of the hydrodynamic properties of micellar systems. Viscosity theory has developed sufficiently to provide valuable information about the particle size, shape, charge and the structural problems of the micelles.

The theory of micelle formation has been extensively studied(143,144,145,146) taking into account the energy changes associated with the process. Although small heat changes occur, the micelle formation is predominantly an entropy directed process. The entropy effect arises from the formation of structural regions (ice bergs) around nonpolar solutes(4,6) and the interactions between polar head groups and water molecules (hydrophobic interactions) which cause the nonpolar portions of the solute molecules to transfer from an aqueous environment to the nonpolar regions(4). By this process they increase their flexibilites.

At this stage there are abrupt changes in the colligative properties of the amphiphiles and at a critical concentration due to the discussed thermodynamic process micelles are formed.

It is found that there is a change at certain concentrations on the $1/\eta_{red}$ - concentration curve of the n-alkyl bromide in aqueous solution and in the solutions containing aliphatic alcohol. When the hydrophobic tails leave the water energy is gained. Consequently the charged heads are brought to the certain configurations, in order to develop a basic micellar structure.

The polar head groups are located at the micelle-water interfaces while the hydrophobic parts of the aggregates form the interior of the micelle(147).

Various models have been proposed for the micelle structure. McBain(148) introduced two kinds of micelles, ionic spherical and neutral lamellar. Hartley(143) proposed only one type of micelle, a spherical one.Mattoon et al.(149) postulated a two layer sandwich micelle as another possible model.

Debye and Anacker(144,150) showed by light scattering experiments that the micelles are small in solutions of low ionic strength. They become large as the ionic strength increases. They concluded that in the aqueous solution of n-alkylbromide containing KBr, the micelles are rod-like. Trap-Hermans(151), Cohen-Vassiliades(152) and Hermann (153) by using light scattering, Reiss-Husson-Luzzati(154) applying small angle X-Ray scattering introduced also the idea of rod like micelles. Stigter(155,156) postulated spherical, Poland-Scheraga(145,157), Shinoda(158) discussed cylindrical models of the micelles.

The micelle interior generally has been treated as a liquid hydrocarbon state(159,160,161). However there have been some indications that the micellar interior could have some amount of water molecules(162;163,164,165). According to this approach water molecules could penetrate in to the micelle up to the distances of approximately three to six carbon atoms.

The structure of the interior of a micelle has been considered as quasi-crystalline hydrocarbon structure(158).

The number of carbon atoms in the hydrocarbon chains of homologous amphiphiles is one factor determining the critical micelle concentration. It has been shown that the C.M.C's decrease logarithmically with the increase in the number of carbon atoms (n) for various amphiphiles. The relation could be given by the equation(158)

$$\log_{10} C_0 = A - Bn \qquad \text{II-31}$$

The C.M.C's of the n-alkylbromides in aqueous solution decrease linearly obeying the above expression (Fig.II.4). The intrinsic viscosities of the micelles increase also with the increasing chain lengths (Fig.II.6). Since the intrinsic viscosity $[\eta]$ is the function of the size and shape of the particle, the relationship between density of the micelle and $[\eta]$ can be given by an equation(166)

$$[\eta] = \frac{K}{100d} \qquad \text{II-32}$$

The shapes of the micelles of the n-alkylammonium bromides in aqueous solutions are discussed in terms of Huggins constant, viscosity, disymmetry and light scattering measurements. For the rigid spherical particle, the Huggins constant is equal $\simeq$ 2.0. The relationship between concentration effect and the particle shape has been given by Huggins(167).

$$\frac{\eta_{sp}}{C - C_0} = [\eta] + Hk[\eta]^2 C \qquad \text{II-33}$$

where H_k is the Huggins constant. In our case the value of H_k of C_{16} has been calculated in terms of the slope of the curve $\left(\frac{\eta_{sp}}{C - C_0}\right)$ versus $\left(C - C_0\right)$ (0.004) divided by $[\eta]^2$ (176). The obtained H_k value (0.44) is much smaller than that of ≃ 2.0. The dissymmetry of the solutions measured by light scattering at 60° and 120°, are very close to unity, (1.010). In order to introduce the possible shapes of the micelles, it is necessary to expand our considerations for the other kind of shapes, which could be the possible shapes of the micelles in our systems.

Let us first consider the possibility of nonspherity. The other likely shapes of the micelles are disc and rod. The disc shapes of the micelles have been discussed by Harkins(149,167,168) and he concluded that they have a thickness of twice of the length of the surfactant molecule. If we assume the distance between $-\overset{1}{\underset{1}{N}}-CH_2-$ is approximately equal to $-CH_2-CH_2-$ distance, one can calculate from the bond lengths and bond angles a length (fully extended), close to 25Å for C_{16} in aqueous solution. So the thickness of the disc micelle will be 50Å. We can calculate the volume of a micelle, taking into account the macroscopic density of C_{16} (1.1423 g/ml), and the micellar molecular weight (M = 31250, N ≃ 86 from light scattering). Considering the volume of the micelle, one can calculate that each monomer occupies a volume of about 528 Å^3. The micelle then should have a volume about 45410 Å^3. In order for a disc of thickness 50Å, to have the required volume, it should have a radius of 17Å. This disc might approximate a prolate spheroid of revolution of axial ratio 1.47, which should give rise to an intrinsic viscosity 0.023 g/dl (169,170).

On the other hand, the rod like model should have the diameter of 50Å.

This model could approximate to an oblate spheroid of revolution of axial ratio $^{1}/AR = 2.2$ The micelle of such shape should have the intrinsic viscosity 0.026 g/dl (169,170). Neither model suffices to explain $[\eta] = 0.096$ g/dl for C_{16} that was found experimentally. However the above theoretical approximations indicate that the micelles are spherical. It is generally believed that the ionic detergent micelles with molecular weights in the region of $1 \times 10^4 - 1 \times 10^5$, contain 20-100 monomers and have average radii of 12-30Å (171,172) are spherical. Schick et al.(172) has shown that with molecular weights in excess of 5×10^5 the micelles are rod shaped, and are large compared with the low molecular weights aggregates(172).

In view of the treatment of the micelles, and the observations about the micellar shapes given in the literature, it is concluded that the micelles are spherical. Since part of the volume of the any shape of micelle is occupied by liquid hydrocarbon chains, it is reasonable to assume that the density of a micelle of n-dodecyltrimethyl ammonium bromide in aqueous solution, could be fairly close to that of the liquid dodecane which is 0.802 g/ml at 25°C(155,156).

Theoretically $[\eta]$, calculated from the equation (II-32) for C_{12} micelles is 0.0312 g/dl. Since the $[\eta]$ of the rigid, non-interacting sphere which has unity density is equal to $[\eta]$, 0.025 g/dl. The deviation from the Einstein expression(126,127) could be attributed to the ionic micellar nature of the colloidal particle. The existence of the charges on the kinetic units increase the $[\eta]$, due to the electroviscous effect which has been discussed in Section II.Ia.

Booth(44) showed that the viscosities of the suspension particles, which are noninteracting charged spheres with Gouy Chapman double layer, could be given by an equation such as(147)

$$\eta = \eta_o[1 + 2.5\phi E] \qquad \text{II-34}$$

The interaction between a charged sphere and its double layer is given by

$$E = 1 + \sum_{1}^{\infty} b_i(e\xi/kT)^i \qquad \text{II-35}$$

which includes a correction for the electroviscous effect. If we generalize the above equation to include particles of all shapes, then we have

$$[\eta] = E\beta/100d \qquad \text{II-36}$$

It is also reasonable to discuss $[\eta]$ of the micelle from the solvation point of view. As the micelles have hydrophilic surfaces this approach could give valuable information about the hydration phenomenon of the micelles. McBain et al.(173) have shown that potassium laurate molecules are hydrated, and he suggested that each monomer contains 10 bound water molecules.

In view of this fact, we assume that the micelles are hydrated. Consequently this hydration contributes to the increases in viscosity and $[\eta]$ due to increase of its kinetic volume in terms of hydration.

The intrinsic viscosity is related to the shape and volume of the micelle by an equation(174);

$$[\eta] = \frac{NoK\ Vh}{100M} \qquad \text{II-37}$$

Since the micelles are assumed to be spherical, one can calculate the hydrated volumes of the micelles. (Table II.I.4). It is also possible to estimate the anhydrous volume by using an equation such as (174)

$$Va = M\bar{\nu}/No \qquad \text{II-38}$$

From the above observations, the deviation from theoretically calculated value of $[\eta]$, can be postulated by a quantitative treatment such that one can calculate the weight of water hydrating one gram of surfactant(175,176) using

$$100 \times [\eta] = 2.5(\bar{v} + w\,dw) \qquad \text{II-39}$$

The values obtained are 1.458 g /g.surfactant and 1.841 g /g.surfactant for the anhydrous micelles of C_{10} and C_{12}, which correspond to 22 and 31 water molecules for each monomer of the micelles of C_{10} and C_{12} respectively. It increases with increasing chain length (Table II.I.4).

According to Oncley's(177) calculations, the maximum hydration w compatible with $[\eta] = 0.045$ is 0.6 g /g. surfactant, whereas the limiting w value for $[\eta] = 0.049$ is 0.74 g /g. surfactant. These maximum hydration values refer to spheres. Since we have higher $[\eta]$ than the values given by Oncley, the deviations from given values could be attributed to the heavily hydrated spherical micelles.

This is due to the stronger interactions of the water molecules with the hydrophilic polar head groups in the Stern layer, in terms of hydrophobic interactions. Consequently water molecules are bound to the head groups with possible covalent hydrogen bonds.

The degree of hydration of the micelle undoubtedly depends on the number of counter ions adsorbed in the Stern layer, and the possible interactions between hydrated ions and polar head groups and water molecules.

II.Ih2 - The effects of the aliphatic alcohols.

The nature of the effects produced by alcohols upon the critical micelle concentrations of aqueous solutions of surface active agents is a matter of some dispute. In aqueous solutions containing a certain alcohol concentration, if it is assumed that the alcohol molecule and the soap ion in the micelle dissolve each other according to regular solution theory, then we can write(178)

$$C_S = C_S{}^{\circ}\, N_S\, (N_S + N_A) \;\ldots\; N_S/(N_S + N_A) = 1 \qquad \text{II-40}$$

and

$$C_A = KC_A{}^{\circ}\, N_A/(N_S + N_A) \;\ldots\; N_A/(N_A + N_S) \ll 1 \qquad \text{II-41}$$

The alcohol molecules in bulk solution are in equilibrium with the alcohol molecules in the micelles. Hence we could express the concentration of the alcohol in the mixed micelle

$$C_A \propto N_A/(N_A + N_S)\, \exp\left[-\,(X-X')kT\right] \qquad \text{II-42}$$

if we substitute the molar fraction of the alcohol then we obtain,

$$x \propto C_A \;\; \mathrm{Exp}(m'w)/kT \qquad \text{II-43}$$

The molar fraction of the alcohol in the micelle increases as the bulk concentration decreases, and the equilibrium concentration of soap ion in the bulk decreases in terms of the molar fraction of the soap ion in the micelle. In this work methanol, ethanol, n-propanol and n-butanol have been used as additives to investigate their effect on the formation of micelles, and to study hydrophobic interactions in aqueous solutions of decyl and dodecyl trimethylammonium bromides.

On the addition of a series of alcohols to aqueous solutions of C_{10} and C_{12}, it was observed that the relative viscosities of the systems increased the same as in aqueous solutions, with the increasing concentrations of the alcohols. On the other hand, $[\eta]$ values of the micelles increased also with increasing chain lengths of the alcohol molcules. But it decreased with the increasing concentration of the particular alcohol. (FigsII.11, II.11.A).

The increase in relative viscosity (relative to the solvent) is due to hydrophobic interactions between apolar regions of the soap and alcohol molecules(4,6), OH polar groups and icebergs(123,124,125), the alcohol molecules and polar heads of the amphiphiles(124,125) and the possible binding of the nonpolar parts of the alcohols to the apolar sides of the monomers(122).

The clusters around the nonpolar groups are not much affected by the alcohols at low concentrations, due to their behaviour as structure promoters(97). When the concentrations of the alcohols is increased alcohol rich systems are obtained. Hence the structure of water molecules are destroyed by the alcohols molcules in such systems. Owing to their polymeric characters(118,78), the alcohols molcules increase the hydrogen bonding mechanism by the interactions of water molecules while they associate with polar-OH groups in the solutions.

As has been explained, the effect of the alcohol on the water structure increases with the increasing alcohol concentration. This situation directly affects the micelle formation mechanism, and the micellar shape, size and the structure.

It is universally accepted that the alcohol penetrates into the micellar core through the bulk solution and the Gouy-Chapman-Stern electrical double layer and it changes the electrokinetic property of the system(158,179) forming a mixed micelle.

In the case of asymmetrical particles(175), the specific viscosity of the system is affected by the particle shape and size.

The Einstein equation(126,127) can be rewritten by including rigid particles with non spherical shapes.

$$\lim_{C\to 0}\left[\left(\frac{\eta-\eta_o}{\eta_o}\right)\Big/C\right] = [\eta] = V \times K/100 \qquad \text{II-44}$$

The ratio $\frac{\eta-\eta_o}{\eta_o}\Big/C$ is strongly dependent on the axial ratio of the particles.

The axial ratio of the particle is defined as $a/b = p$ where b is the semiaxis of the revolution, and a is the equatorial radius.

If the ratio is less than 1 the shape is oblate ellipsoid, equal to 1 for sphere and greater than 1 is for a prolate ellipsoid.

For the large value of the axial ratio of the nonspherical rigid particle, Kuhn and Kuhn(181) introduced an equation to calculate the axial ratio for prolate or oblate ellipsoids

$$K = 2.5 + (32/15\pi)(p^{-1}-1) - 0.628(p^{-1}-1)/(p^{-1}-0.075) \qquad 0 < p \leqslant 1 \qquad \text{II-45}$$

$$K = 2.5 + 0.4075(p-1)^{1.508} \qquad 1 \leqslant p \leqslant 15 \qquad \text{II-46}$$

$$K = 1.6 + \frac{p^2}{5}\left(\frac{1}{3(\ln 2p-1.5)} + \frac{1}{\ln 2p - 0.5}\right) \qquad p > 15 \qquad \text{II-47}$$

Other possible effects are the electroviscous effect and hydration. It is apparent that the hydration of the micelles is influenced by the solvation effects of the alcohol molcules. Hence the quantity of the hydration varies with the concentration of the added alcohol.

Since the frictional dissipation energy exists in the system due to the presence of the assymetrical particles, it is reasonable to introduce these two effects, shape and size of the micelle as driving forces to increase the $[\eta]$ viscosities of the micelles.

The results of measurements of C_{10} and C_{12} in aqueous solutions containing varying amounts of methanol show that the C_0 decreases up to a certain concentration (5.88×10^{-2} m.dm^{-3} and 1.2×10^{-2} m.dm^{-3} for C_{10} and C_{12} respectively. Tables II.I.2, II.I.3, Fig.II.9), then increases gradually as the concentration increases.

Brown et al.(182) showed that the C.M.C. of dodecylammonium chloride in methanol-water mixture first decreases, then the C.M.C. shows a marked shift on the equivalent conductance - $\sqrt{c}$ curve at the higher concentration. Similar effects have been observed by Evers(183) and Grieger(184) in aqueous solutions of hexadecyl and octadecyl quaternery ammonium salts.

It is apparent that methanol has a less hydrophobic group than the other lower alcohols. Hence it has a less structure promoting effect(97), which does not increase water structure, due to its proton acceptor(116) character. Consequently the hydrophobic interactions are weakened in the mixed solution. Since the methanol molecules are oriented with respect to water molecules, the solubilization involves penetration of the methanol molecules into the micelles. This(185) penetration phenomenan occurs with the polar groups orientated towards water and the hydrocarbon chain lying between those of the soap molecules in the micelles. However the lower dielectric constant might affect the dielectric distribution of the micelles and their kinetic properties.

At low dielectric constant, the stability of the micelle increases due to a decrease in the degree of dissociation of the micelle.

The micellar properties in the methanol-water systems could be attributed to those factors which have been discussed, ethanol behaves in the same way (Fig.II.9). Its dielectric constant lowering effect is greater than that of methanol. It has also higher hydrophobic side which favours hydrophobic interactions between various orientations of the molecules in terms of its higher proton acceptor capacity(116).

The behaviour of other alcohols are more complex. It is generally accepted that the additions of n-PrOH and n-BuOH even at low concentrations decrease the C_o(158,186). This decreasing effect in BuOH is higher than that of n-PrOH (TablesII.I.2,B,C,II.I.3.B,C, Fig.II.9). The decrease of the C_o is due to the decrease of free energy of the system, and the surface charge density, in terms of the entropy effect of the hydrophobic interaction in the mixed solution.

Those alcohols have longer chain lengths than that of previous alcohols and at low concentrations they increase water structure(97). On the other hand the hydrophobic interactions are more favourable between possible orientated configurations. They react more effectively because they are stronger proton acceptors. The lower dielectric constant causes ion-pair formation in these systems. The observed micellar molecular weight from light scattering shows an increase with the addition of 1M C_2H_5OH, then it decreases as the concentration increases. (Chapter VI).

The addition of alcohol to the system affects the hydrodynamic properties of micelles. The increase in relative viscosity (Fig.II.7, Table,II.I.2,1.2148 for C_{10} of 0.1 $m.dm^{-3}$ containing 1M CH_3OH) is higher compared with the respective viscosity (1.0761, Table II.I.1) of aqueous solution of C_{10}. This increase is due to solute-solute, and solvent-solute interactions. It shows an increase with increasing concentration of alcohol (1.321 and 1.4103 for C_{10} containing 2M and 3M CH_3OH respectively).

However the observed $[\eta]$ of micelles is less (0.0415 $g.dl^{-1}$ and 0.056 $g.dl^{-1}$ for C_{10} containing 1M CH_3OH and 1M C_2H_5OH Tables II.I.2, II.I.2.A) than that of aqueous solution (0.06 $g.dl^{-1}$ Table II.I.1). The solutions containing various concentration of C_3H_7OH and C_7H_9OH show a similar pattern (Tables II.I.2.B,C, II.I.3.B,C).

The decrement in $[\eta]$ of micelles is due to the effect of alcohols on the hydration of micelles, and the electroviscous(42,43,44) effect. In this work observations indicate that the number of water molecules bound to the micelles decreases as the concentration increases (decrement in hydration) and a similar effect is postulated for the electroviscous effect in the micellar system. As can be seen in Fig.II.12, $[\eta]$ increases non linearly as the chain length of alcohol molecule increases. After 1M C_2H_5OH, on the addition of 1M C_3H_7OH

the increment in $[\eta]$ is not significant (0.0495 g.dl^{-1} for C_{12}) compared with the same solution containing 1M C_2H_5OH (0.044 g.dl^{-1}).

The $[\eta]$ of micelles decreases when the number of carbon atoms in alcohol molecules is higher than three. (Fig.II.12). Hence, it is apparent that the dehydration effect of alcohols increases as the straight chain length increases. Although $[\eta]$ decreases with concentration, and alcohol molecules behave as a structure breaker at high concentration, the increment in relative viscosity can be attributed to the change of micellar shape, and size of the micelle. According to light scattering data the AMW of micelles first increases, (5.263×10^4 and 4×10^4 for C_{12} containing 1M C_2H_5OH and 0.5MC_3H_7OH respectively, Chapter VI) then decreases with increasing concentration.

The shape function of the micelles has been calculated using equation (II-44) (4.7 and 3.9 for C_{12} containing 1M and 2M C_2H_5OH respectively Table II.I.5). Then the axial ratio of the micelle (4.1 and 3.3 for the mixed micelle of C_{12} containing 1M and 2M C_2H_5OH respectively Table II.I.5) has been determined by substitution of the shape function into equation (II-46). The observed shape functions and axial ratios are comparable with the data given by Mehl et al.(169), and Scheraga(170) for oblate and prolate particles.

The obtained viscosity, and light scattering data for alkylammonium bromides introduce the idea that the micelles are of the prolate type rather than the other shapes. The stability of micelles has been discussed by Emerson-Holtzer(179) in terms of hydrophobic interactions, temperature effect, and the dielectric effect of the medium. They have concluded that as the temperature increases, the stability of micelles (DTAB and SDS) decreases. The lowering dielectric constant of the medium, and rise in temperature behave as micelle breakers since the repulsive forces between the head groups increase.

As has been discussed in this section, and in Section II.Ic, the effect of decreasing the dielectric constant of the medium increases as the alcohol chain length increases. The hydrophobic character of the alcohol molecule behaves as structure promoting at low concentration, due to an increase in structural order of water molecules.

The micellar properties at low temperature have been interpreted by means of the predominance of hydrophobic interactions over the dielectric effect of medium, and at high temperature the dielectric effect over the hydrophobic interactions(179). But at any particular temperature, two factors have been introduced for the stability of mixed micelles.

1) The effect of hydrophobic surface, through the contribution of free energy of the hydrocarbon chain to the micellization.
2) The increment in the effect of dielectric constant of the medium when it is lowered by the addition of alcohol molecule.

Due to these factors the mixed micelles are more stable than the ordinary micelles at low concentrations of alcohol. But the hydrophobic interactions between the hydrocarbon chains near the micelle surface is considerably changed.

The deeper penetration of alcohol molecules disrupt the contact of the monomers. The effect of alcohol molecules on the stability of the micelle increases with increasing concentration and chain length. Consequently at higher concentration they break the micelles, while they disrupt the hydrophobic interactions between water networks and monomers.

In the light of this observation, it is reasonable to assume that the effect of the dielectric constant of the medium on the dipole orientation and dielectric distribution(36) of molecules, causing a change in electrokinetic properties of micelles, and hydrophobic interactions play an important role in the stability of mixed micelles.

II.Ii - Conclusions.

The observed micellar properties of alkyltrimethyl ammonium bromides in aqueous solution, and such solutions containing aliphatic alcohols, have been investigated by a viscosity method, surface tension measurement and light scattering data.

It is apparent that micelle formation is an entropy directed process, which is directed by hydrophobic interactions, which operate between the possible orientated configurations, and highly structured hydrogen bonded water molecules.

The observations indicate that the intrinsic viscosity of the micelles increases as the hydrocarbon group increases.

The increment in $[\eta]$ has been discussed in terms of the electroviscous effect, hydration and hydrophobic interactions between non-polar-polar groups.

On the addition of aliphatic alcohol to aqueous solutions of surfactants, due to the penetration of alcohol into interior of the micelle, the micellar properties are altered. Although the increase in relative viscosity is higher compared with the aqueous solution, the increment in $[\eta]$ is not significant compared with $[\eta]$ in aqueous solution. This observation has been attributed to the decrement in hydration, and electroviscous effect. The decrement in $[\eta]$ increases as the alcohol concentration increases.

On the other hand, the increment in relative viscosity, and $[\eta]$ have been discussed in terms of the changed micellar shape, and hydrophobic interactions. Possible shapes have been examined for the mixed micelles in terms of shape function, and axial ratio of the micelles.

The combination of the hydrodynamic and light scattering data indicate that the mixed micelles are prolate shaped, while the micelles of surfactants in aqueous solution are spherical. However, the observed C_o on the addition of methanol and ethanol to the system differs appreciably from that found with propanol and butanol. The C_o decreases up to a certain concentration with addition of organic additive, then it increases (methanol and ethanol).

In the case of higher alcohols C_o decreases with increasing concentration. The effect of alcohols on C_o has been discussed by means of hydrophobic interactions between alcohol, surfactant and water molecules. Alcohols at low concentration have structure promoting effect while they behave as structure breakers at high concentration.

Dipole orientation of the molecules due to the decrement in dielectric constant of the solution also contributes to the effects found.

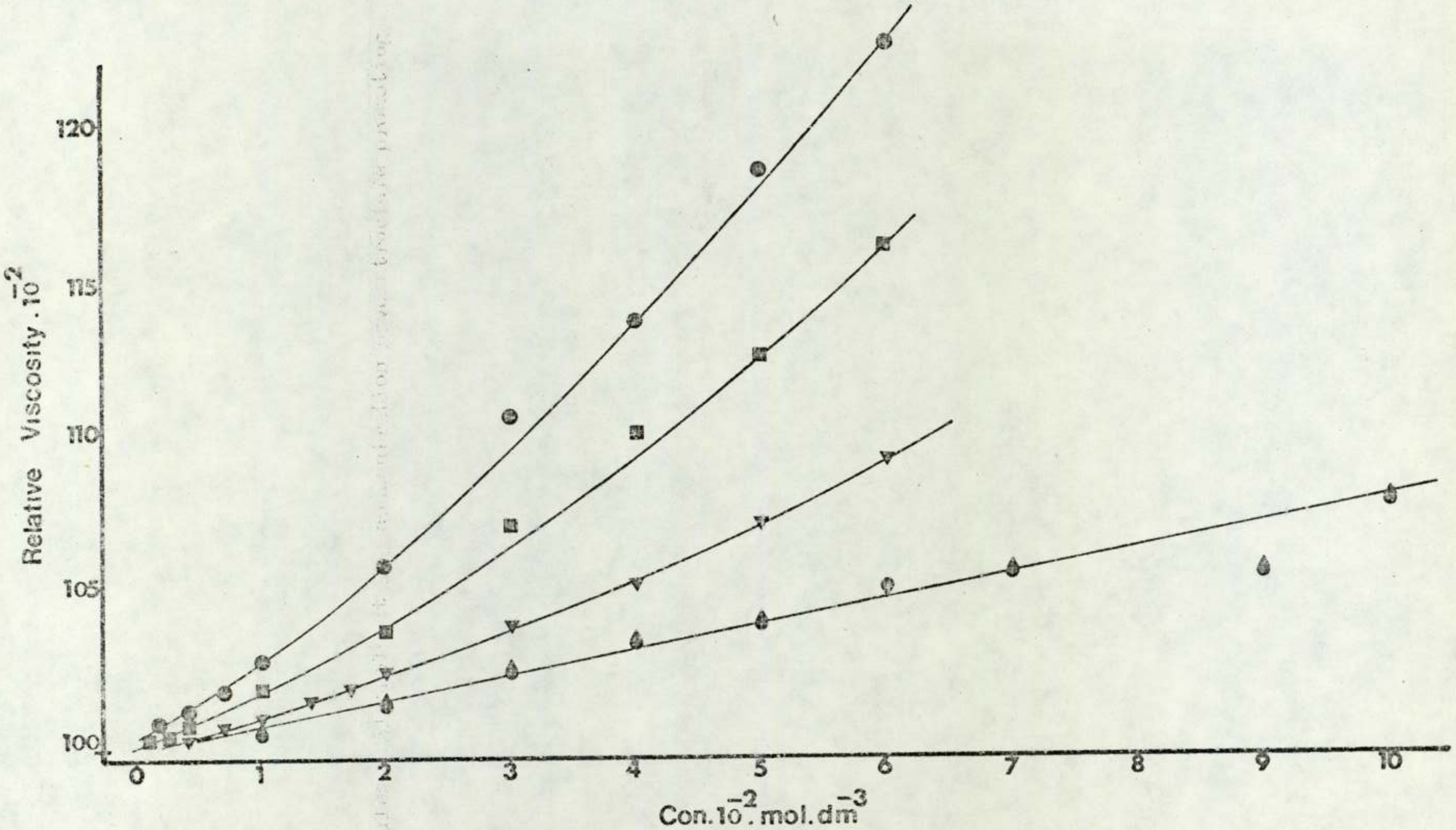


Fig. II.1 Plots of the relative viscosities versus concentration for the alkyltrimethyl ammonium bromides in water at 25° C; ♦ C_{10}, ▲ C_{12}, ■ C_{14}, and ● C_{16}

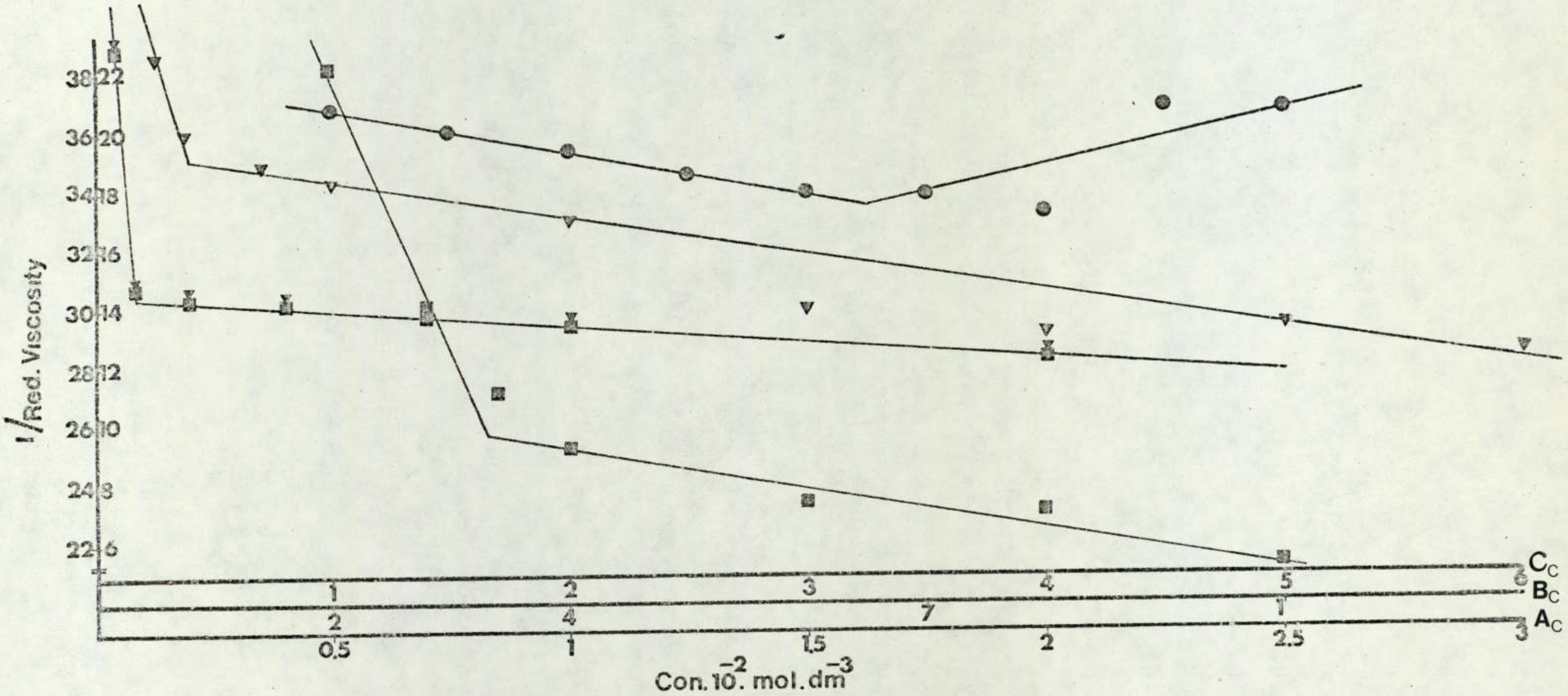


Fig. II.2 Reciprocal reduced viscosity as a function of the concentration of alkyltrimethyl ammonium bromide at 25° C; ● C_{10}, ■ C_{12}, ▲ C_{14}, and ■ C_{16}; B_C C_{10}, C_C C_{12}, and A_C C_{14}, C_{16}

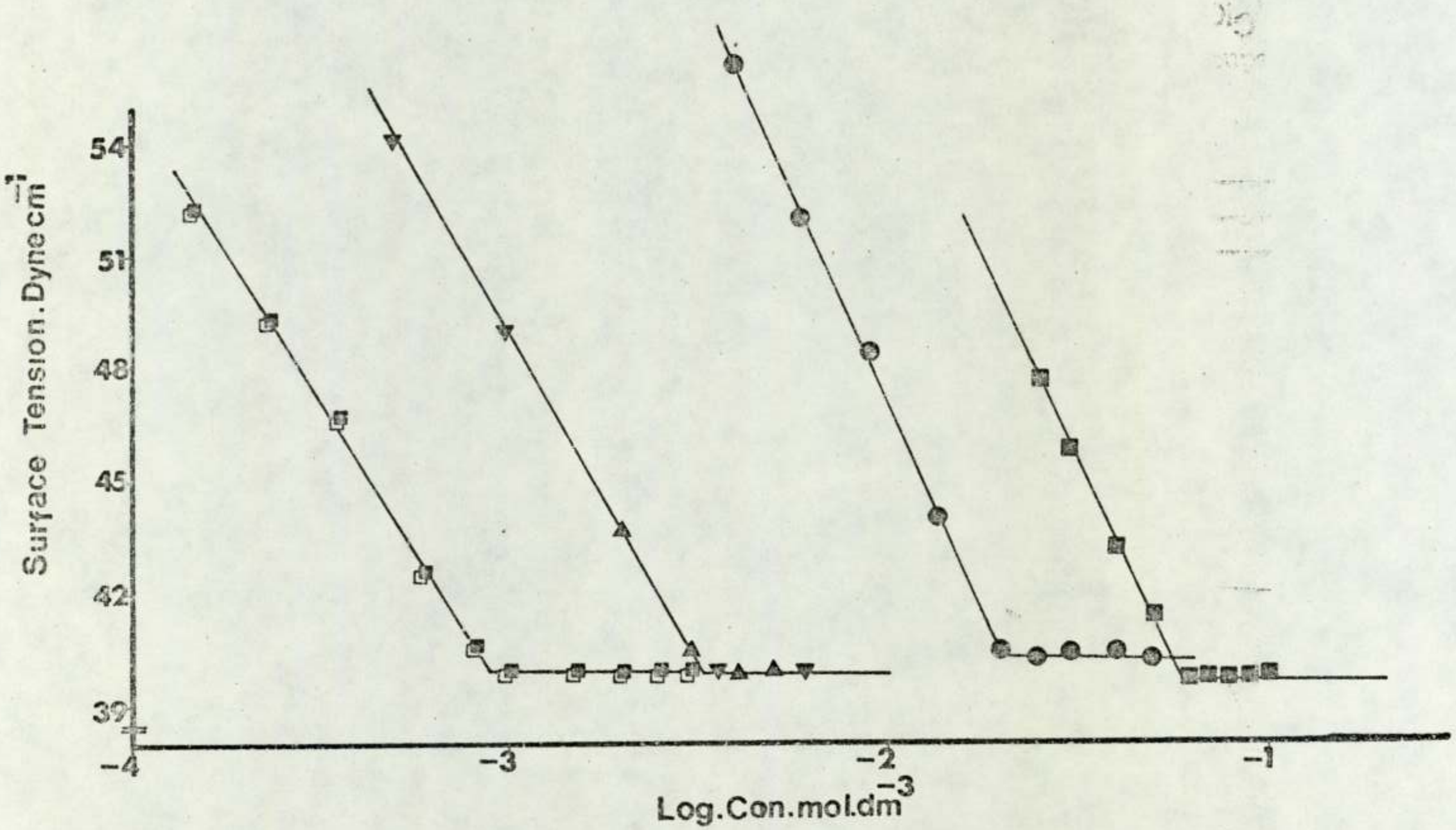


Fig. II.3 Surface tension versus log. concentration curves for the alkyltrimethyl ammonium bromides at 25° C; ■ C_{10}, ● C_{12}, ▲ C_{14}, and ▣ C_{16}

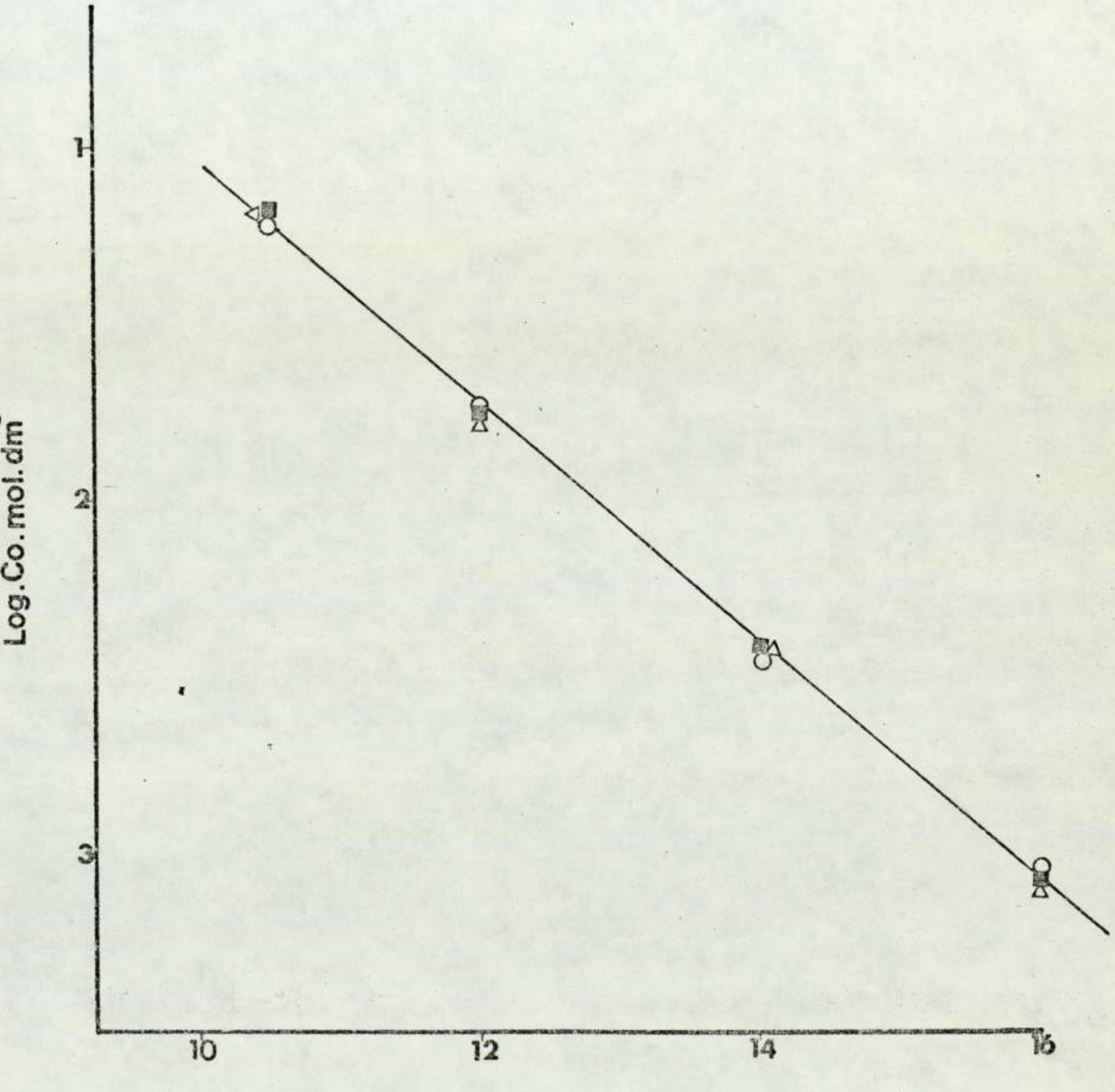


Fig.II.4 The variation of log. Co of alkyltrimethyl ammonium bromide with the hydrocarbon chain length at 25° C; ■ Viscosity, ○ Surface Tension, △ Light Scattering

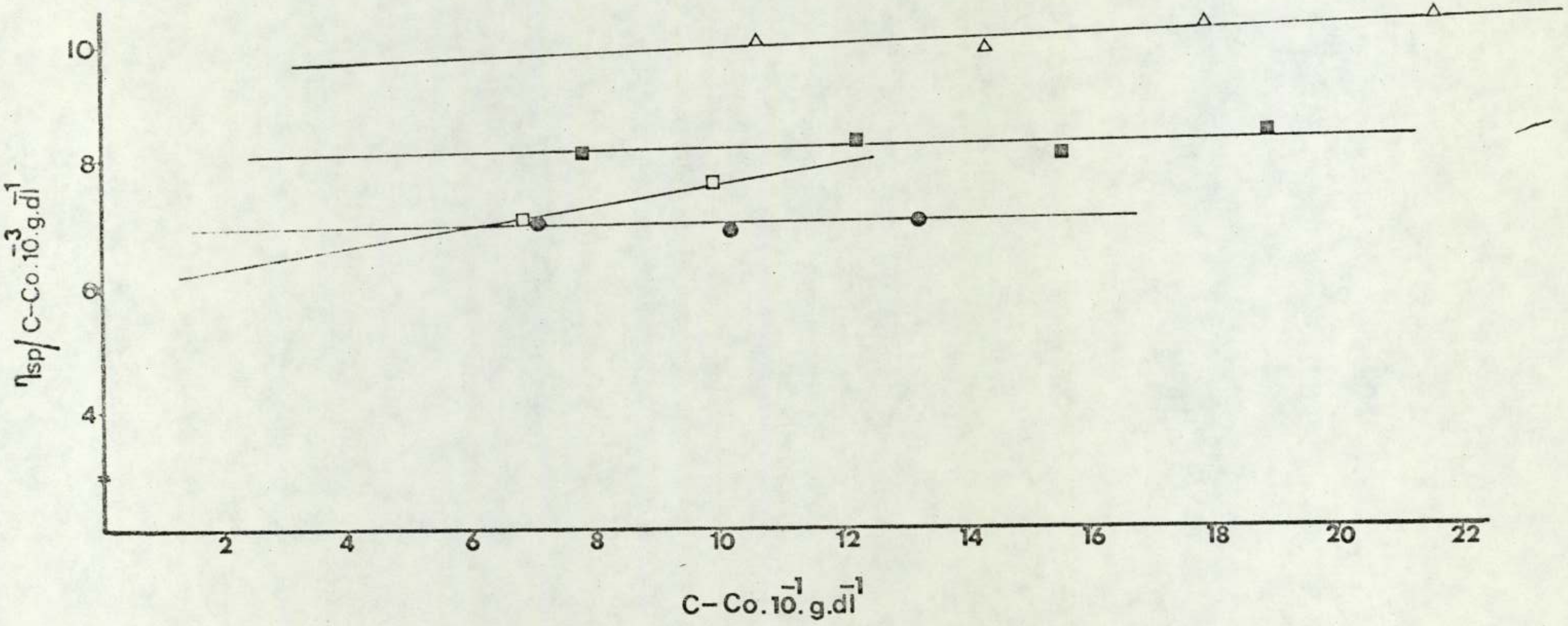


Fig. II.5 Plots of reduced viscosity versus concentration for the alkyltrimethyl ammonium bromides in water at 25° C; □ C_{10} , ● C_{12} , ■ C_{14} , and △ C_{16}

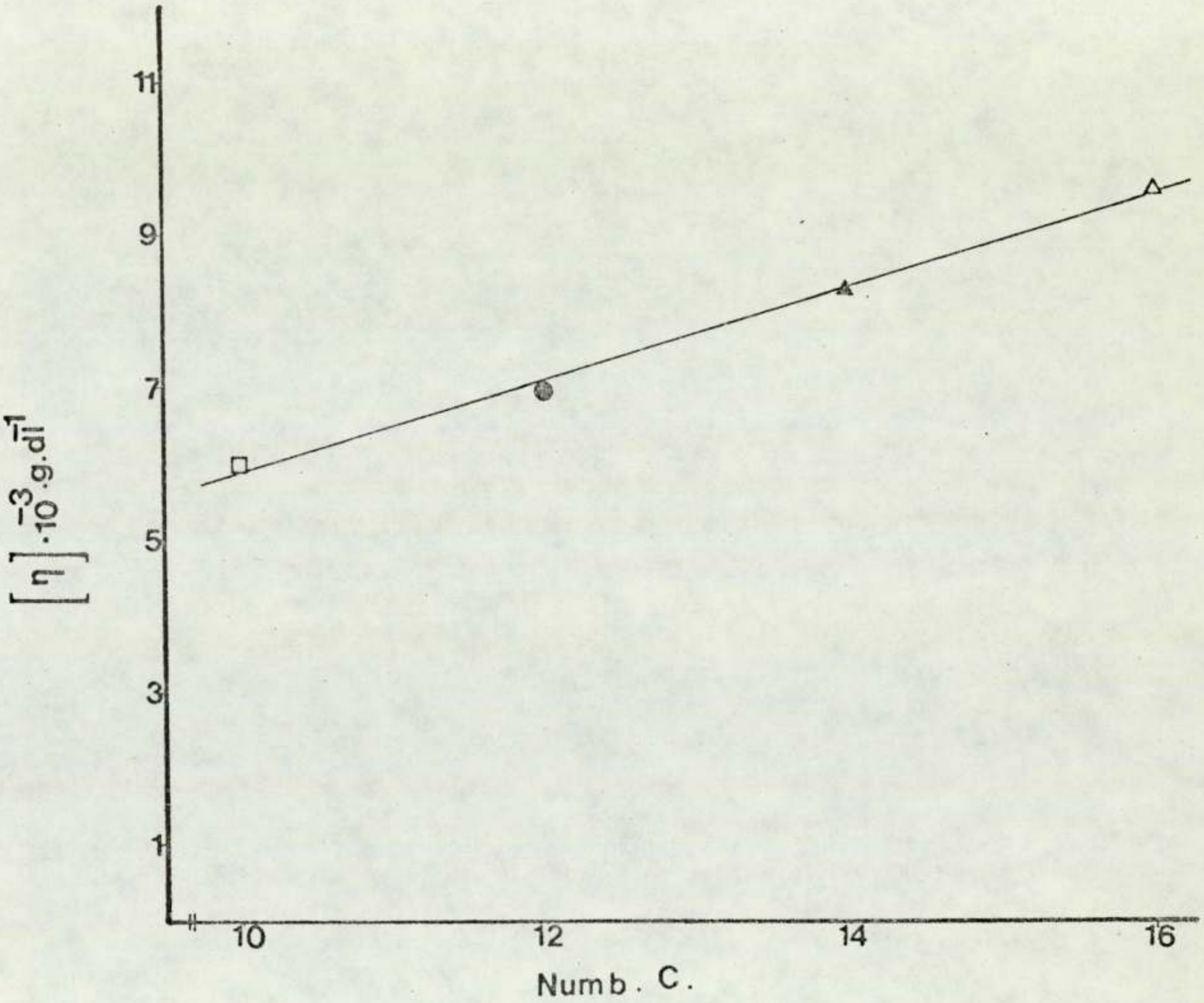


Fig. II.6 Dependence of the intrinsic viscosity of Co of the alkyltrimethyl ammonium bromide on the hydrocarbon chain length at 25° C;

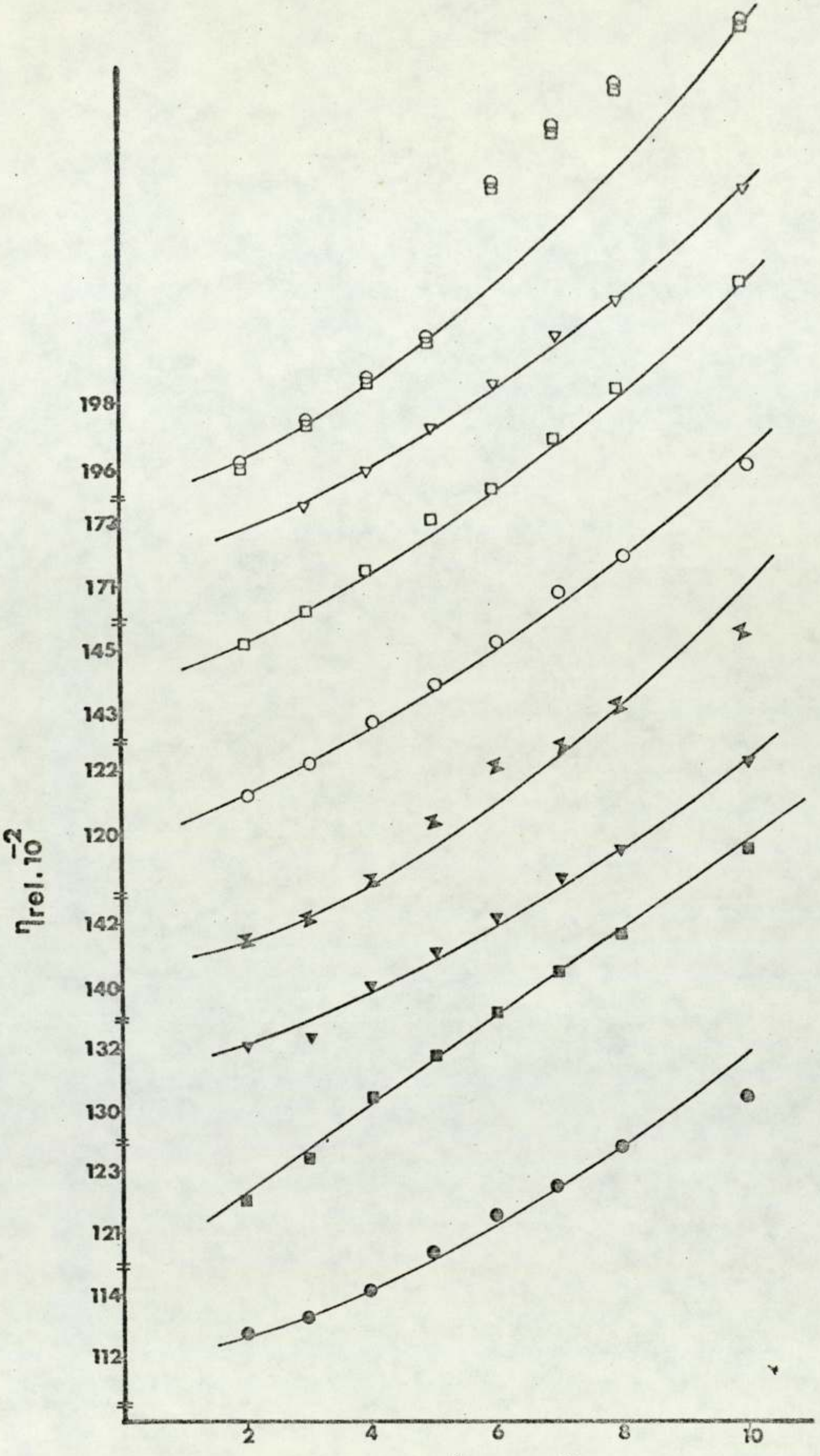


Fig. II.7 Relative viscosities versus concentration of the decyltrimethyl ammonium bromide containing various concentration of the aliphatic alcohols in water at 25° C; Me-OH: ● 1M, ▪ 2M, ▲ 3M, and ⧗ 4M; Et-OH: ○ 1M, □ 2M, △ 3M, and ⊜ 4M

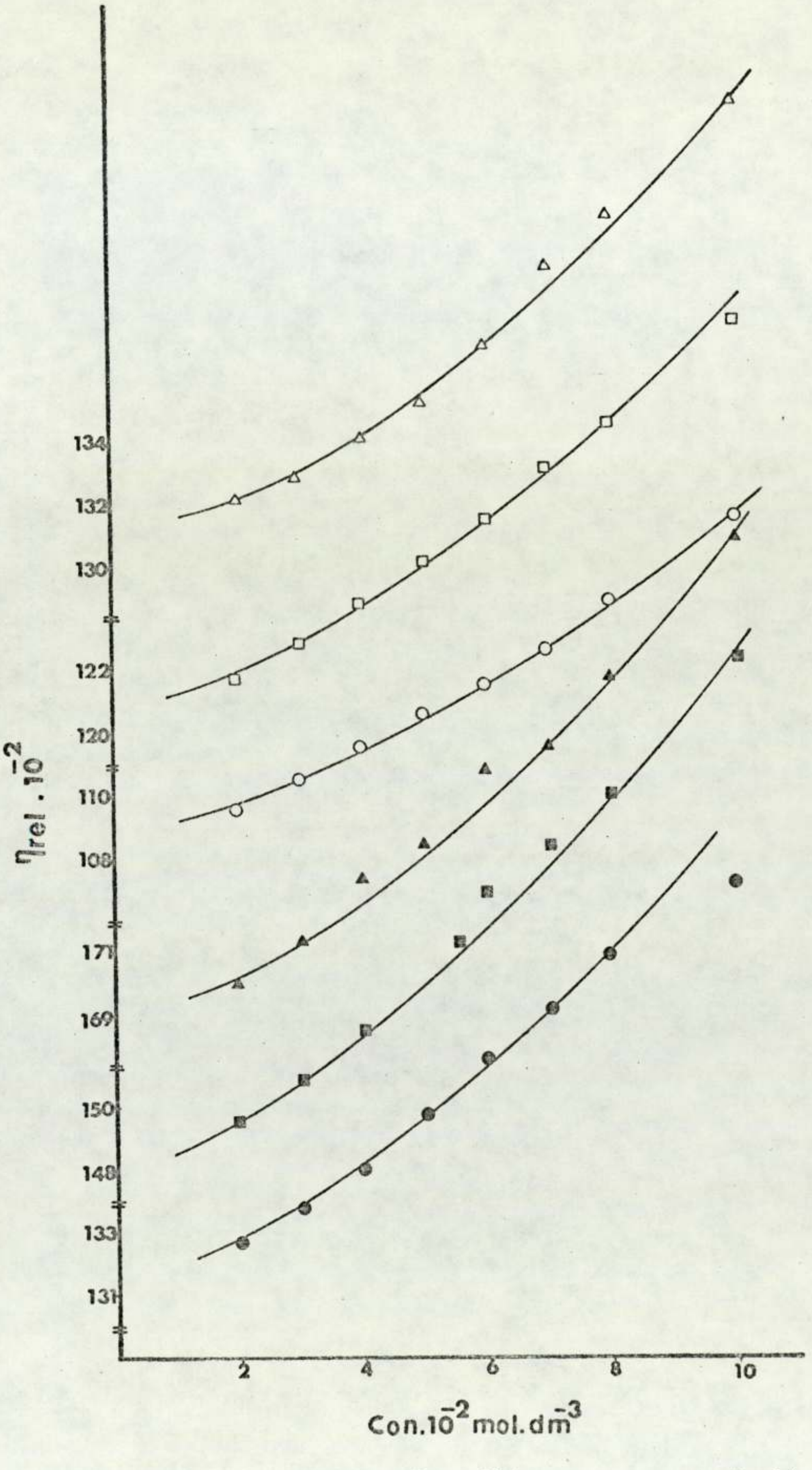


Fig. II.7.A. Relative viscosities versus concentration of the decyltrimethyl ammonium bromide containing various concentration of the aliphatic alcohols in water at 25° C; Pr-OH: ● 1M, ■ 1.5M, and ▲ 2M; Bt-OH: ○ 0.2M, □ 0.5M, and △ 0.8M

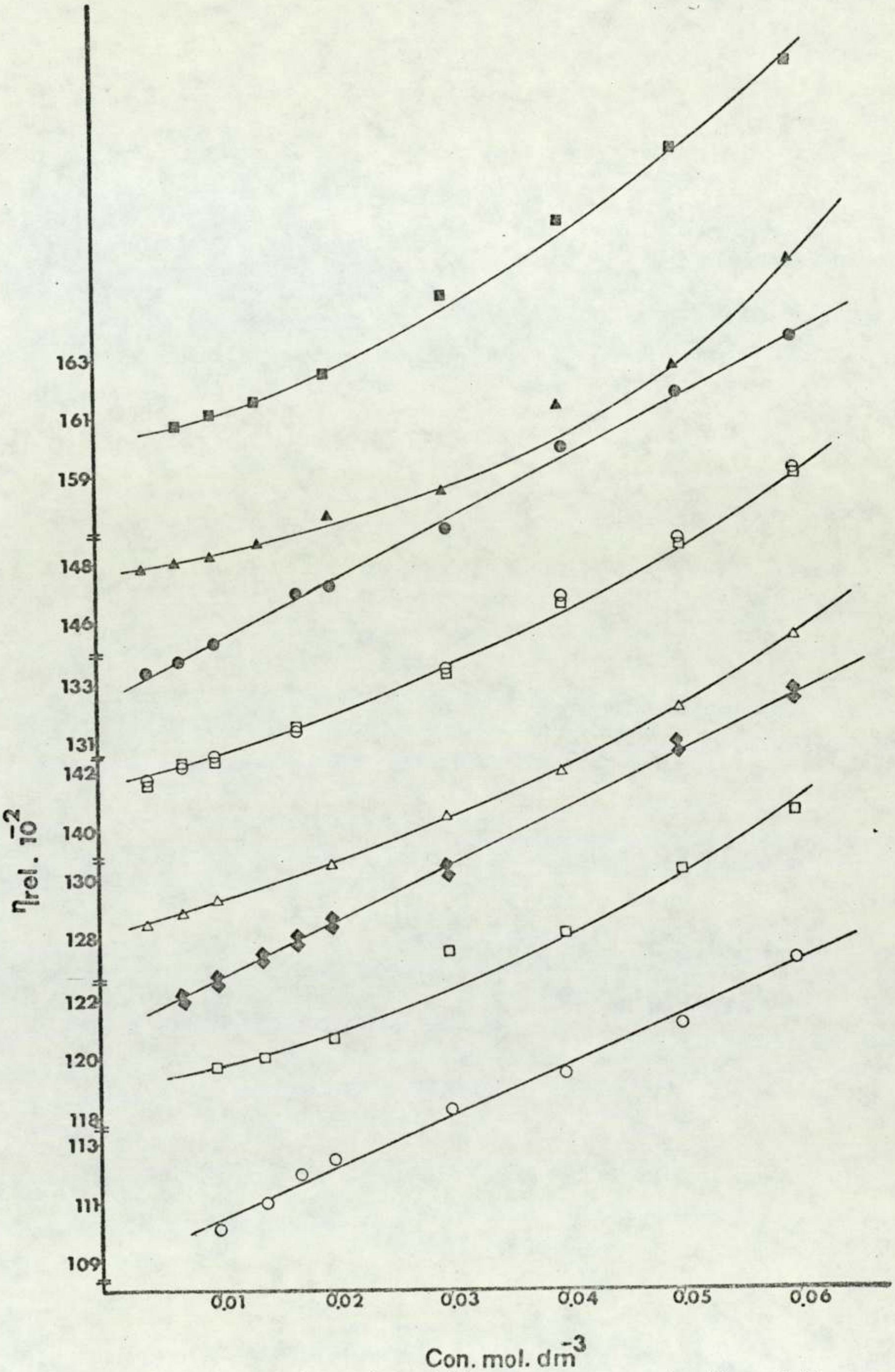


Fig. II.7.B Relative viscosities versus concentration of the dodecyltrimethyl ammonium bromide containing various concentration of the aliphatic alcohols in Water at 25° C; Me-OH: ○ 1M, □ 2M, △ 3M, and ⊟ 4M; Et-OH: ◆ 1M, ● 1.5M, ▲ 2M, and ■ 2.5M

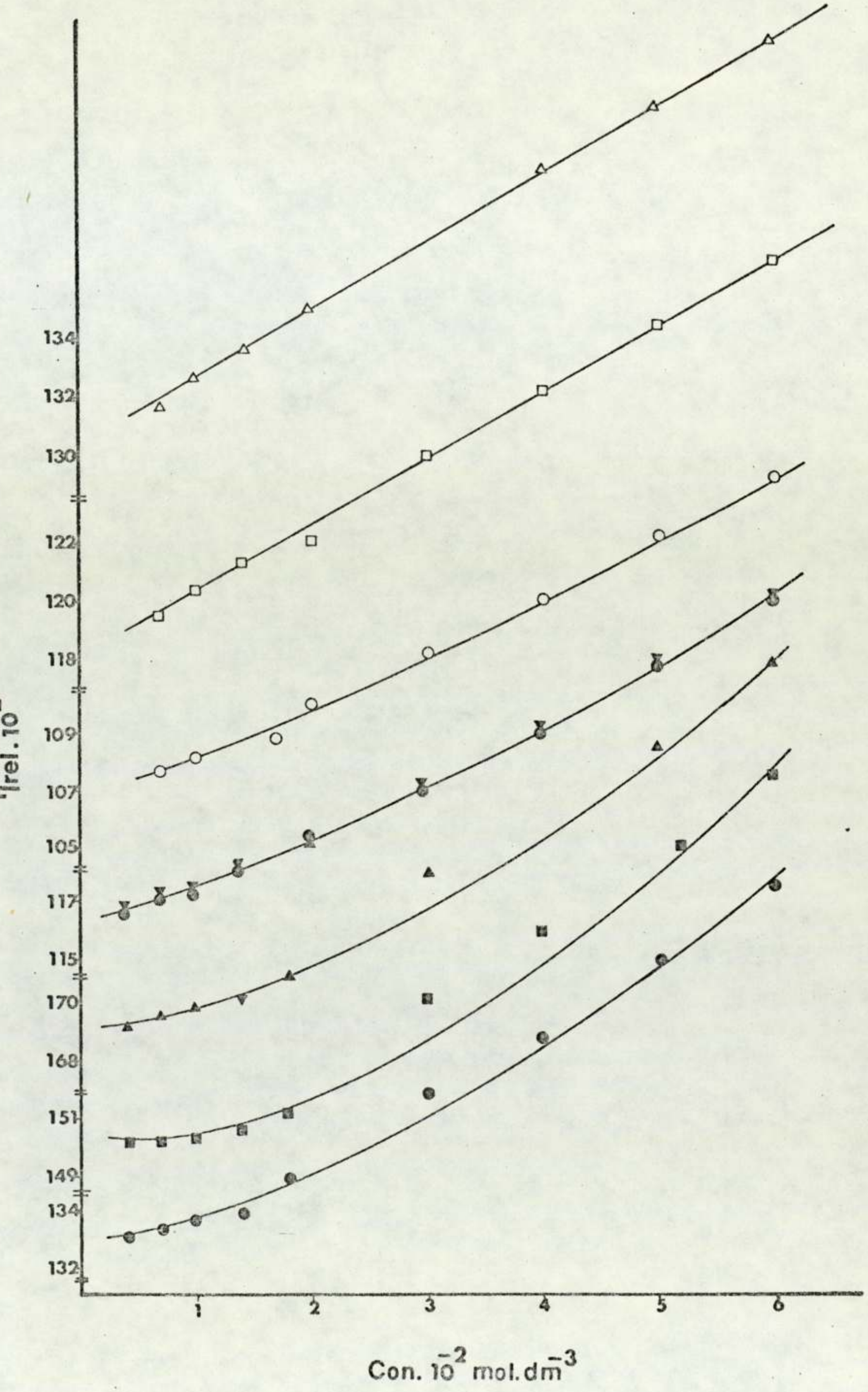


Fig. II.7.C Relative viscosities versus concentration of the dodecyltrimethyl ammonium bromide containing various concentration of the aliphatic alcohols in Water at 25° C; Pr-OH: ● 1 M, ■ 1.5M, ▲ 2 M, and ⧗ 0.5 M Bt-OH: ○ 0.2M, □ 0.5 M, and 0.8 M

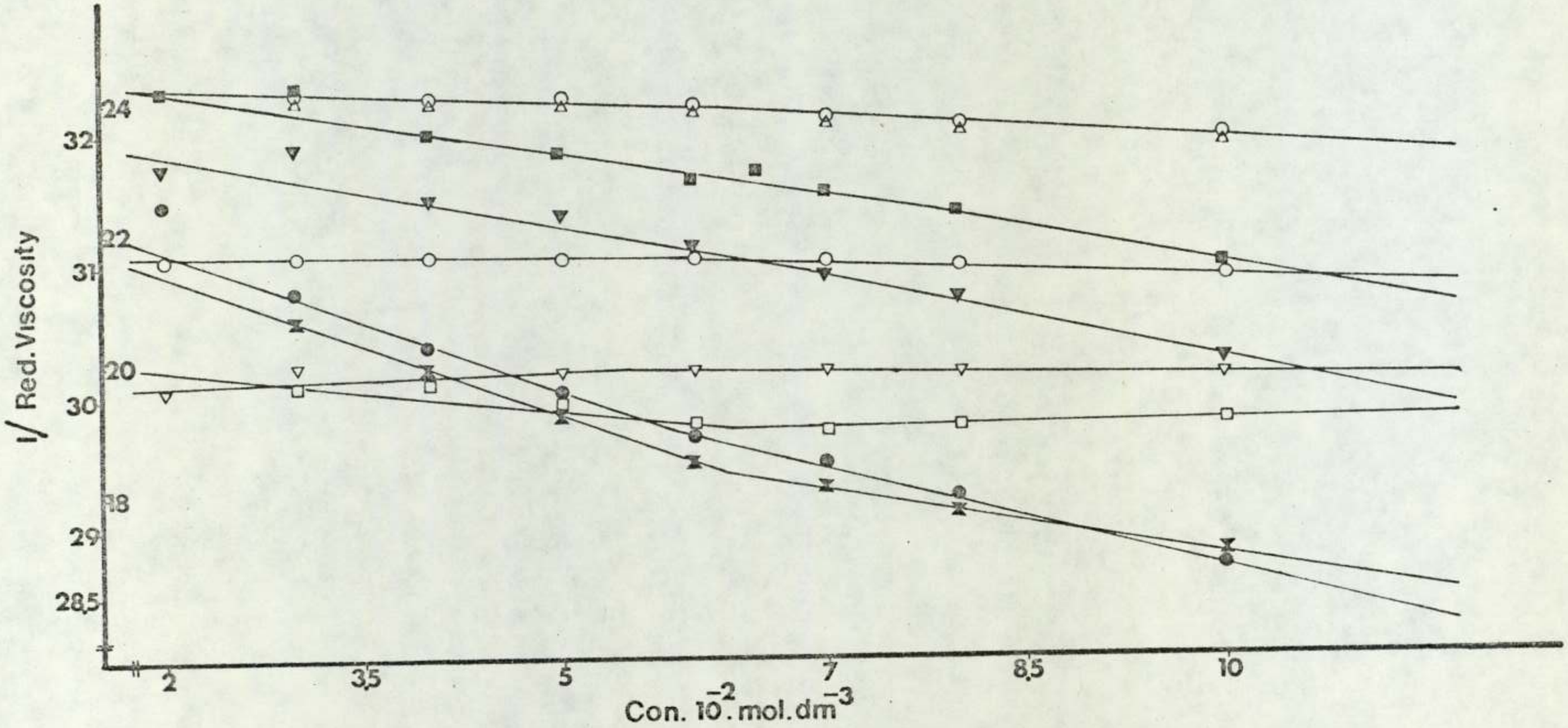


Fig. II.8 Reciprocal reduced viscosities as a function of the concentration for the decyltrimethyl ammonium bromide containing various concentration of methanol and ethanol in water at 25° C; Me-OH: ⧗ 1M, ● 2 M, ▲ 3M, and ■ 4 M, Et-OH: ○△ 1 M, ○ 2 M, △ 3 M, and □ 4 M

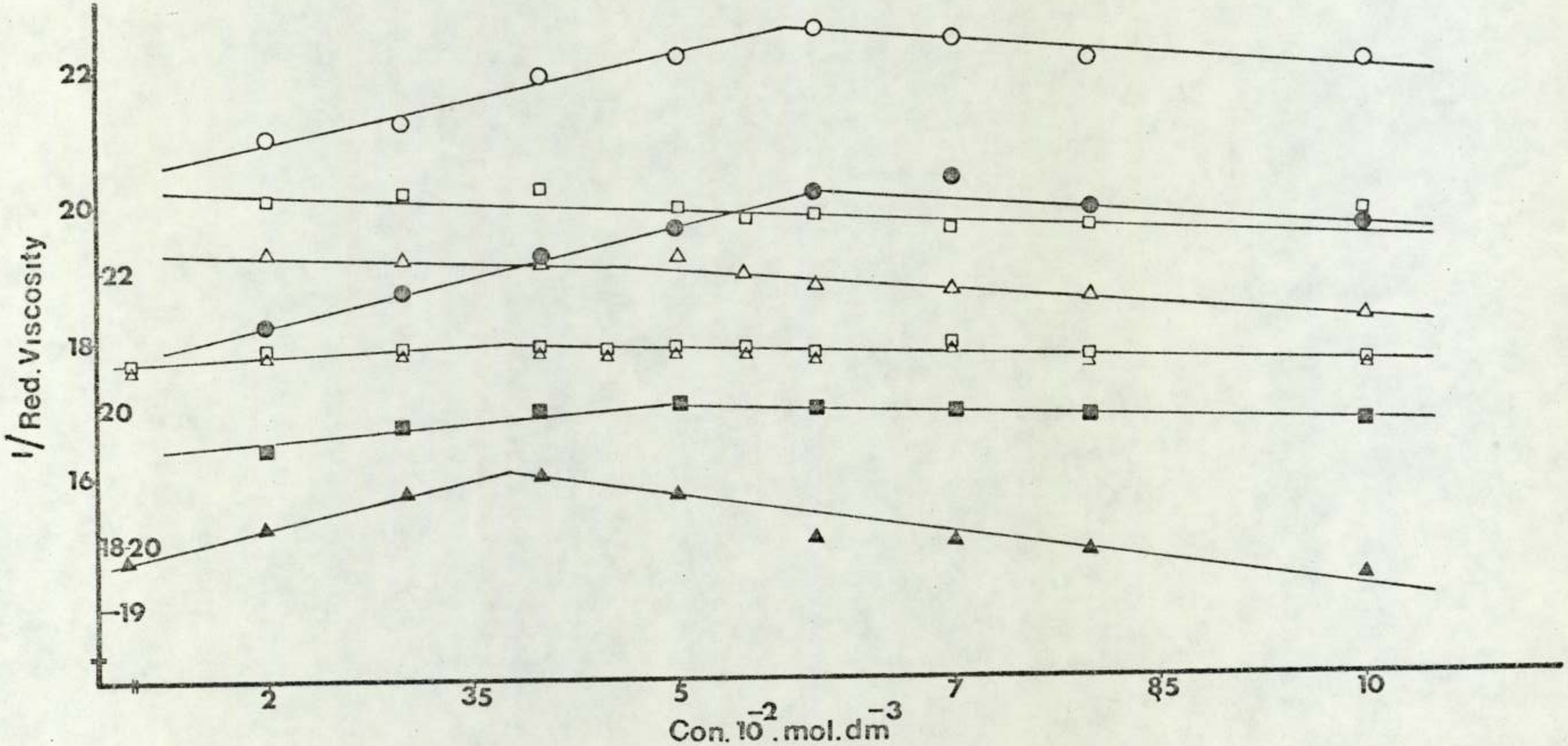


Fig. II.8.A Reciprocal reduced viscosities as a function of the concentration for the decyltrimethyl ammonium bromide containing various concentration of propanol and butanol in water at 25° C;
Pr–OH: ○ 0.5 M, □ 1 M, △ 1.5 M, and ⊠ 2 M, Bt-OH: ● 0.2, ■ 0.5 M, and ▲ 0.8 M

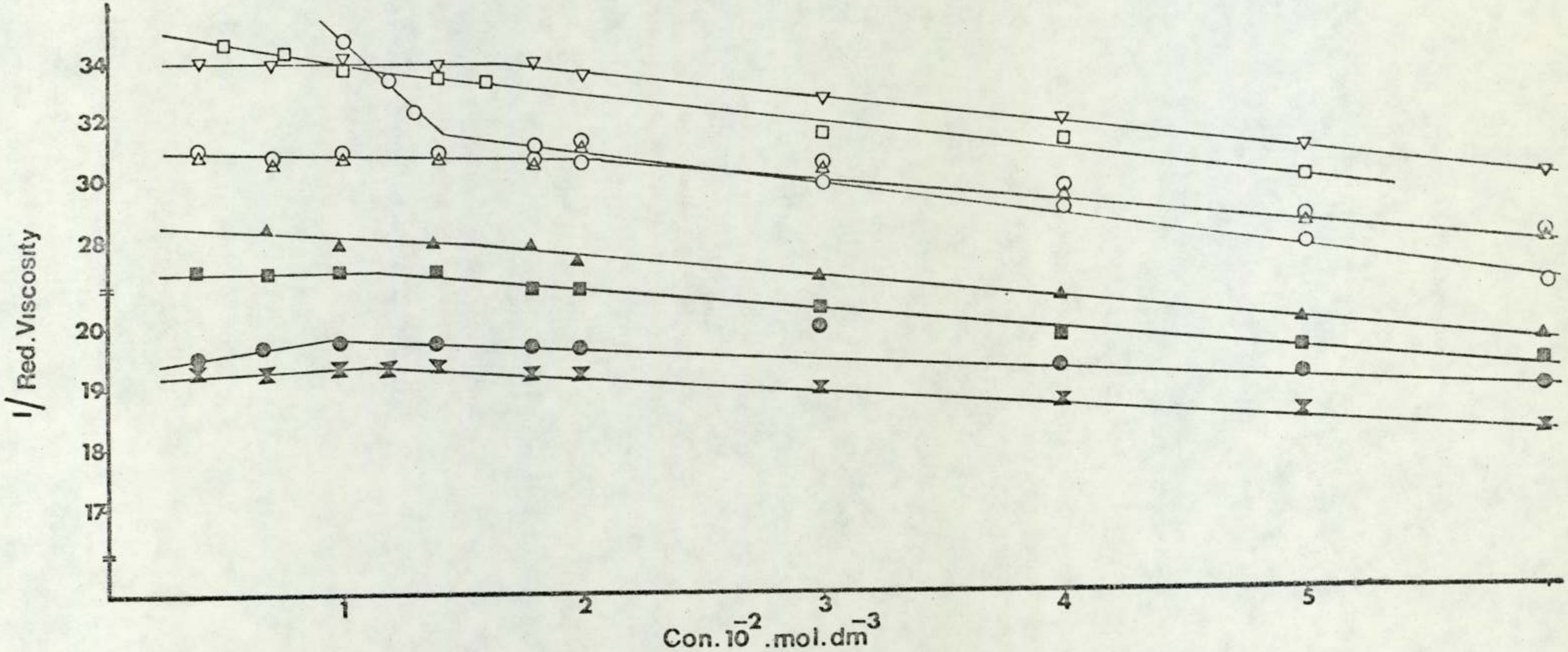


Fig. II.8.B Reciprocal reduced viscosities as a function of the concentration for the dodecyltrimethyl ammonium bromide containing various concentration of methanol and ethanol in water at 25° C;
Me–OH: ○ 1 M, □ 2 M, △ 3 M, and ⊗ 4 M, Et–OH: ▲ 1 M, ■ 1.5 M, ● 2 M, and ⧗ 2.5

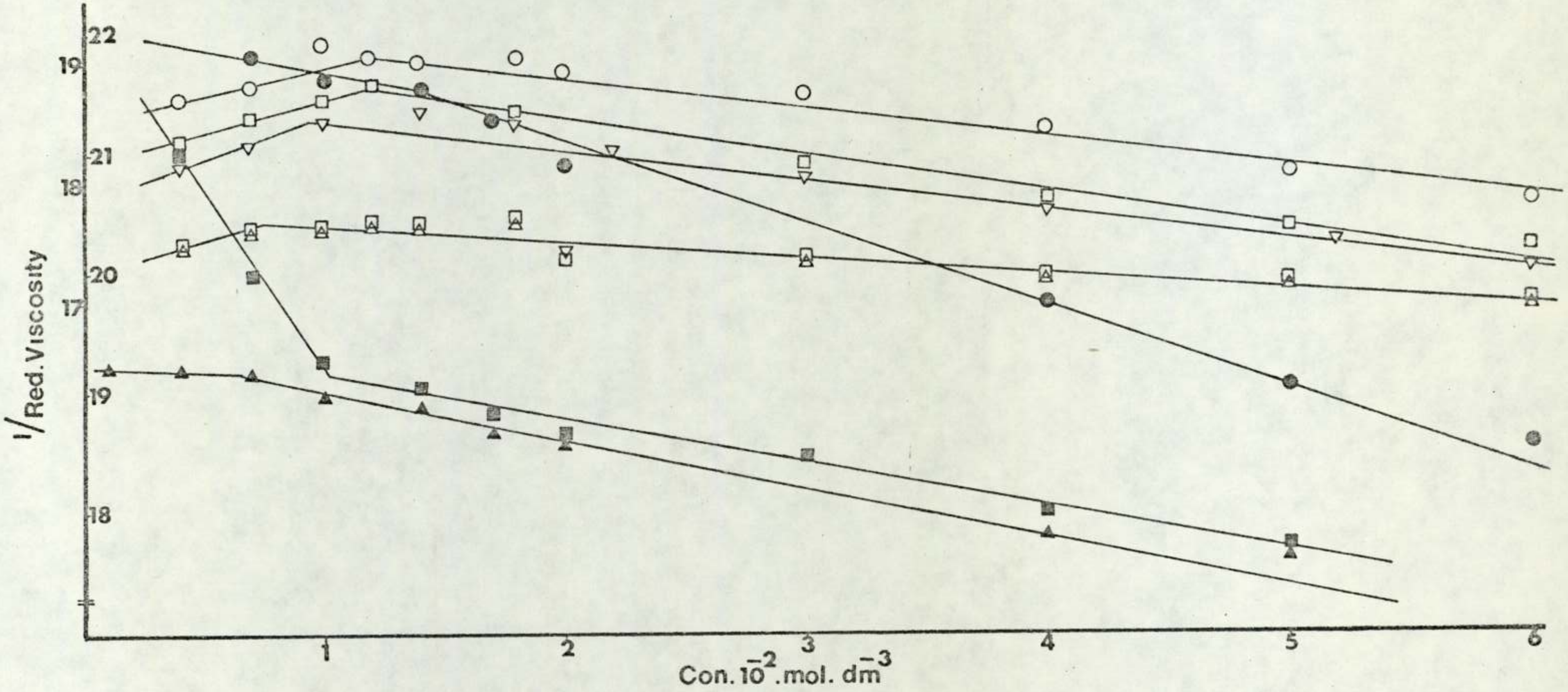


Fig. II.8.C Reciprocal reduced viscosities as a function of the concentration for the dodecyltrimethyl ammonium bromide containing various concentration of propanol and butanol in water at 25° C;
Pr-OH: ○ 0.5 M, □ 1 M, △ 1.5 M, and ⊠ 2 M, Bt-OH: ● 0.2 M, ■ 0.5 M, and ▲ 0.8 M

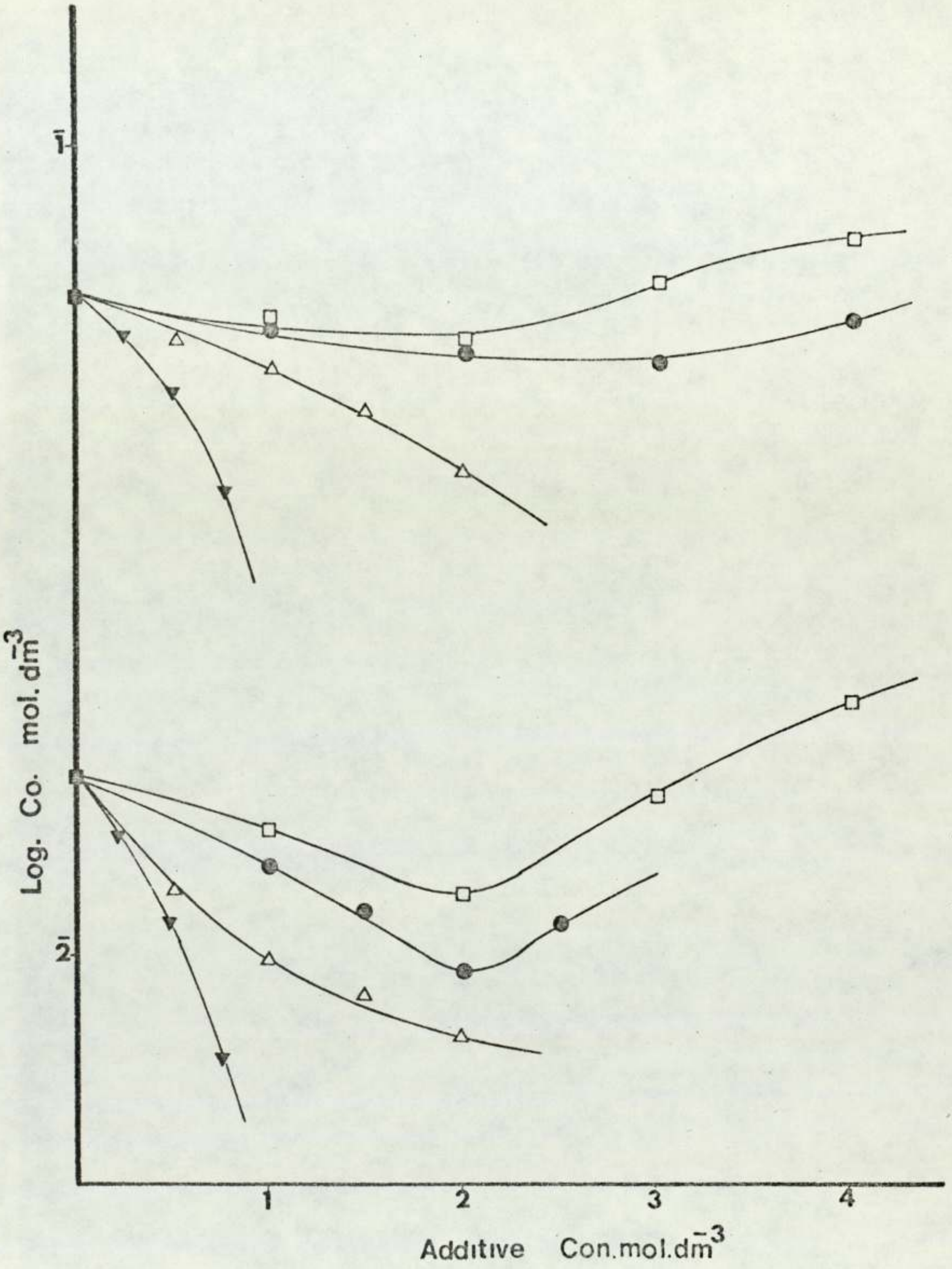


Fig.II.9 The effect of the various concentration of aliphatic alcohols on the Co of alkyltrimethyl ammonium bromides at 25° C; C_{10} : □ Me-OH, ● Et-OH, △ Pr-OH, and ▼ Bt-OH; C_{12} : □ Me-OH, ● Et-OH, △ Pr-OH, and ▼ Bt-OH

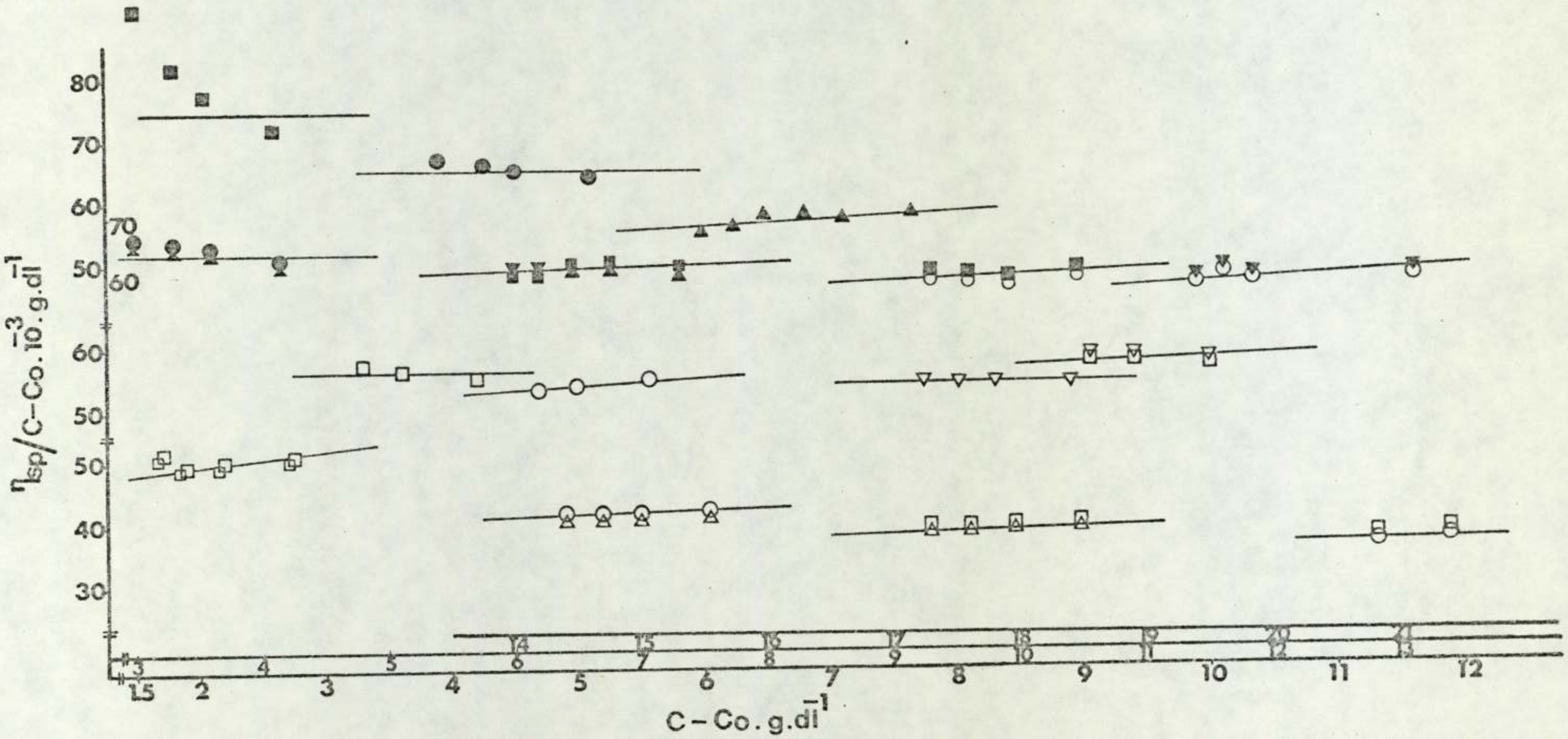


Fig. II.10 Dependence of the reduced viscosity of decyltrimethyl ammonium bromide on the concentration of aliphatic alcohols at 25° C; Bt-OH: ■ 0.2 M, ● 0.5 M, and ▲ 0.8M, Pr-OH: ● 0.5 M, ⧗ 1 M, ⧗ 1.5 M, and ○ 2 M Et-OH: □ 1 M, ○ 3 M, △ 2 M, and ▽ 4 M, Me-OH: ⊞ 1 M, ○ 2 M, ⊠ 3 M, and ⊟ 4 M

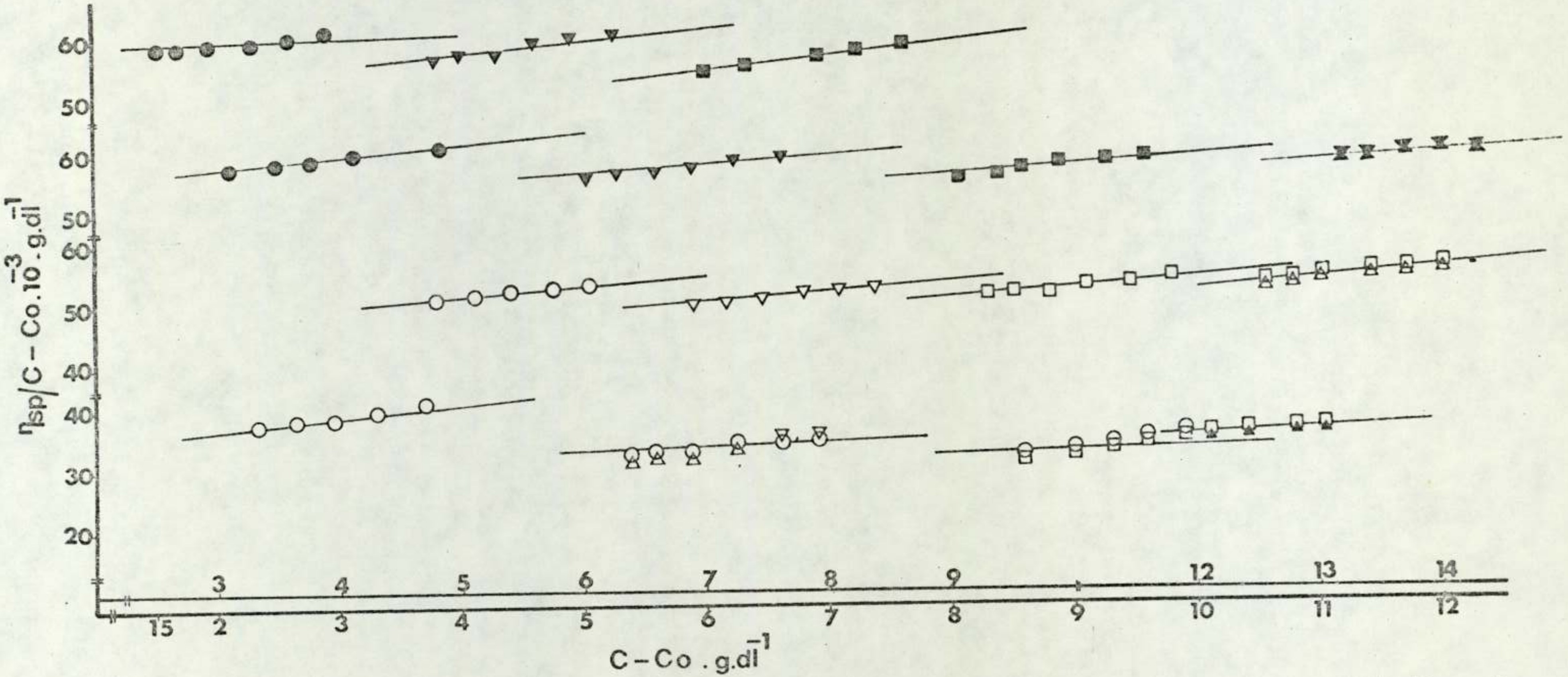


Fig. II.10.A Dependence of the reduced viscosity of dodecyltrimethyl ammonium bromide on the concentration of aliphatic alcohols at 25° C; Bt-OH: ● 0.2 M, ▽ 0.5 M, and ■ 0.8 M, Pr-OH: ● 0.5 M, ▼ 1 M, ■ 1.5 M, and ⧗ 4 M, Et-OH: ○ 1 M, △ 1.5 M, □ 2 M, and ⊠ 2.5 M, Me-OH: ○ 1 M, ⍝ 2 M, ⊟ 3 M, and ⊠ 4 M

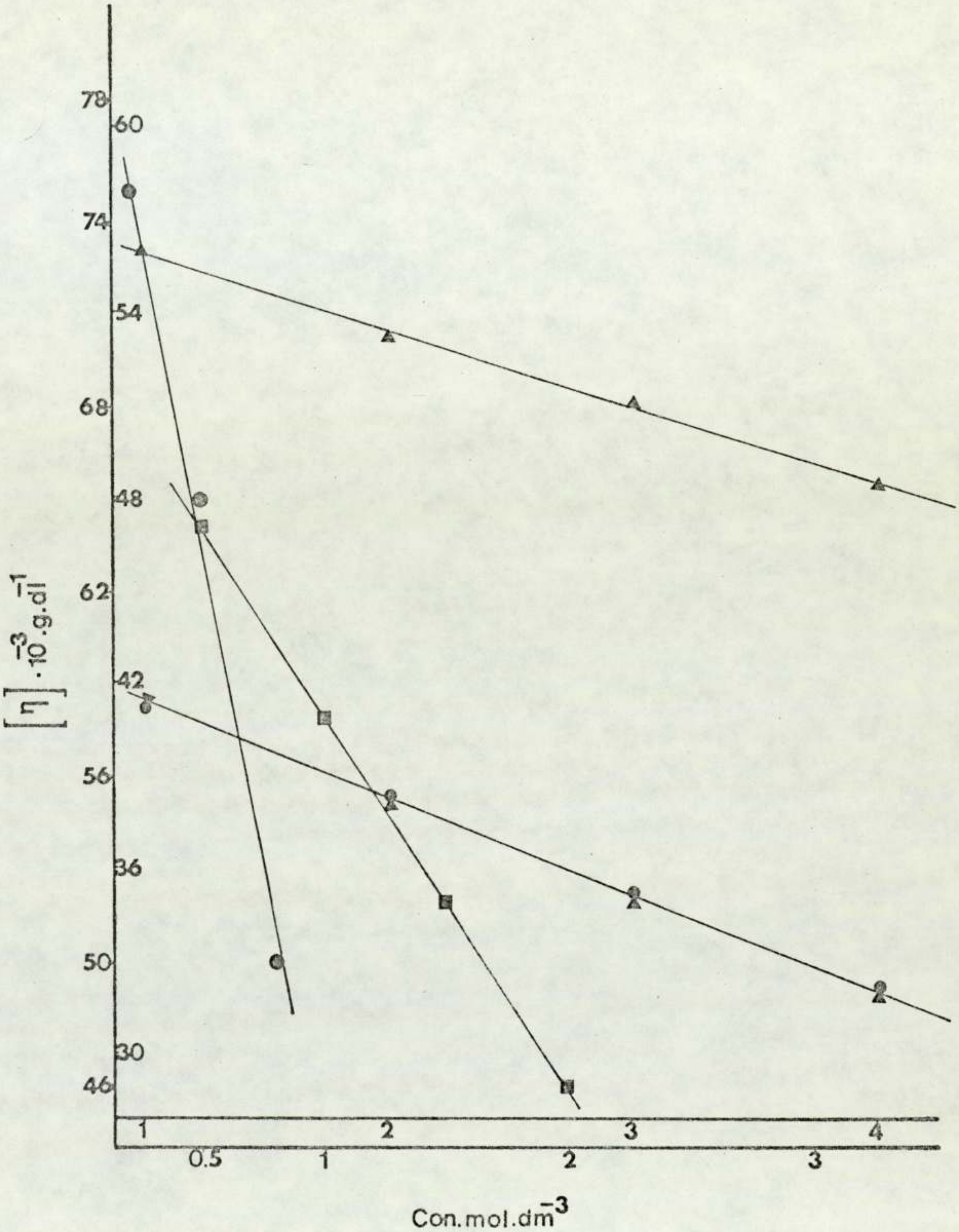


Fig. II.11 Dependence of the intrinsic viscosity of Co of the decyltrimethyl ammonium bromide on organic additives in water at 25° C; ♀ Me-OH, ▲ Et-OH, ■ Pr-OH, and ● Bt-OH

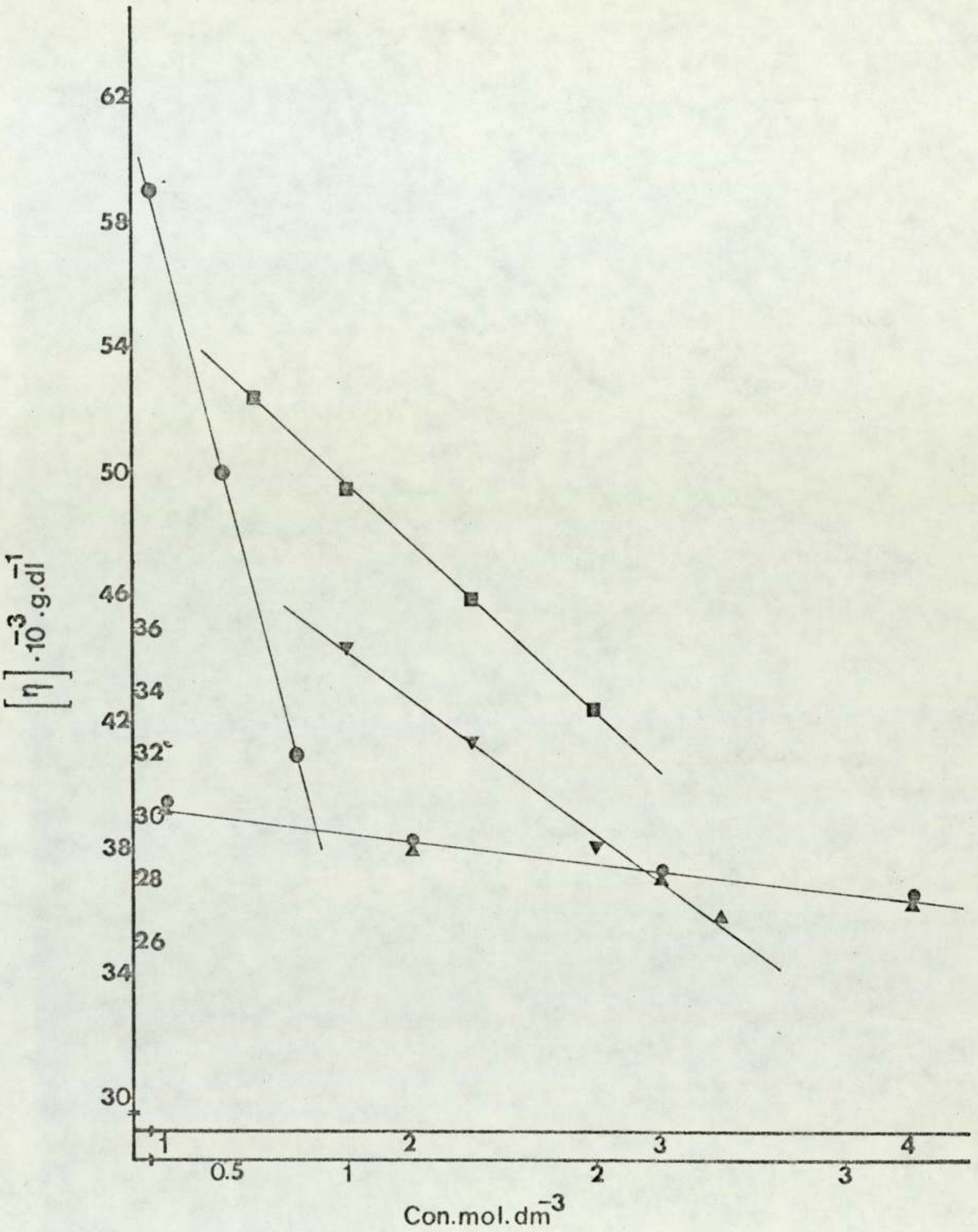


Fig. II.11.A Dependence of the intrinsic viscosity of Co of the dodecyltrimethyl ammonium bromide on organic additives in water at 25° C; ♀ Me-OH, ▲ Et-OH, ■ Pr-OH, and ● Bt-OH

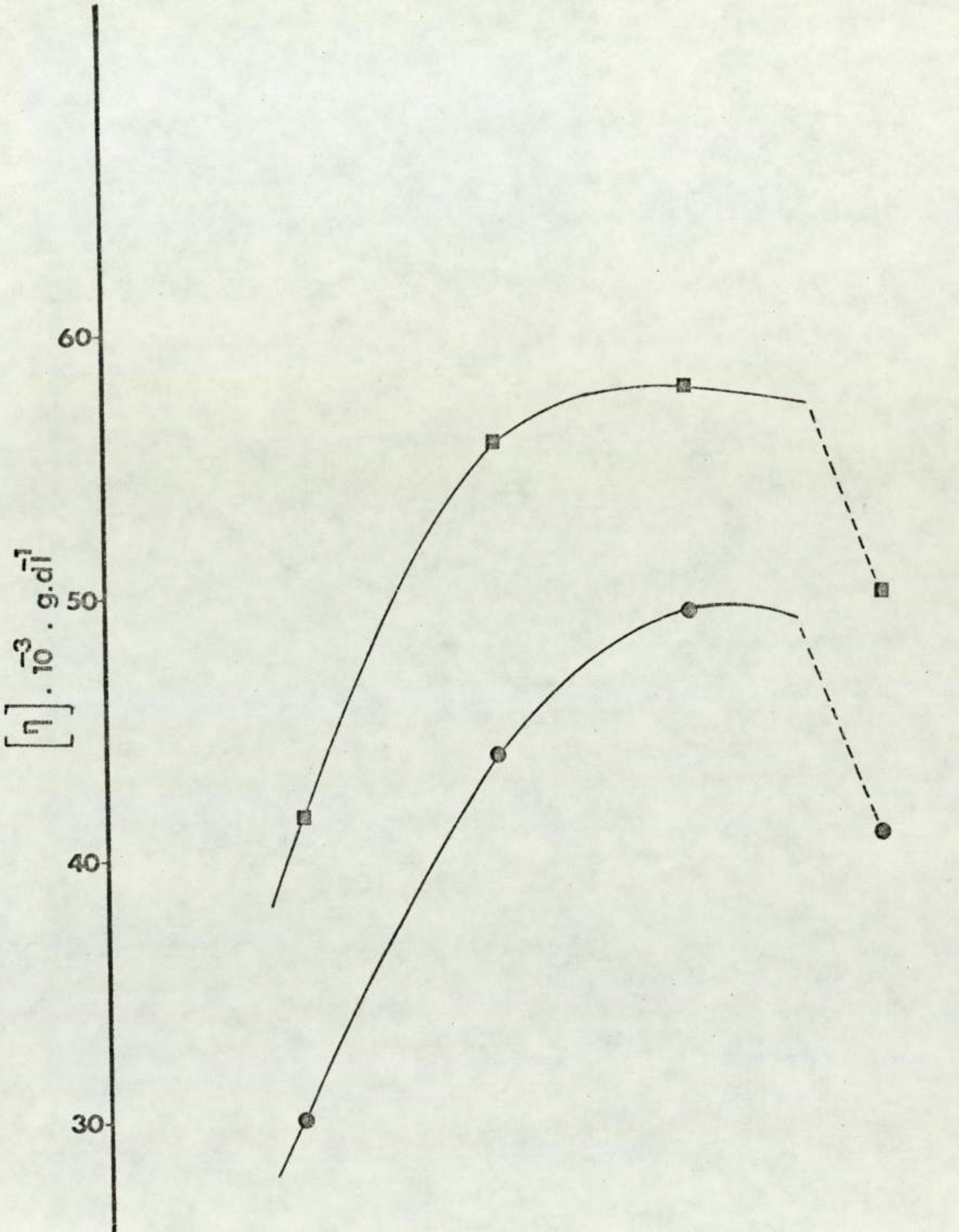


Fig. II.12 Intrinsic viscosities of the Co of C_{10} and C_{12} containing IM various aliphatic alcohols in water as function of the hydrocarbon chain length;

VISCOSITY AND SURFACE TENSION DATA FOR THE SOLUTIONS

OF ALKLAMMONIUM BROMIDES IN WATER AT 25° C

TABLE II.I.1

Vicosity									Surface Tension		
C $mol.dm^{-3}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$\frac{\eta-1}{C-C_o}$ $g.dl^{-1}$	$[\eta]$ $10^{-2}.g.dl^{-1}$	$\frac{1}{\eta_{sp}/C}$	C $mol.dm^{-3}$	C_o $mol.dm^{-3}$	γ $dyne.cm^{-1}$	C_o $mol.dm^{-3}$
C_{10}											
1×10^{-1}	1.00020	0.9630	1.0761	0.0761	0.0775	6.0	36.84	6.5×10^{-2}	1×10^{-1}	39.95	6.0×10^{-5}
9×10^{-2}	0.99910	0.9401	1.0505	0.0505	0.0720		37.00		9×10^{-2}	39.91	
7×10^{-2}	0.99861	0.9468	1.0580	0.0580	0.414		33.78		8×10^{-2}	39.75	
6×10^{-2}	0.99831	0.9391	1.0494	0.0494			34.03		7×10^{-2}	39.73	
5×10^{-2}	0.99810	0.9310	1.0403	0.0403			34.74		6.5×10^{-2}	39.78	
4×10^{-2}	0.99791	0.9232	1.0316	0.0316			35.50		5×10^{-2}	41.32	
3×10^{-2}	0.99771	0.9157	1.0233	0.0233			36.09		4×10^{-2}	43.10	
2×10^{-2}	0.99753	0.9085	1.0152	0.0152			36.84		3×10^{-2}	45.82	
1×10^{-2}	0.99741	0.8974	1.0027	0.0027					2.5×10^{-2}	47.60	
C_{12}											
6×10^{-2}	0.99841	0.9789	1.0938	0.0938	0.0704	6.9	19.71	1.68×10^{-2}	6×10^{-2}	40.10	1.9×10^{-2}
5×10^{-2}	0.99823	0.9593	1.0711	0.0711	0.0699		21.43		5×10^{-2}	40.20	
4×10^{-2}	0.99805	0.9410	1.0505	0.0505	0.0707		24.44		4×10^{-2}	40.32	
3×10^{-2}	0.99788	0.9307	1.0399	0.0399	0.0981		23.14		3×10^{-2}	40.35	
2×10^{-2}	0.99774	0.9167	1.0244	0.0244			25.31		2.5×10^{-2}	40.20	
1.7×10^{-2}	0.99771	0.9117	1.0188	0.0188			27.28		2×10^{-2}	40.30	
1.4×10^{-2}	0.99768	0.9077	1.0144	0.0144			30.11		1.4×10^{-2}	44.00	
1×10^{-2}	0.99761	0.9024	1.0081	0.0081			38.146		1.9×10^{-2}	48.32	

TABLE II.I.1.A

7 x 10^{-3}	0.99757	0.9990	1.0046	0.0046	–	–	–	–	6 x 10^{-3}	52.10	–
4 x 10^{-3}	0.99753	0.8981	1.0035	0.0035					5 x 10^{-3}	56.00	
C_{14}											
6 x 10^{-2}	0.99852	1.0389	1.1609	0.1609	0.0849	8.2	12.59	3.7x10^{-3}	8 x 10^{-3}	39.87	3.4x10^{-3}
5 x 10^{-2}	0.99835	1.0173	1.1257	0.1257	0.0810		13.38		7 x 10^{-3}	39.90	
4 x 10^{-2}	0.99812	0.9876	1.1036	0.1036	0.0840		13.00		6 x 10^{-3}	39.90	
3 x 10^{-2}	0.99790	0.9601	1.0728	0.0728	0.0820		13.85		5 x 10^{-3}	39.35	
2 x 10^{-2}	0.99771	0.9283	1.0374	0.0374			17.06		4 x 10^{-3}	39.93	
1 x 10^{-2}	0.99750	0.9113	1.0183	0.0183			18.33		3.5x 10^{-3}	39.95	
7 x 10^{-3}	0.99746	0.9122	1.0190	0.0190			18.99		3 x 10^{-3}	40.45	
4 x 10^{-3}	0.99740	0.9010	1.0067	0.0067			20.17		2 x 10^{-3}	43.90	
2.5x 10^{-3}	0.99737	0.8982	1.0037	0.0037			22.59		1 x 10^{-3}	49.00	
1 x 10^{-3}	0.99731	0.8976	1.003	0.003					5 x 10^{-4}	54.25	
C_{16}											
6 x 10^{-2}	0.99861	1.0959	1.2246	0.2246	0.104	9.6	9.73	8 x10^{-4}	3 x 10^{-3}	40.0	8.8x10^{-4}
5 x 10^{-2}	0.99841	1.0613	1.1859	0.1859	0.103		9.81		2.5x 10^{-3}	39.97	
4 x 10^{-2}	0.99819	1.0179	1.1375	0.1375	0.096		10.59		2 x 10^{-3}	39.95	
3 x 10^{-2}	0.99798	0.9903	1.1069	0.1069	0.1004		10.22		1.5x 10^{-3}	40.0	
2 x 10^{-2}	0.99776	0.9468	1.0581	0.0581	0.828		12.56		1 x 10^{-3}	40.0	
1 x 10^{-2}	0.99754	0.9189	1.0269	0.0269			13.54		8 x 10^{-4}	40.72	
7 x 10^{-3}	0.99748	0.9112	1.0183	0.0183			13.97		6 x 10^{-4}	42.71	
4 x 10^{-3}	0.99742	0.9042	1.0103	0.0103			14.15		3.5x 10^{-4}	46.90	
2 x 10^{-2}	0.99740	0.8994	1.0051	0.0051			14.42		2.3x 10^{-4}	49.62	
7 x 10^{-3}	0.99737	0.8964	1.0017	0.0017			14.67		1.5x 10^{-4}	52.45	
4 x 10^{-4}	0.99737	0.8954	1.0006	0.0006			22.85				

HYDRO DYNAMIC DATA FOR THE SOLUTIONS OF DECYL TRIMETHYL AMMONIUM BROMIDE CONTAINING ALIPHATIC ALCOHOLS AT 25° C

TABLE II.I.2

C mol.dm^{-3}	da q.ml^{-1}	η cp	η_r	η_{sp}	C−C$_o$ g.dl^{-1}	$\frac{\eta-1}{C-C_o}$ g.dl^{-1}	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ g.dl^{-1}	C$_o$ mol.dm^{-3}
1M Me-OH									
0.1	0.99521	1.0872	1.2148	0.2148	4.247	0.0505	27.95	0.0415	6.24x10^{-2}
0.08	0.9947	1.0623	1.1871	0.1871	3.6964	0.0506	29.11		
0.07	0.9945	1.0522	1.1758	0.1758	3.4961	0.0503	29.38		
0.065	0.99439	1.0456	1.1684	0.1684	3.2759	0.051	29.84		
0.06	0.99421	1.0427	1.1652	0.1652			29.57		
0.05	0.99392	1.0326	1.1538	0.1538			29.92		
0.04	0.99365	1.0228	1.1429	0.1429			30.25		
0.03	0.99321	1.0130	1.1320	0.1320			30.64		
0.02	0.99306	1.0097	1.1283	0.1283			29.34		
2M									
0.1	0.99071	1.1822	1.3210	0.3210	7.561	0.0425	28.68	0.0380	5.88x10^{-2}
0.08	0.99012	1.1592	1.2953	0.2953	7.004	0.0421	29.28		
0.07	0.98985	1.1482	1.2830	0.2830	6.7201	0.0421	29.56		
0.06	0.98921	1.1383	1.2720	0.2720	6.4398	0.0422	29.73		
0.05	0.98861	1.1272	1.2595	0.2595			30.08		
0.04	0.98842	1.1164	1.2475	0.2475			30.41		
0.03	0.98812	1.1051	1.2349	0.2349			30.85		
0.02	0.98781	1.0926	1.2210	0.2210			31.54		
3M									
0.1	0.98490	1.2621	1.4103	0.4103	10.485	0.0391	30.25	0.035	6.9x10^{-2}
0.08	0.98420	1.2398	1.3854	0.3854	9.9244	0.0388	30.75		
0.07	0.98401	1.2301	1.3744	0.3744	9.6441	0.0388	30.90		
0.06	0.9837	1.2192	1.3623	0.3623	9.3638	0.0387	31.16		
0.05	0.98341	1.2089	1.3510	0.3510			31.38		
0.04	0.98352	1.20	1.3410	0.3410			31.48		
0.03	0.98120	1.1881	1.3276	0.3276			31.90		
0.02	0.98089	1.1816	1.3206	0.3206			31.74		

TABLE II.I.2.A

C mol.dm^{-3}	da g.dl^{-1}	η cp	η_r	η_{sp}	$C-C_o$ g.dl^{-1}	$\frac{\eta-1}{C-C_o}$ g.dl^{-1}	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ g.dl^{-1}	C_o mol.dm^{-3}
4M									
0.1	0.98041	1.3462	1.5043	0.5043	13.419	0.0375	30.96		
0.08	0.97981	1.3241	1.4795	0.4795	12.858	0.0372	31.39		
0.07	0.97952	1.3140	1.4683	0.4683			31.55		
0.065	0.97931	1.3080	1.4616	0.4616			31.70		
0.06	0.97920	1.3074	1.4610	0.4610			31.66	0.032	7.85×10^{-2}
0.05	0.97891	1.2939	1.4458	0.4458			31.88		
0.04	0.97852	1.2843	1.4352	0.4352			32.03		
0.03	0.97620	1.2722	1.4216	0.4216			32.38		
0.02	0.9778	1.2653	1.4139	0.4139			32.31		
1 M, Et-OH									
0.1	0.99212	1.1776	1.3159	0.3159	5.690	0.0555	23.45		
0.08	0.99161	1.1543	1.2898	0.2898	5.1294	0.0565	23.63		
0.07	0.99140	1.14241	1.2765	0.267	4.849	0.0570	23.75		
0.06	0.99112	1.1298	1.2625	0.2625			23.95		
0.05	0.99081	1.1173	1.2485	0.2485			24.17	0.056	6.14×10^{-2}
0.04	0.99061	1.1070	1.2370	0.2370			24.16		
0.03	0.99021	1.0952	1.2239	0.2239			24.33		
0.02	0.99002	1.0859	1.2134	0.2134			24.20		
2M									
0.1	0.98482	1.4003	1.5647	0.5647	10.387	0.0543	21.27		
0.08	0.98425	1.3712	1.5322	0.5322	9.826	0.0541	21.52		
0.07	0.98411	1.3583	1.5179	0.5179	9.546	0.0542	21.57		
0.06	0.98371	1.3457	1.5037	0.5037	9.265	0.0543	21.62		
0.05	0.98340	1.3346	1.4914	0.4914			21.60	0.053	5.82×10^{-2}
0.04	0.98320	1.3207	1.4758	0.4758			21.72		
0.03	0.98291	1.3083	1.4619	0.4619			21.76		
0.02	0.9827	1.2993	1.4518	0.4518			21.63		

TABLE II.I.2.B

C $mol.dm^{-3}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$C-C_0$ $g.dl^{-1}$	$\frac{\eta-1}{C-C_0}$ $g.dl^{-1}$	$\frac{\frac{1}{\eta}}{c}$	$[\eta]$ $g.dl^{-1}$	C_0 $mol.dm^{-3}$
3M									
0.1	0.97841	1.6444	1.8375	0.8375	15.074	0.0555	19.84	0.0510	$5.53x10^{-2}$
0.08	0.97782	1.6161	1.8059	0.8059	14.513	0.0545	19.93		
0.07	0.97752	1.6028	1.79106	0.79106	14.23	0.0541	19.95		
0.06	0.97731	1.5901	1.7769	0.7769			19.95		
0.05	0.97692	1.5775	1.7628	0.7628			19.95		
0.04	0.97661	1.5646	1.7484	0.7484			19.96		
0.03	0.97632	1.5551	1.7378	0.7378			19.87		
0.02	0.97601	1.5547	1.7372	0.7372			19.51		
4M									
0.01	0.97192	1.8837	2.1043	1.1043	19.479	0.056	19.22	0.0484	$6.25x10^{-2}$
0.08	0.97131	1.8619	2.0806	1.0806	18.922	0.0574	19.12		
0.07	0.97102	1.8511	2.0685	1.0685	18.638	0.0570	19.083		
0.06	0.97071	1.8370	2.0527	1.0527			19.12		
0.05	0.97042	1.7923	2.0028	1.0028			19.77		
0.04	0.97021	1.7791	1.9881	0.9881			19.79		
0.03	0.96981	1.7681	1.9757	0.9757			19.74		
0.02	0.96962	1.7558	1.9621	0.9621			19.76		
0.5M.PrOH									
0.1	0.99531	1.1296	1.2623	0.2623	4.168	0.0629	22.14	0.064	$5.85x10^{-2}$
0.08	0.99502	1.1072	1.2373	0.2373	3.607	0.0657	22.117		
0.07	0.99471	1.0924	1.2207	0.2207	3.327	0.066	22.51		
0.06	0.99442	1.0799	1.2067	0.2067	3.046	0.067	22.66		
0.05	0.99403	1.0724	1.1984	0.1984			22.2		
0.04	0.99372	1.0630	1.1878	0.1878			21.96		
0.03	0.99343	1.0572	1.1813	0.1813			21.20		
0.02	0.99312	1.0464	1.1694	0.1694			21.05		

TABLE II.I.2.C

C mol.dm^{-3}	da g.ml^{-1}	η cp	η_r	η_{sp}	C − C$_o$ g.dl^{-1}	$\frac{\eta - 1}{C - C_o}$ g.dl^{-1}	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ g.dl^{-1}	C$_o$ mol.dm^{-3}
1 M									
0.1	0.9904	1.4389	1.4423	0.4423	7.313	0.0604	19.92		
0.08	0.99031	1.269	1.4180	0.4180	6.752	0.0619	19.74		
0.07	0.99021	1.2552	1.4026	0.4026	6.472	0.062	19.79		
0.06	0.9901	1.2396	1.3852	0.3852	6.1918	0.062	19.96		
0.055	0.990	1.2352	1.3803	0.3803	6.0516	0.062	19.85	0.058	5.35x10^{-2}
0.050	0.9891	1.2251	1.3690	0.3690			20.08		
0.04	0.98899	1.2086	1.3506	0.3506			20.34		
0.03	0.98819	1.1980	1.3387	0.3387			20.22		
0.02	0.9881	1.1879	1.3274	0.3274			20.08		
1.5 M									
0.1	0.98571	1.4707	1.6434	0.6434	10.468	0.0614	18.36		
0.08	0.98551	1.4338	1.6022	0.6022	9.897	0.0608	18.67		
0.07	0.9854	1.4178	1.5843	0.5843	9.617	0.0607	18.76		
0.06	0.98531	1.4064	1.5716	0.5716	9.336	0.0612	18.80		
0.055	0.98526	1.3903	1.5536	0.5536			19.05	0.052	4.82x10^{-2}
0.05	0.98521	1.3766	1.5383	0.5383			19.34		
0.04	0.98512	1.3658	1.5262	0.5262			19.24		
0.03	0.98502	1.3535	1.5125	0.5125			19.22		
0.02	0.98401	1.3371	1.4942	0.4942			19.35		
2 M									
0.1	0.9813	1.6482	1.8417	0.8417	13.713	0.0614	17.60		
0.08	0.98112	1.6091	1.7981	0.7981	13.153	0.0606	17.86		
0.07	0.98101	1.5894	1.7761	0.7761	12.872	0.0603	18.02		
0.06	0.98093	1.5823	1.7686	0.7686	12.592	0.061	17.83		
0.055	0.98041	1.5696	1.7539	0.7539	12.452	0.0605	17.98	0.046	3.96x10^{-2}
0.05	0.97991	1.5612	1.7445	0.7445			18.02		
0.04	0.97941	1.5514	1.7337	0.7337			17.91		
0.03	0.97862	1.5356	1.7159	0.7159			17.96		
0.02	0.97783	1.5227	1.7015	0.7015			17.93		
0.01	0.97701	1.5172	1.6953	0.6953			17.68		

TABLE II.I.2.D

C $mol.dm^{-3}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$C-C_0$ $g.dl^{-1}$	$\frac{\eta-1}{C-C_0}$ $g.dl^{-1}$	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ g.dl	C_0 $mol.dm^{-3}$
0.2 M,Bt-OH									
0.1	0.9973	1.0644	1.1894	0.1894	2.625	0.0721	22.62		
0.08	0.99711	1.0402	1.1623	0.1623	2.064	0.0786	22.94		
0.07	0.99701	1.0265	1.1470	0.1470	1.784	0.0824	23.42		
0.06	0.99692	1.0173	1.1368	0.1368	1.5038	0.091	23.12		
0.05	0.98681	1.0092	1.1277	0.1277			22.57	0.075	$5.9x10^{-2}$
0.04	0.9967	1.0001	1.1175	0.1175			22.14		
0.03	0.99661	0.9907	1.1071	0.1071			21.69		
0.02	0.9965	0.9813	1.0965	0.0965			21.16		
0.01	0.9964	0.9711	1.0851				20.71		
0.5M									
0.1	0.9939	1.1902	1.3300	0.330	5.109	0.064	19.72		
0.08	0.9937	1.1620	1.2981	0.2981	4.548	0.065	19.95		
0.07	0.99362	1.1488	1.2838	0.2838	4.268	0.066	19.97		
0.06	0.9935	1.1354	1.2687	0.2687	3.987	0.067	20.05		
0.05	0.99339	1.1226	1.2544	0.2544			20.07	0.065	$5.\ x10^{-2}$
0.04	0.9933	1.1108	1.2412	0.2412			20.01		
0.03	0.9932	1.1004	1.2296	0.2296			19.79		
0.02	0.9931	1.0893	1.2172	0.2172			19.64		
0.8M									
0.1	0.9903	1.2957	1.4479	0.4479	7.6626	0.0584	19.49		
0.08	0.98981	1.2642	1.4126	0.4126	7.102	0.057	19.80		
0.07	0.9897	1.2493	1.3960	0.3960	6.822	0.058	19.92		
0.06	0.98961	1.2341	1.3791	0.3791	6.541	0.0579	20.07		
0.05	0.9895	1.2104	1.3526	0.3526	6.261	0.0563	20.78	0.050	$3.8x10^{-2}$
0.04	0.98941	1.1991	1.3401	0.3401	6.081	0.0559	21.03		
0.03	0.9893	1.1877	1.3272	0.3272			20.68		
0.02	0.98922	1.1836	1.3226	0.3226			20.115		
0.01	0.98910	1.1764	1.3145	0.3145			19.72		

HYDRO DYNAMIC DATA FOR THE SOLUTIONS OF DODECYL TRIMETHYL AMMONIUM BROMIDE CONTAINING ALIPHATIC ALCOHOLS AT 25°C

TABLE II.I.3

C $mol.dm^{-3}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$C - C_o$ $g.dl^{-1}$	$\frac{\eta-1}{C-C_o}$ $g.dl^{-1}$	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ $g.dl^{-1}$	C_o $mol.dm^{-3}$
1 M Me-OH									
0.06	0.99261	1.0667	1.1920	0.1920	4.644	0.0413	26.33		
0.05	0.99221	1.0475	1.1705	0.1705	4.296	0.0397	27.82		
0.04	0.99181	1.0320	1.1532	0.1532	3.986	0.0384	28.95		
0.03	0.99142	1.0215	1.1415	0.1415	3.678	0.0384	29.16		
0.02	0.99102	1.0061	1.1243	0.1243	3.371	0.0368	30.73	0.0302	1.44×10^{-2}
0.018	0.99074	1.0029	1.1207	0.1207	3.309	0.0364	31.13		
0.016	0.99034	0.9977	1.1144	0.1144			32.16		
0.014	0.99012	0.9955	1.1125	0.1125			32.31		
0.012	0.98982	0.9905	1.1068	0.1068			33.44		
0.01	0.98953	0.9847	1.1004				34.97		
2 M									
0.06	0.98791	1.1459	1.2839	0.2839	7.888	0.0359	29.086		
0.05	0.98763	1.1318	1.2647	0.2647	7.580	0.0349	30.023		
0.04	0.9874	1.1122	1.2428	0.2428	7.27	0.0334	31.45		
0.03	0.98717	1.1014	1.2308	0.2308	6.963	0.0331	31.76		
0.02	0.98694	1.081	1.2077	0.2077	6.654	0.0312	33.82	0.0292	1.2×10^{-2}
0.018	0.98690	1.088	1.2164	0.2164	6.593	0.032	32.17		
0.016	0.98682	1.0797	1.2065	0.2065	6.5314	0.031	33.42		
0.014	0.98676	1.0771	1.2036	0.2036	6.469	0.0314	33.59		
0.01	0.98664	1.0723	1.1983	0.1983			33.88		
3 M									
0.06	0.98215	1.2375	1.3828	0.3828	10.9324	0.0350	29.93		
0.05	0.98182	1.2163	1.3592	0.3592	10.624	0.0338	31.05		
0.04	0.98159	1.1977	1.3384	0.3384	10.314	0.0328	32.048		
0.03	0.98135	1.1829	1.3218	0.3218	10.007	0.0322	32.74		
0.02	0.98112	1.1670	1.3041	0.3041	9.698	0.0313	33.64	0.0282	1.72×10^{-2}
0.018	0.98106	1.1622	1.2988	0.2988	9.637	0.0310	34.02		
0.014	0.98101	1.1604	1.2966	0.2966			33.85		
0.01	0.98085	1.1567	1.2925	0.2925			33.907		
0.007	0.98079	1.1536	1.2891	0.2891			33.93		
0.004	0.98073	1.1505	1.2856	0.2856			34.08		

TABLE II.I.3.A

C $mol.dm^{-3}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$C-C_o$ $g.dl^{-1}$	$\frac{\eta-1}{C-C_o}$ $g.dl^{-1}$	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ $g.dl^{-1}$	C_o $mol.dm^{-3}$
4 M									
0.06	0.9767	1.3642	1.5244	0.5244	14.026	0.0373	27.96	0.0275	2.08×10^{-2}
0.05	0.9765	1.3440	1.5018	0.5018	13.718	0.0365	28.61		
0.04	0.9763	1.3246	1.4802	0.4802	13.408	0.0358	29.25		
0.03	0.9760	1.3031	1.4561	0.4561	13.101	0.0348	30.13		
0.02	0.97582	1.2814	1.4318	0.4318			31.10		
0.018	0.97576	1.2837	1.4344	0.4344			30.77		
0.014	0.97564	1.2787	1.4289	0.4289			30.88		
0.01	0.97561	1.2753	1.4251	0.4251			30.94		
0.007	0.97542	1.2725	1.4219	0.4219			30.88		
0.004	0.9755	1.2687	1.4177	0.4177			30.97		
1 M, Et-OH									
0.06	0.99032	1.1854	1.3246	0.3246	6.057	0.0535	19.89	0.044	1.29×10^{-2}
0.05	0.99002	1.1695	1.3068	0.3968	5.749	0.0533	20.04		
0.04	0.9899	1.1511	1.2863	0.2863	5.439	0.0526	20.39		
0.03	0.98988	1.1310	1.2637	0.2637	5.132	0.0514	20.97		
0.02	0.98951	1.1157	1.2468	0.2468	4.824	0.0512	21.16		
0.018	0.98942	1.1103	1.2406	0.2406	4.762	0.0512	21.45		
0.014	0.98927	1.1051	1.2348	0.2348			21.43		
0.01	0.98910	1.1001	1.2293	0.2293			21.43		
0.007	0.98889	1.0930	1.2213	0.2213			21.78		
1.5 M									
0.06	0.98671	1.2974	1.4498	0.4498	8.4005	0.0535	19.47	0.0415	1.16×10^{-2}
0.05	0.98652	1.2773	1.4272	0.4273	8.0925	0.0528	19.78		
0.04	0.98563	1.2627	1.4110	0.4110	7.783	0.0528	19.81		
0.03	0.98558	1.2376	1.3830	0.3830	7.475	0.0512	20.45		
0.02	0.98548	1.2193	1.3630	0.3630	7.167	0.0505	20.76		
0.018	0.98542	1.2176	1.3606	0.3606	7.105	0.0513	20.70		
0.014	0.98537	1.2056	1.3472	0.3472	6.982	0.0502	21.14		
0.01	0.98531	1.2016	1.3428	0.3428			21.06		
0.007	0.98525	1.1978	1.3385	0.3385			21.05		
0.004	0.98520	1.1945	1.3348	0.3348			21.00		

TABLE II.I.3.B

C mol.dm^{-3}	da g.ml^{-1}	η cp	η_r	η_{sp}	$C-C_0$ g.dl^{-1}	$\frac{\eta-1}{C-C_0}$ g.dl^{-1}	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ g.dl^{-1}	C mol.dm^{-3}
2 M									
0.06	0.98272	1.4177	1.5842	0.5843	10.764	0.0543	18.94		
0.05	0.98260	1.3939	1.5576	0.5576	10.456	0.0533	19.28		
0.04	0.98251	1.3763	1.5379	0.5379	10.146	0.0530	19.42		
0.03	0.98239	1.3466	1.5047	0.5047	9.838	0.0513	20.08		
0.02	0.98228	1.3414	1.4990	0.4990	9.5306	0.0523	19.70		
0.018	0.98224	1.3392	1.4964	0.4964	9.469	0.0524	19.67	0.038	9.73x10^{-3}
0.014	0.9822	1.3315	1.4879	0.4879	9.3457	0.0522	19.76		
0.01	0.98219	1.3257	1.4814	0.4814			19.79		
0.007	0.98215	1.3246	1.4802	0.4802			19.63		
0.004	0.98211	1.323	1.4789	0.4789			19.49		
2.5 M									
0.06	0.9793	1.5504	1.7325	0.7325	13.0179	0.0562	18.25		
0.05	0.97912	1.5227	1.70163	0.70163	12.7095	0.0551	18.62		
0.04	0.9790	1.50263	1.67911	0.67911	12.399	0.0547	18.77		
0.03	0.97891	1.4811	1.6551	0.6551	12.0920	0.0542	18.99		
0.02	0.97882	1.4577	1.6289	0.6289	11.784	0.0533	19.29		
0.018	0.9788	1.4537	1.6245	0.6245	11.722	0.0532	19.33	0.0358	1.13x10^{-2}
0.014	0.97876	1.4478	1.6178	0.6178	11.599	0.0533	19.34		
0.012	0.97872	1.4460	1.6158	0.6158			19.30		
0.01	0.97871	1.4423	1.6116	0.6116			19.33		
0.007	0.97860	1.4399	1.609	0.609			19.26		
0.004	0.97851	1.4337	1.6021	0.6021			19.33		
0.5 MPr-OH									
0.06	0.99351	1.1402	1.2741	0.2741	4.485	0.061	17.71		
0.05	0.9934	1.1208	1.2524	0.2524	4.177	0.060	18.01		
0.04	0.99332	1.1001	1.2292	0.2292	3.867	0.059	18.48		
0.03	0.99316	1.0825	1.2096	0.2096	3.559	0.058	18.74		
0.02	0.99312	1.0662	1.1946	0.1946	3.252	0.058	18.91		
0.018	0.99309	1.0614	1.1861	0.1861	3.182	0.058	19.10	0.0524	1.2x10^{-2}
0.014	0.99302	1.0561	1.1801	0.1801			19.07		
0.012	0.9930	1.0528	1.1764	0.1764			19.12		
0.01	0.99271	1.04929	1.1725	0.1725			19.21		
0.007	0.99252	1.04820	1.1713	0.1713			18.79		
0.004	0.99231	1.0440	1.1671	0.1671			18.72		

TABLE II.I.3.C

C $mol.dm^{-3}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$C-C_o$ $g.dl^{-1}$	$\frac{\eta-1}{C-C_o}$ $g.dl^{-1}$	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ $g.dl^{-1}$	Co $mol.dm^{-3}$
				1M					
0.06	0.98890	1.2991	1.4517	0.4517	7.564	0.0597	17.41		
0.05	0.98887	1.2776	1.4276	0.4276	7.252	0.0589	17.65		
0.04	0.98874	1.2569	1.4045	0.4045	6.932	0.0583'	17.87		
0.03	0.98861	1.2366	1.3819	0.3819	6.6349	0.0575	18.15		
0.02	0.9885	1.2178	1.3608	0.3608	6.326	0.0570	18.36		
0.018	0.98847	1.2107	1.3529	0.3529	6.265	0.0563	18.59	0.0495	$9.7x10^{-3}$
0.014	0.98844	1.1977	1.3384	0.3384	6.142	0.0551	19.04		
0.012	0.98841	1.1973	1.3379	0.3379			18.87		
0.01	0.98837	1.1969	1.3374	0.3374			18.72		
0.007	0.98814	1.1948	1.3352	0.3352			18.57		
0.004	0.98811	1.1934	1.3336	0.3336			18.38		
				1.5M					
0.06	0.9845	1.4576	1.6288	0.6288	10.585	0.0594	17.27		
0.052	0.9843	1.4372	1.6059	0.6059	10.348	0.0585	17.57		
0.04	0.9842	1.4105	1.5761	0.5761	9.967	0.0578	17.78		
0.03	0.98417	1.3884	1.5515	0.5515	9.659	0.0571	18.02		
0.022	0.98412	1.3675	1.5281	0.5281	9.416	0.056	18.36		
0.018	0.9841	1.3534	1.5124	0.5124	9.291	0.0555	18.67	0.046	$9.1x10^{-3}$
0.014	0.98406	1.3491	1.5075	0.5075	9.166	0.0557	18.61		
0.012	0.98402	1.3479	1.5063	0.5063	9.1051	0.0556	18.53		
0.01	0.98399	1.3465	1.5047	0.5047			18.47		
0.007	0.98396	1.3452	1.5032	0.5032			18.34		
0.004	0.98392	1.3443	1.5021	0.5021			18.19		
				2M					
0.06	0.9800	1.6262	1.8171	0.8171	13.651	0.0598	16.97		
0.05	0.97984	1.6008	1.7889	0.7889	13.342	0.0591	17.19		
0.04	0.97978	1.5841	1.7702	0.7702	13.032	0.0591	17.21		
0.03	0.97963	1.5615	1.7449	0.7449	12.725	0.0585	17.37		
0.02	0.97948	1.5472	1.7289	0.7289	12.410	0.0587	17.33		
0.018	0.97945	1.5305	1.7103	0.7103	12.355	0.0576	17.70	0.0425	$7.1x10^{-3}$
0.014	0.979411	1.5239	1.7028	0.7028	12.231	0.0574	17.71		
0.012	0.97937	1.5202	1.6988	0.6988			17.72		
0.01	0.97934	1.5193	1.6977	0.6977			17.66		
0.007	0.97931	1.5182	1.6965	0.6965			17.56		
0.004	0.97927	1.5137	1.6915	0.6915			17.56		

TABLE II.I.3.D.

C mol.dm^{-3}	da g.ml^{-1}	η cp	η_r	η_{sp}	C−C$_o$ g.dl^{-1}	$\frac{\eta-1}{C-C_o}$ g.dl^{-1}	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ g.dl^{-1}	C$_o$ mol.dm^{-3}
0.2M,Bt-OH									
0.06	0.9959	1.0553	1.1792	0.1792	2.9155	0.0614	18.59	0.059	1.4x10^{-2}
0.05	0.99581	1.0363	1.1580	0.1580	2.6071	0.0606	19.14		
0.04	0.99572	1.0177	1.1372	0.1372	2.2988	0.0597	19.78		
0.03	0.9956	1.0010	1.1184	0.1184	1.9910	0.0595	20.33		
0.02	0.9955	0.9845	1.1002	0.1002	1.682	0.0595	20.94		
0.017	0.995471	0.9790	1.0879	0.0879	1.5885	0.0592	21.34		
0.014	0.99544	0.9735	1.0879	0.0879			21.59		
0.01	0.99541	0.9691	1.0829	0.0829			21.58		
0.007	0.99537	0.9645	1.0778	0.0778			21.80		
0.5M									
0.06	0.9926	1.1791	1.3175	0.3175	5.247	0.0605	17.49	0.050	1.0x10^{-2}
0.05	0.99249	1.1601	1.2963	0.2963	4.939	0.060	17.70		
0.04	0.99239	1.1405	1.2744	0.2744	4.6311	0.059	18.00		
0.03	0.99232	1.1190	1.2504	0.2504	4.322	0.057	18.49		
0.02	0.99220	1.1005	1.2297	0.2297	4.014	0.057	18.68		
0.017	0.99217	1.0953	1.2239	0.2239	3.922	0.057	18.88		
0.014	0.99214	1.0953	1.2239	0.2239	3.814	0.056	19.18		
0.01	0.992110	1.0792	1.2059	0.2059			19.48		
0.007	0.99207	1.070	1.1956	0.1956			20.04		
0.004	0.99204	1.0576	1.1818	0.1818			21.06		
0.001	0.99201	1.0538	1.1776	0.1776			21.04		
0.8M									
0.06	0.9892	1.2933	1.4452	0.4452	7.579	0.0587	17.47	0.041	6.5x10^{-3}
0.05	0.98912	1.2718	1.4211	0.4211	7.271	0.0579	17.74		
0.04	0.9890	1.2547	1.4021	0.4021	6.963	0.0577	17.81		
0.02	0.98881	1.2098	1.3518	0.3518	6.346	0.0554	18.60		
0.017	0.98877	1.2040	1.3454	0.3454	6.253	0.0551	18.68		
0.014	0.98874	1.1989	1.3397	0.3397	6.246	0.0544	18.97		
0.01	0.98871	1.1897	1.3294	0.3294	6.037	0.0545	18.93		
0.007	0.98867	1.1807	1.3194	0.3194	5.945	0.0537	19.23		
0.004	0.98867	1.1769	1.3151	0.3151			19.20		
0.001	0.98861	1.1722	1.3098	0.3098			19.24		

HYDRODYNAMIC DATA FOR THE MICELLES OF ALKYLTRIMETHYL AMMONIUM BROMIDES AT 25° C

TABLE II.I.4

S.A.A	Vh	Va	Wg.g^{-1}	$\overline{\upsilon}$	Light Scattering		Viscosity	K
	ml.10^{-19}	ml.10^{-19}		ml.g^{-1}	Incorrect R^{O}.A°	Correc. R^{C}.A°	R^{V}.A°	
C_{10}	0.4025	0.158	1.458	0.94542	16	18	21	
C_{12}	0.705	0.2360	1.841	0.92445	18	20	25	2.5
C_{14}	1.232	0.352	2.348	0.93783	20	22	30	
C_{16}	1.990	0.479	2.923	0.92465	23	24	36	

MICELLAR DIMENSIONS OF THE DODECYLTRIMETHYL AMMONIUM BROMIDE

IN WATER CONTAINING ALIPHATIC ALCOHOLS

TABLE II.I.5

C $mol.dm^{-3}$	K	A_R	A_a A°	A_b A°
Et-OH				
1 M	4.7	4.1	70	17
2 M	3.9	3.3	56	17
Pr-OH				
0.5 M	5.4	4.7	70	15
1.0 M	5.1	4.4	62	14
1.5 M	4.7	4.1	53	13
Bt-OH				
0.5 M	5.1	4.4	57	13
1.0 M	4.6	3.9	43	11

CHAPTER III - The effects of additives on B-coefficients of Alkylammonium bromides in aqueous solutions

III-Ia - Theory of viscosity of the electrolyte solutions.

In electrolyte solutions the presence of coulomb forces between the ions effect the viscosity of the medium. The change in viscosity of the dispersion medium has been successfuly examined by Falkenhagen et al.(188,189,190). According to his theory, a part of stress in an ionic solution is produced by the deformation of the ionic atmosphere. According to the Debye-Hückel(191) theory each ion in the solution, is surrounded by an atmosphere of ions of opposite sign, at an average distance of $1/\kappa$.

If we assume that we have such a situation in the unperturbed solution, then the distribution will possess a spherical symmetry. Due to the velocity gradient in the solution, the atmosphere of an ion is deformed from a spherical to an ellipsoidal form. As a result of this process, the electrostatic forces and thermal motion tend to restore the atmospheres to their original form. The magnitude of the deformation of the ionic atmosphere, could be given by an expression(188) such as,

$$\frac{a_i}{\kappa^2 kT} \frac{\partial v_x}{\partial y} \qquad \text{III-1}$$

and the forces between two ions of charge e at distance $1/\kappa$ is $e^2\kappa^2/D$, and the total transfer of forces act between the ion and its atmosphere is $1/\kappa$ times the quantity of the $e^2\kappa^2/D$ or $e^2\kappa D$.

Substituting this quantity into expression (III-1) and considering the displacement of the ionic atmosphere, we get the following expression,

$$\frac{e^2 a_i}{\kappa D kT} \frac{\partial \nu_x}{\partial y} \qquad \text{III-2}$$

which is the order of the magnitude of the stress transferred between the ion and its atmosphere.

By substitution of $\kappa = \left[\frac{4\pi\epsilon^2}{DkT} \sum_{i=1}^{s} n_i z_i^2 \right]$ into expression III- 2 the electrostatic contribution to the stress is obtained

$$S_a \sim \kappa a_i \frac{\partial v_x}{\partial y} \qquad \text{III-3}$$

when $\frac{1}{a_i} = \omega_1 = \omega_2 = \dots \omega_s$ this becomes,

$$S_a = \frac{1}{480\pi} a_i \kappa \frac{\partial v_x}{\partial y} \qquad \text{III-4}$$

The stress between the solvent molecules is given by the equation

$$S_b = \eta_0 \frac{\partial v_x}{\partial y} \qquad \text{III-5}$$

Hence the contribution of the ionic atmosphere to the viscosity is,

$$\eta_1 = \frac{a_i \kappa}{480\pi} \qquad \text{III-6}$$

This Falkenhagen's result, was later confirmed experimentally by Jones-Dole(192) for the dilute solutions.

III-Ib - The B-coefficients of ionic solutions.

Due to the long range nature of coulombic interactions, the properties of ionic solutions are influenced by interionic effects. These properties can be examined by the Debye-Hückel limiting law, by assuming that the ions do not approach each other so closely. Otherwise owing to their hydration envelopes, they interfere with each other introducing an extra term into the activity coefficient(80).

At higher concentrations, it has been observed that the behaviour of the ionic solutions deviate from simple concentration dependence. The properties of aqueous electrolyte solutions are highly specific to the individual ions concerned. In the case of viscosity, Jones-Dole have developed(192) a relationship between concentration dependence, and the viscosity of dilute electrolyte solution, which is given by the equation

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC \qquad \text{III-7}$$

Falkenhagen et al.(188,189,190) showed that the square root term is due to the long range interionic forces, and that the coefficient A can be calculated from the Debye-Hückel(191) limiting law. Since, in general $^A/B \leqslant 1$, the square root term could be neglected at concentrations above 0.002M, when the equation takes the form(193)

$$\eta/\eta_0 = 1 + BC \qquad 0.002M < C < \sim 0.1M \qquad \text{III-8}$$

The B coefficient which is a specific property of the solute, can be derived in terms of the individual contributions of the solute constituent ions. Hence

$$B = {}_{z+}^{B-} + {}_{z-}^{B+} \qquad \text{III-9}$$

The viscosity B coefficients can be either positive or negative. If we consider the B value as a measure of the ion-solvent interactions, then we can introduce the following effects, which influence the B value of the electrolyte solution(194),

1) The interaction of solvent molecules with the ion which causes an increase in viscosity.
2) The effect of the field ion in producing long-range order of solvent molecules, which also causes an increase in viscosity.
3) The destruction of water molecules due to structure breaking effect of the ion, which causes a decrease in viscosity.
4) Steric effects.

In the case of suspensions, Einstein introduced(126,127) an equation for the relative viscosity of the dilute suspension of the rigid spheres which is

$$\eta/\eta = 1 + 2.5\phi$$

Tuan-Fuoss(195) and Moulik(196) have examined the relationship between the Einstein and Jones-Dole equations. As a result of this investigation, they have postulated an expression such as,

$$\phi = c\ V \qquad \text{III-10}$$

then the B coefficient could be related to the molar volume of the solute by,

$$B = 2.5\ V \qquad \text{III-11}$$

If we consider concentrated electrolyte solutions, then the relative viscosity can be represented by a polynomial of the form(193)

$$\eta/\eta_o = 1 + 2.5\phi + k_1\phi^2 + k_2\phi^3 \qquad \text{II-12}$$

Vand(197) has concluded that the second and higher order terms, which were added to the Einstein equation, is due to the particle interactions of various types. The investigation of the viscosity of the concentrated eletrolyte solutions has been extended by Thomas(198). He introduced a second degree equation, which could be defined by an expression,

$$\eta/\eta_o = 1 + 2.5\phi + 10.05\phi^2 \qquad \text{III-13}$$

This expression is valid for highly concentrated suspensions. If we substitute the expression $\phi = c\ Ve$ into the equation (III-13) we obtain(193)

$$\eta/\eta_o = 1 + 2.5\ c\ Ve + 10.05\ c^2\ Ve^2 \qquad \text{III-14}$$

This equation may be rearranged to solve for Ve, which is the effective rigid molar volume of the salt,

$$Ve = \frac{-2.5\ c + \sqrt{(2.5c)^2 - 4(10.05c^2)(1 - \eta/\eta_o)}}{2(10.05)c^2} \qquad \text{III-15}$$

Cox-Wolfenden(199) examined the individual B coefficients of the ions of lithium iodate, in terms of the temperature coefficient of mobility of the ions. They calculated the B coefficients of several ions, considering the ionic volumes which are inversely proportional to the cube of the ionic mobilities. The negative values of B coefficients have been interpreted, by means of the depolymerization of the solvent by the ions. In aqueous solution of electrolyte, the ionic radius is altered by the change in nature of the number of neighbour molecules by the ion considered.

Kaminsky(194) studied the B_{ion} values of KCl at different temperatures, by examining the ionic mobilities of K^+ and Cl^- ions. He has found that the difference is less than 3%. As a result of this fact, he concluded that at every temperature B_{K^+} is equal to B_{Cl^-}. These values are very close to the B_{ion} values of KCl derived by Cox-Wolfenden(199).

On the other hand he observed that the B_{ion} values for NH_4^+ are very close to zero. The reason has been attributed to the structure of the ion which does not influence the structure of the solvent.

However in the case of the alkali metals, alkaline earths and halogens, at wide temperature range, the B_{ion} values decrease as the crystal ionic radii increase. But the temperature coefficient of B_{ion} values increases as the crystal ionic radius increases. He discussed also the negative values of B coefficients, in terms of the structure breaking influence of the ions on the solvent structure.

III-Ic - Cosphere effects.

Born(200) first considered the effect of static dielectric on the ionic mobilities, and put forward the suggestion that the solvent dipoles in the cosphere of ion could be orientated by the motion of the ion. These orientated dipoles relax at finite time to their random orientations.

This observation has been examined and in semi-empirical form presented by Fuoss(201). Later Boyd(202) extended this approach. Fernandez-Prini-Atkinson(203) suggested that the dielectric constant of the cosphere of an ion could be altered due to the high charge density of the small ion. They were able to obtain a constant, which accounts for the mobilities of the ions in a number of aprotic solvents.

There has been an indication that the viscosity of the cosphere of an ion, is also influenced by the ionic charge. This effect on the viscosity would affect the mobilities. In this case the dielectric saturation effect appears as a second-order correction.

Endom et al.(204) observed that the larger metal ions decrease the amount of long range order in the cosphere in aqueous solutions. Giese(205) et al. showed that water molecules have greater rotational and translational freedom in the vicinity of the metal ions than in bulk water. In the Frank-Wen(c) treatment, the cosphere contains two regions. The region 'A' which is adjacent to the ion surface contains water molecules and the other region B which is further away from the centre of the ion. In this region A it is believed that the tetrahedrally bonded water molecules are disrupted by the ionic charges. It is further assumed that the region A is bigger than that of region B for the ions of high charge density, whereas the ions of low charge density have the reverse situation.

This approach has been employed by Kay-Evans(206) to examine the ionic transport phenomenon and the cospheres of the large univalent ions in aprotic solvents. When the ion is sufficiently large, the solvent molecules in the cosphere, could be orientated into favourable positions by neighbouring molecules. This behaviour arises from ions (i.e. tetraalkylammonium), which contain an inert surface.

As a result of this fact one can postulate that a cosphere of this type of ions contain greater degrees of hydrogen bonding than the bulk water does. It has also been observed that these ions increase the viscosity of water.

Another view of the structural cosphere effect has been introduced(101) from conductance data for D_2O solutions. The higher viscosity of D_2O solution over that of H_2O at 25°C, has been attributed to their hydrogens bonding characteristics. They have further showed that the structure breakers have higher mobility in D_2O than in H_2O, which is the reverse for the structure makers.

III-Id - Information from Experimental Data.

The viscosities of aqueous solutions of alkyltrimethyl ammonium bromides, and the solutions containing additives have been measured, as mentioned in Chapter II. The Jones-Dole equation(192) (III-7) has been used to analize the hydrodynamic data of the electrolyte solutions.

In order to evaluate A and B coefficients equation (III-7) can be written as

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} \qquad \text{III-16}$$

The plots of $\frac{n_r - 1}{\sqrt{c}}$ versus $\sqrt{c}$ are shown in Figs.III.1, III.2, III.3, III.4. The A intercept obtained is very small (0,009) in the aqueous solutions studied (Fig.III.1). The plot of equation (III-16) was found to be linear with $\sqrt{c}$ for C_{10}. But in the case of higher chain lengths, it is observed that the linear relationship with $\sqrt{c}$ is up to 0,15M, then it increases nonlinearly as the concentration increases. (Fig.III.1, Table III.I.1).

Frank-Evans(4) postulated that the presence of apolar solute increases water structure surrounding the solute. In the light of this approach, Krishnan-Friedman(91) and other investigators(100,106,107) have observed that the long apolar groups govern the interactions of the ions with water structure.

They showed that the apolar solution effects were large, for the structural contribution to the thermal properties of the solutions. As a result of these observations, they concluded that the apolar side of the ion behaves as structure maker in the solution.

Due to the apolar group of the ion, the viscosity of water increases by increasing the ice-like structure (structure maker). The calculated positive B coefficients (0.78 and 1.52 for C_{10} and C_{14} respectively) indicate that the alkylchain length of the ions tend to order the solvent structure, and increase the viscosity of the solution(207). The positive B coefficients of the hydrated ions appear to be proportional to the effective radius of Frank's(6) A region, in which the water is highly ordered. On the other hand the ions might also have small B regions. But the effect of this region is negligibly small.

It is apparent that the structure breaking effect decreases with the increase in radius of the ion(194). This can be explained in terms of the low charge density of the large ions. However, the increase in the ice-like structure, is proportional to the size of the nonpolar region(207).

When the surface charge is low, the electrostatic ion-solvent interactions do not affect the hydrogen bonded structure of the solvent(208). The order producing ions with positive B coefficients increase the energy and entropy of the activation for viscous flow, which increases with the increase in the chain length of ion. This is due to the increase in ice like structure around the apolar group(140,209).

The division of the B coefficients into individual ionic values is a kind of arbitrary process, because it is rather difficult to evaluate the corresponding transport numbers of the individual ions. The B_{ion} values of K^+ and C^- have been computed by Cox-Wolfenden(199), Kaminsky(194) and Gurney(69). The obtained ionic values were in good agreement with each other.

In order to obtain individual B_{ion} coefficients of the alkylammonium bromides, Kaminsky's procedure has been considered and his data was used for Br^- ion (-0.042, Table III.I.1).

Relatively small ions(194), multivalent ions, such as Li^+, Na^+, H_3O^+, Ca^{2+}, Mg^{2+} increase the viscosity of water. They polarize, immobilize and electrostrict nearest-neighbour water molecules(131). They are said to have net structure-making effects. Large mono valent ions have a net structure-breaking(131) (entropy increasing effect). Thus ions, such as Cl^-, Br^-, I^-, NO_3^-, Cs^-, K^+ increase the fluidity of water. The water molecules which are not in the vicinity of these ions become more mobile than those in pure water. As the temperature of water is increased, the net structure breaking influence of ions like Cl^-, Br^- and I^- decreases as the number of hydrogen bonded water molecules decreases.

Consequently the existence of negative viscosity B coefficients of the ions arises from the structure breaking effect. In view of the Frank-Wen(6) model, the negative B coefficients indicate that for large ions, because of the weak electric field, the B-region encroaches upon the A-region. The order destroying ions possess negative activation energies.

The cosphere of the positive ion causes a local increase in the viscosity, while cospheres of negative ions cause a decrease in the viscosity(69). If a cancellation occurs than the B coefficient will be near to zero. When the B coefficient is negative, it can be postulated that one of the ions is diminishing the viscosity.

On the addition of aliphatic alcohols to the aqueous solution of decyltrimethyl ammonium bromide, it is observed that the viscosity B coefficient becomes negative, as the concentration of alcohol increases. (0,641, 0,529 and -0,870 for C_{10} containing 0.4M, 1M and 2M CH_3OH respectively Fig.III.2, Table III.I.1,A). On the other hand, the decreasing effect of the alcohol increases linearly as the chain length increases (Fig.III.5). The observed negative values of the viscosity B coefficients can be discussed in terms of the effect of alcohols on the solvent structure and the possible interactions.

It is generally considered(91,97,210) that the apolar region of the alcohol molecule behaves as an apolar solute, which affects the solvent structure. The addition of alcohol to water causes at first an increase in the solvent structure(at low concentration structure maker). As the alcohol content is progressively increased, the structure is destroyed by the alcohol molecules, consequently the networks around the apolar groups are influenced by the apolar sides of the alcohol molecules, and the binding of alcohol molecule to the alkyl group of the ion might occur. Due to the high concentration of alcohol in the solution, polymeric hydrogen bonding mechanism takes place. These interactions alter the physico-chemical environment of the alkyl group and bromide ion in the solution.

Cox-Wolfenden(199) stated that the negative viscosity B coefficient is due to the depolymerization of thewater structure.

Gurney(69) explained that if a solute at room temperature causes the local loosening of the water structure, then the viscosity B coefficient is negative.

In this work it is reasonable to assume that the negative values of B coefficients arise from the destruction of networks around the apolar region by alcohol molecules. The alkyl group associated with alcohol molecule may behave as a structure breaker. As a result of this fact the negative B coefficient will increase as the particular alcohol concentration increases.

III.Ie - Conclusions.

The viscosity B coefficients of alkylammonium bromides in aqueous solutions are all positive. The B coefficient increases as the chain length increases. The increment of B is due to the long apolar group , which promotes the hydrogen bonded water structure.

The electrostatic ion-solvent interactions do not affect the hydrophobic interactions, due to the low surface charge of the apolar group. The energy and entropy of the activation for viscous flow, increase with increasing chain length. On the other hand, the Br^- ion behaves as a structure breaker and introduces the negative B coefficient.

The addition of alcohol to the system, affects the positive viscosity B coefficient of the ion. It becomes negative as the concentration of alcohol increases. This behaviour of the B coefficient is due to the effect of alcohol molecules on the solvent structure, the networks around the nonpolar groups, and the structure breaker effects of the alkyl and Br^- ions is a positive explanation of the negative B coefficients.

VISCOSITY B COEFFICIENTS FOR THE ALKYLTRIMETHYL AMMONIUM BROMIDES IN WATER AND CONTAINING ALIPHATIC ALCOHOLS AT 25° C

TABLE III.I.1

C mol. dm^{-3}	$\sqrt{C}$	$\frac{[\eta_r - 1]}{\sqrt{C}}$	B	Ionic B Coefficient	
				$R-\overset{\mid}{\underset{\mid}{N}}-^{+}$	Br^{-}
C_{10}					-0.042
0.1	0.3162	0.241	0.78	0.822	
0.08	0.2830	0.239			
0.07	0.2645	0.220			
0.06	0.2449	0.202			
0.05	0.2236	0.180			
0.04	0.20	0.158			
C_{12}					
0.06	0.2449	0.383	0.95	0.992	
0.05	0.2236	0.317			
0.04	0.20	0.253			
0.03	0.1732	0.231			
0.02	0.1414	0.172			
0.017	0.1304	0.144			
0.014	0.1183	0.121			
0.004	0.0632	0.055			
C_{14}					
0.05	0.2236	0.561	1.52	1.562	
0.04	0.20	0.461			
0.03	0.1732	0.378			
0.02	0.1414	0.265			
0.01	0.10	0.184			
0.004	0.0632	0.106			
0.0025	0.05	0.074			
C_{16}					
0.05	0.2236	0.831	2.5	2.542	
0.04	0.20	0.687			
0.03	0.1732	0.617			
0.02	0.1414	0.411			
0.01	0.10	0.269			
0.007	0.0836	0.219			
0.004	0.0632	0.162			

TABLE III.I.1.A

C $mol.dm^{-3}$	$\sqrt{C}$	$\frac{[\eta_r - 1]}{\sqrt{C}}$	A	B
C_{10}; 0.4 M, Me-OH				
0.1	0.3160	0.482	0.2675	0.641
0.08	0.2828	0.455		
0.07	0.2646	0.447		
0.06	0.2449	0.433		
0.05	0.2236	0.450		
0.04	0.20	0.432		
1M				
0.1	0.3160	0.680	0.505	0.529
0.08	0.2828	0.663		
0.07	0.2646	0.665		
0.065	0.2549	0.660		
0.06	0.2449	0.674		
0.05	0.2236	0.687		
0.04	0.20	0.715		
0.03	0.1732	0.763		
0.02				
2M				
0.1	0.316	1.016	-	-0.870
0.08	0.2828	1.047		
0.07	0.2646	1.070		
0.06	0.2449	1.110		
0.04	0.20	1.230		
0.03	0.1732	1.350		
0.02				
1 M, Et-OH				
0.1	0.316	0.999	-	-0.936
0.08	0.2828	1.027		
0.07	0.2646	1.047		
0.06	0.2449	1.071		
0.05	0.2236	1.109		
0.04	0.20	1.180		
2M				
0.1	0.316	1.787	-	-0.303
0.08	0.2828	1.880		
0.07	0.2646	1.960		
0.06	0.2449	2.050		
0.05	0.2236	2.190		

TABLE III.I.1.B

C mol. dm^{-3}	$\sqrt{C}$	$\frac{[\eta_r - 1]}{\sqrt{C}}$	A	B
0.5 M, Pr-OH				
0.1	0.316	0.829	-	-0.257
0.08	0.2828	0.841		
0.07	0.2646	0.835		
0.06	0.2449	0.844		
0.05	0.2236	0.886		
0.04	0.20	0.939		
1 M				
0.1	0.316	1.399	-	-2.3
0.08	0.2828	1.482		
0.07	0.2646	1.520		
0.06	0.2449	1.570		
0.05	0.2236	1.640		
0.2 M, Bt-OH				
0.1	0.316	0.599	0.415	0.540
0.08	2.2828	0.575		
0.07	0.2646	0.556		
0.06	0.2449	0.558		
0.05	0.2236	0.570		
0.04	0.20	0.587		
0.5 M				
0.1	0.316	1.044	-	-0.681
0.08	0.2828	1.056		
0.07	0.2646	1.076		
0.06	0.2449	1.096		
0.05	0.2236	1.135		
0.04	0.20	1.120		
0.8 M				
0.1	0.316	1.417	-	-1.72
0.08	0.2828	1.463		
0.07	0.2646	1.50		
0.06	0.2449	1.547		
0.05	0.2236	1.574		
0.04	0.20	1.70		

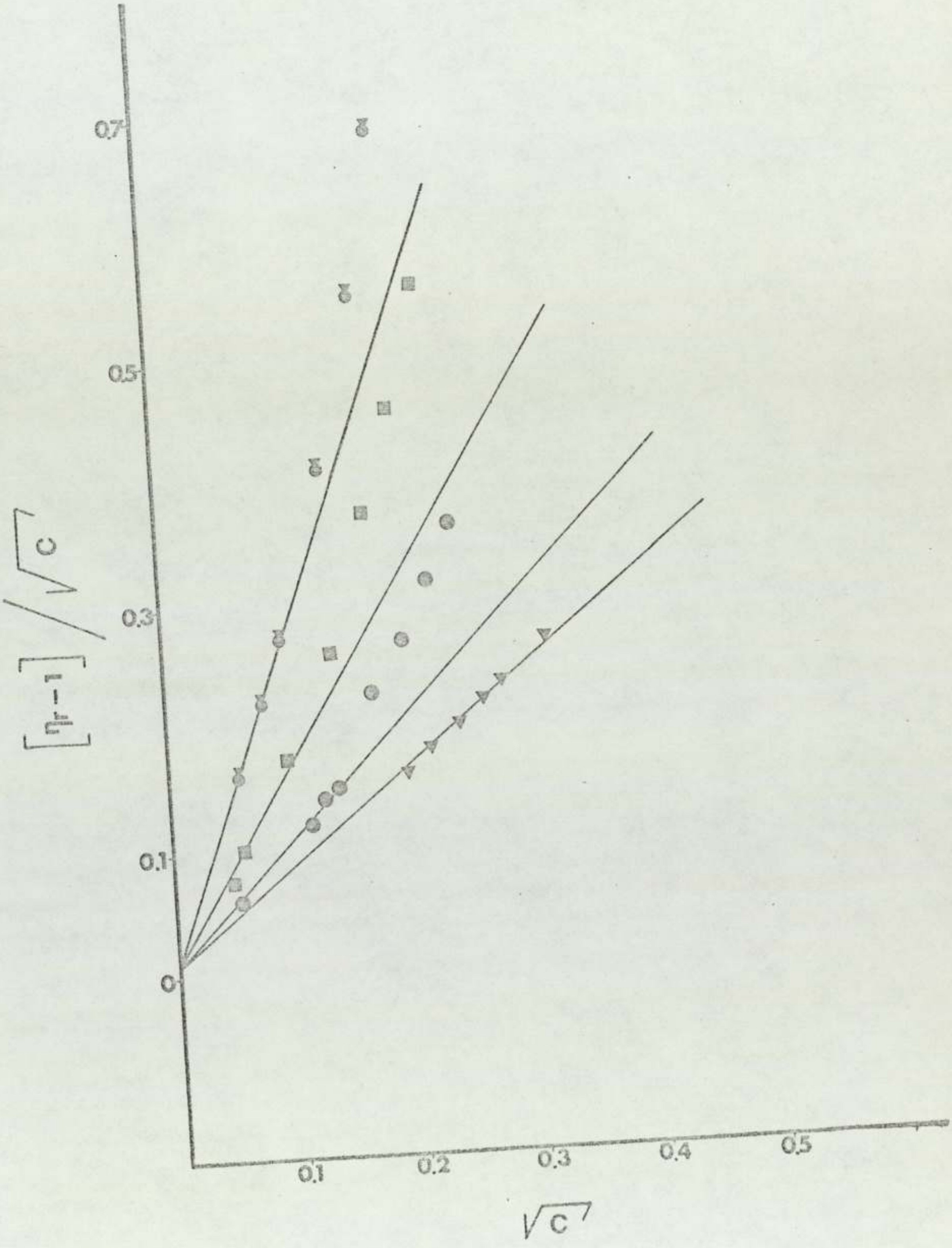


Fig.III.I Plots of $[\eta_r-1]/\sqrt{C}$ versus $\sqrt{C}$ for the alkyl-ammonium bromides in water at 25° C; ▲ C_{10}, ● C_{12} ■ C_{14}, and ▼ C_{16}

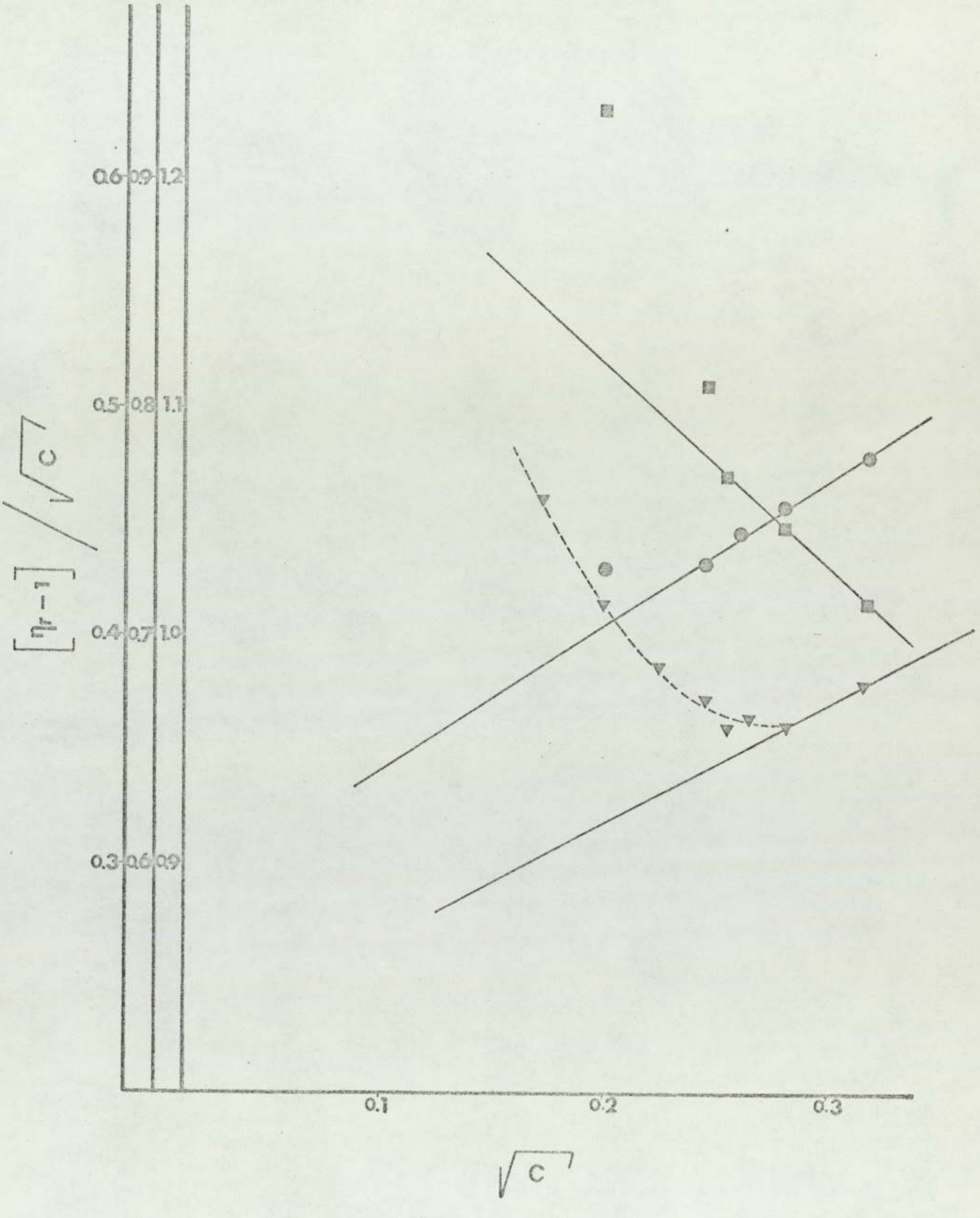


Fig.III.2 Plot of $[\eta-1]/\sqrt{C}$ versus $\sqrt{C}$ for the decyl trimethyl ammonium bromide containing various concentration of the methanol in water at 25° C; Me-OH: ● 0.4M, ▲ 1M, and ■ 2M

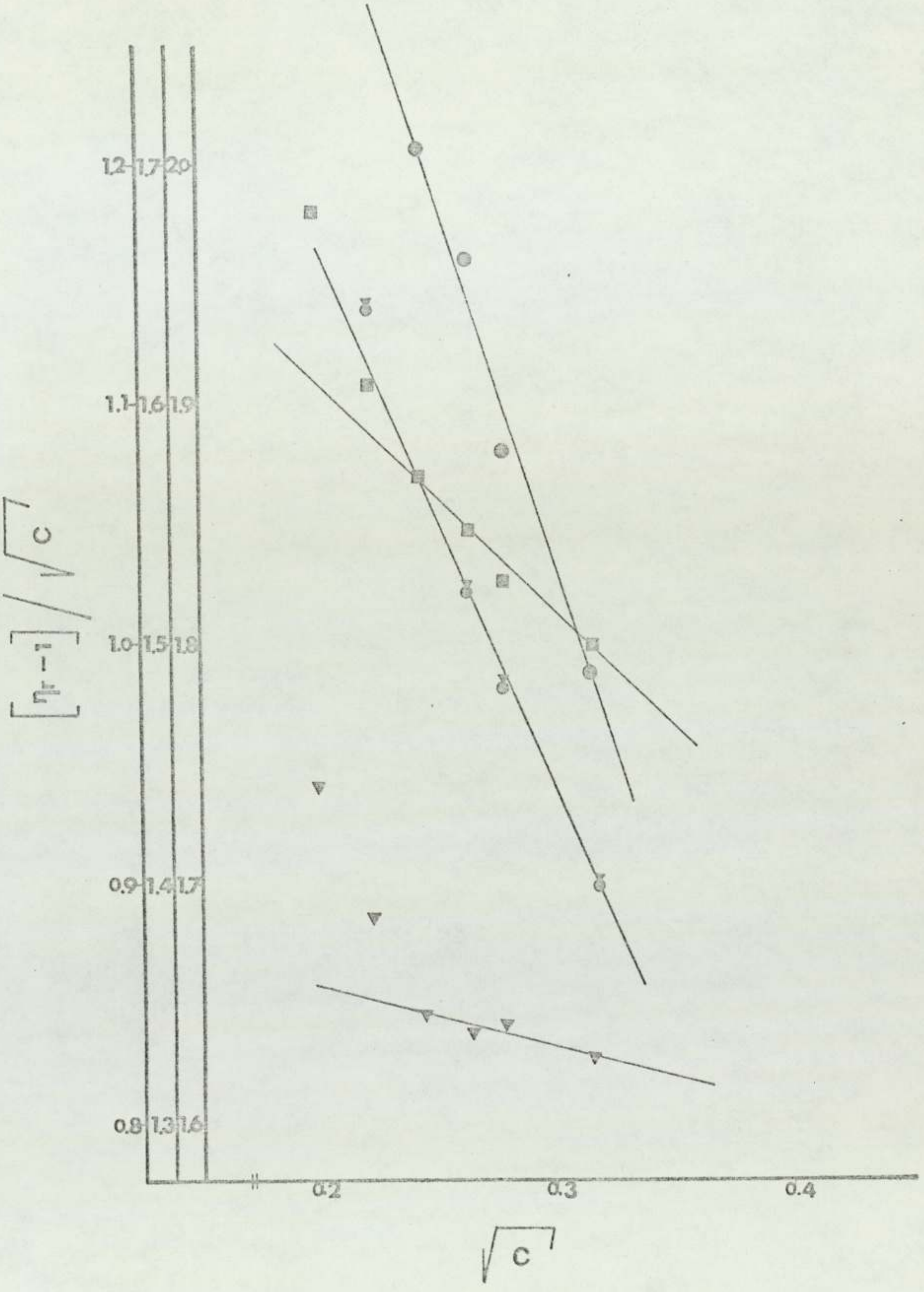


Fig.III.3 Plot of $[\eta-1]/\sqrt{C}$ versus $\sqrt{C}$ for the decyl trimethyl ammonium bromide containing various concentration of the aliphatic alcohols in water at 25° C; Et-OH: ● 1 M, ■ 2 M; Pr-OH: ▲ 0.5 M, ▽ 1 M

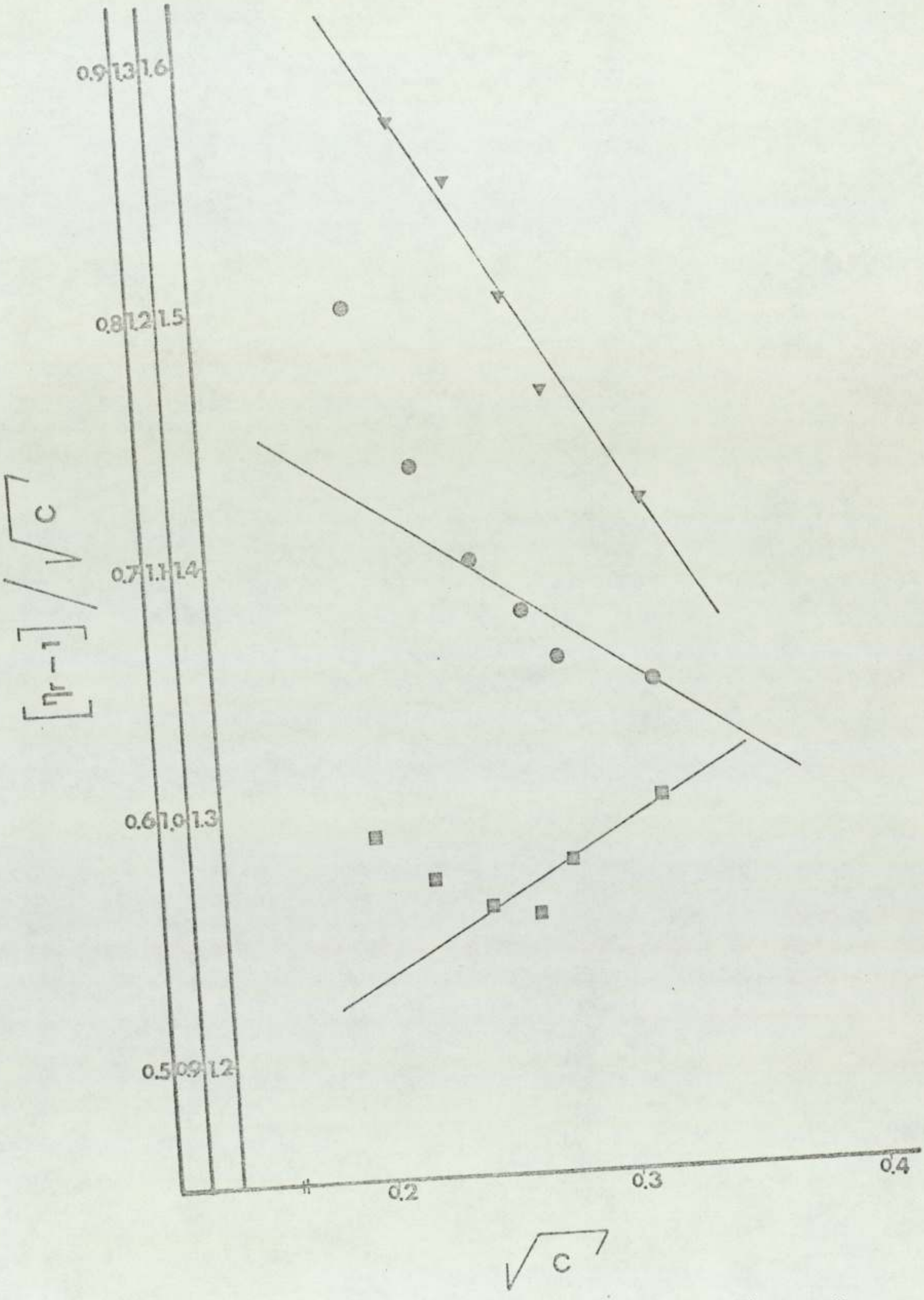


Fig. III.4 Plot of $[\eta - 1] / \sqrt{C}$ versus $\sqrt{C}$ for the decyltrimethyl ammonium bromide containing various concentration of the butanol in water at 25° C; Bt-OH: ■ 0.2 M, ● 0.5M, and ▲ 0.8 M

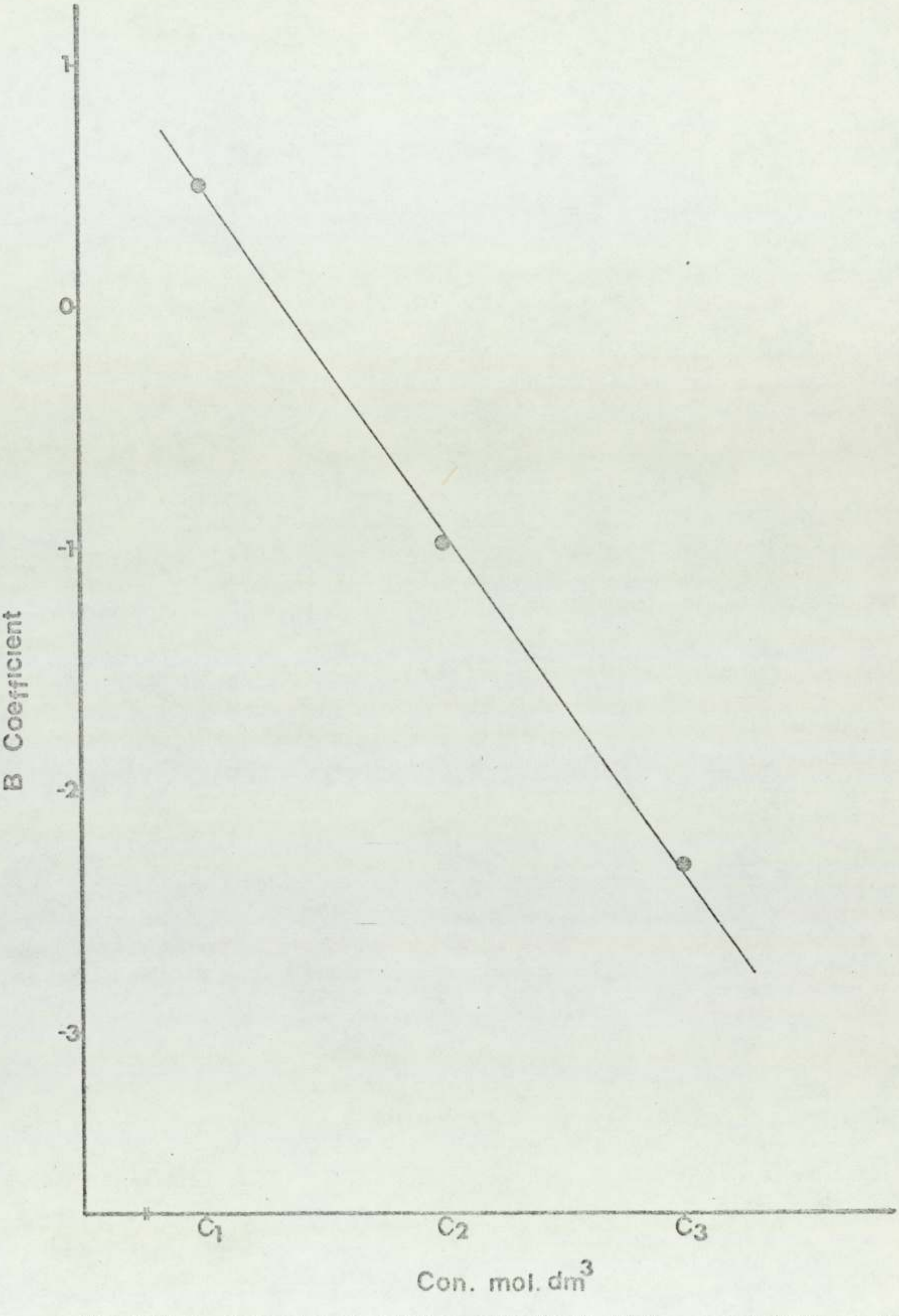


Fig.III.5 Dependence of B coefficient of C_{10} containing I M aliphatic alcohols in water on the hydrocarbon chain length of the alcohol

CHAPTER IV - Partial Molal Volume properties of Alkyl ammonium Bromides.

IV.Ia - Partial molar volumes of solutions

IV-Ib - Volumetric Properties of Solutions

IV-Ic - The nature of partial molal volume of micelles of alkylammonium bromides

IV-Id - Conclusions

IV.Ia - The partial molar volumes of solutions.

Certain characteristics common to all partial molal quantities can be considered, in order to obtain any extensive property of a given solution. It is assumed for the present that the temperature and pressure are constant$^{(88,141)}$.

Consider Y as an extensive property of a given solution such as volume, heat capacity, or internal energy which is a function of temperature, pressure and the amounts of the several constituents$^{(88)}$. So Y depends only on $n_1, n_2 \ldots$ However we can define the partial molal values by the equations,

$$\overline{Y}_1 = \left(\frac{\partial Y}{\partial n_1}\right)_{p,T,n_1,n_3 \ldots} \qquad \overline{Y}_2 = \left(\frac{\partial Y}{\partial n_2}\right)_{p,T,n,n_3 \ldots} \qquad \text{IV-1}$$

which takes the form for general partial differentiation,

$$dY = \left(\frac{\partial Y}{\partial n_1}\right)_{p,T,n_2,n_3 \ldots} dn_1 + \left(\frac{\partial Y}{\partial n_2}\right)_{p,T,n_1,n_3} dn_2 + \ldots \qquad \text{IV-2}$$

or $dY = \overline{Y}_1 dn_1 + \overline{Y}_2 dn_2 + \ldots$ IV-3

It is apparent that $\overline{Y}_1$ and $\overline{Y}_2$ depend on the total amount of each constituent, and the composition. In view of this expression, we can integrate equation (IV-3) in terms of keeping $n_1, n_2 \ldots$ in constant proportions and we obtain

$$\begin{aligned} dY &= (\overline{Y}_1 x_1 + \overline{Y}_2 x_2 + \ldots)dn \\ Y &= (\overline{Y} x_1 + \overline{Y}_2 x_2 + \ldots)n \\ Y &= n_1 \overline{Y}_1 + \overline{Y}_2 n_2 + \ldots \end{aligned} \qquad \text{IV-4}$$

Since this equation is entirely general, it can be differentiated with respect to any change of composition, then the equation takes the form

$$dY = n\, d\overline{Y}_1 + \overline{Y}_1 dn_1 + n_2 d\overline{Y}_2 + \overline{Y}_2 dn_2 \qquad \text{IV-5}$$

and substitution of equation (IV-3) into equation (IV-5) gives

$$n_1 d\overline{Y}_1 + n_2 d\overline{Y}_2 + \ldots = 0 \qquad \text{IV-6}$$

These equations (IV-4 and IV-6) can be called the partial molal equations(88). If we consider the number of moles of one constituent say n_1, as the main variable in terms of the constancy of p and T, then we can rewrite equation (IV-6) with respect to n_1 and n_2

$$n_1 \left(\frac{\partial \overline{Y}_1}{\partial n_1}\right)_{p,T} + n_2 \left(\frac{\partial \overline{Y}_2}{\partial n_1}\right)_{p,T} + \ldots = 0 \qquad \text{IV-7}$$

when n_1 moles of component 1 are mixed with n_2 moles of component 2, the total volume of the solution V is

$$V = n_1 \left(\frac{\partial V}{\partial n}\right)_{n_2,T,p} + n_2 \left(\frac{\partial V}{\partial n_2}\right)_{n,T,p} \qquad \text{IV-8}$$

where $\left(\frac{\partial V}{\partial n_1}\right)_{n_2,T,p} = \overline{V}_1$ and $\left(\frac{\partial V}{\partial n_2}\right)_{n,T,p} = \overline{V}_2$ are the partial molal volumes of components 1 and 2 respectively.(88) The total volume of the solution is an extensive property of the system. The differential molar volumes or partial molar volumes are usually dependent on concentration.

IV.Ib - The Volumetric Properties of Solutions.

Partial molal volume properties of the dilute solutions of mixed solutes are fruitful sources of information on solute-solvent interactions. Friedman-Scheraga(211) showed that the negative excess limiting partial molal volume, for a series of aliphatic alcohols increases with temperature and molecular size. They attempted to correlate their results, in terms of the Nemethy-Scheraga(7) theory considering that the polar and nonpolar sides of the molecule produce additive volume effects.

Franks-Smith(212) introduced a large negative value of $\overline{V}_1^{op}$ for butanols, and that has been attributed to solvent-structure stabilization. On the other hand, Nakanishi(213) showed that the negative value of $\overline{V}_1^{op}$ depends not only on the molar volume of the solute, but also on the polar and nonpolar groups in the solute molecule.

A further approach has been demonstrated by Franks et al.(214) in view of the effect of polar and nonpolar groups on the volume properties of the system. They conclude that the molar volume of the pure solute cannot give reliable indication of solute size, since similar size of cyclic ethers have different molar volumes. The plots of $\overline{V}_2(x_2)$ of many mixed solutes indicate that long-range interaction between the solute molecules does not exist(80). It is reasonable to assume that it is transmitted specifically by the solvent.

The minimum point of the $\overline{V}_2(x_2)$ curves, can be considered as a point at which reinforcement of solvent sheaths are replaced by the interference between solvent sheaths, as the solvent is no longer sufficient to support the structuring ability of the solute molecule.

It is difficult to interpret volume effects at higher concentrations, due to solute-solute, solute-solvent and solvent-solvent interactions. It has been shown(213) that the slope of partial molal volume-mol fraction curve, depends on the ratio of polar and nonpolar groups in the solute molecule.

As the proportion of polar groups increases, the negative slope of the curve decreases. In the case of hydrophilic solutes, the slope of the curve $\partial\bar{V}_2/\partial x_2$ is near to zero(80).

As a result of this fact Franks suggested(80) that the effect of solute on water structure at long range decreases, as the apolar nature of the solute decreases.

As the nonpolar group of alcohol molecule increases, $\partial\bar{V}_2/\partial x_2$ becomes more negative, and the minimum on the curve moves to a lower x_2. This is due to the structure promoting effect of the alcohol molecule at low concentration. Wada-Umeda(215) examined the volumetric behaviour of the alcohols, certain amines, and cyclic ethers, and showed that the temperature of maximum density of water for lower alcohols, ketones and ethers is positive. This observation indicates that these solutes increase the structure of water molecules.

However, a structure making solute at low concentrate exhibits a negative $\partial\bar{V}_2/\partial T$, whereas a structure breaking solute shows a positive $\partial\bar{V}_2/\partial T$. Usually all solutes behave as structure breakers at sufficiently high concentrations.

IV.Ic - The nature of partial molal volume of micelles of alkylammonium bromides.

In order to study volumetrically the solute solvent interactions in aqueous solutions of alkylammonium bromides, it is necessary to derive partial molal volumes from the measurements carried out at finite concentrations. The apparent molal volume of the solute ϕ(211,216), can be related to the densities by the equation

$$\phi = \frac{M}{p_1} - \frac{1000(p_1 - p_1H_2O)}{mp_1 \; p_1H_2O} \qquad \text{IV-9}$$

The partial molal volume $\bar{V}_1$ can be related to ϕ by an equation

$$\overline{V}_1 = \phi + m \left[\frac{\partial \phi}{\partial m} \right]_{T,p,n_0} \qquad \text{IV-10}$$

If ϕ is plotted against m, and extrapolation of the obtained curve to zero concentration, the intercept gives $\overline{V}_0$ at infinite concentration. The measurement of densities of the solutions has been described in Chapter IIand the same density data (TablesII.I.1, II.I.1.A, II.I.3,A,B,C,D) has been employed for the determination of partial molal volumes of the alkylammonium bromides inaqueous solutions.

The partial molal volumes at different concentrations, have been derived by using equations (IV- 9 and IV-10). In order to obtain the partial molal volume of micellar species, the $\overline{V}$ value has been plotted against concentration ($C-C_0$), and the extrapolation of the curve to C = 0 gives the intercept, which is the $\overline{V}_1$ value of the micelle (Fig.IV.2).

The observed $\overline{V}_1$ value of the micelles for C_{10}, and C_{12} is 265, and 285 ml/mole respectively (Table IV.I.1). The $\overline{V}_1$ value for C_{10} is very close to the value (262 ml/mole), given by Corkill et al.(217) for the respective alkylammonium salt.

However the $\overline{V}_1$ values for higher chain lengths are lower than given by Corkill et al(217)(295 ml/mole for C_{12}). On the other hand, the partial molal volume below C_0, has been derived by using equation (IV- 9) amd plotting ϕ value against concentration C. The extrapolation of the obtained curve to C = 0, gives the partial molal volume $\overline{V}_0$ below the C_0 (Fig.IV.1).

These results follow a similar pattern, the $\overline{V}_0$ value for C_{10} and C_{12} (258.2 and 278.05 ml/mole respectively) are also different from the respective values (255 and 287 ml/mole) given by Corkill et al.(217). (Table IV.I.1). As can be seen in Fig.IV.3 the partial molal volume of alkylammonium bromides in aqueous solution, in both cases increases as the chain length increases. The observed volume change in $\overline{V}_1$ per $-CH_2-$ group is 17 ml/mole ($\overline{V}^o_{1A}$), which agrees well with the values given (17.4 ml/mole) by Corkill et al(217) for alkylammonium bromides, and Huggins(218) (16.7 ml/mole per $-CH_2-$) for n-alkanes at chain lengths C_8-C_{14}.

On the other hand, the volume change per $-CH_2-$ group below C_0 is 15.45 ml/mole ($\overline{V}^o_{1B}$), which is slightly different from Corkhill's(217) value (16.1 ml/mole). Gurney(69) introduced the idea that the partial molal volumes of electrolytes, could be examined in terms of unsolvated ionic radius. In his approach, it is assumed that the hydration sheath around the ion is compressed by electrostatic forces.

However the volume change which occurs in hydrocarbon water systems has been examined by Nemethy-Scheraga(5) in terms of hydrophobic interactions. In view of this treatment, they consider that the pertubation of water molecules by the apolar group of an alkyl chain, causes a volume change.

It is apparent that the partial molar volume of a solution species, does not depend on the environment. It describes solvent-solute interactions. Micelle formation is accompanied by an increase in $\overline{V}_1$, which is due to the elimination of hydrocarbon water contact. The formation of micelles involves the transfer of hydrocarbon from an aqueous to a non-polar region with an increase in volume(219). The observed volume change $\Delta\overline{V}_1$ at the C_0 for C_{10}, and C_{12} is 6.8 ml/mole and 7.1 ml/mole respectively, (Table VI.I.1). These results are very close to the values given by Corkhill et al(217)(6.9 and 8.5 ml/mole).

The alkyl chain length of surfactants studied possess a high hydrocarbon water interfacial energy(220), and this tends to reduce surface area. When complete reduction in interfacial energy is reached, the chain is more free to expand. As a result of this process, the partial molal volume $\overline{V}_1$ increases(221).

The volumetric change which occurs during the micellization process, has been discussed by Benjamin (219), in terms of hydrophobic interactions. According to his view, one can consider the volume change as due to the decreased hydration of the head group, and possible electrostriction effects. If this view is correct, one could consider the head group, and adjacent alkyl chain to remain unchanged during the micellization process.

The micelles have a high charge density due to their head groups, which are adsorbed in the Stern layer(155). The changing environment of the head group, can be expected to give a small contribution to $\overline{V}_1$. The $\Delta\overline{V}_1$ has been plotted as a function of chain length(217,219) (Fig.IV.3), and as can be seen, with extrapolation of the curve, the $\Delta\overline{V}_1$ becomes zero for the lower chain lengths of 3-5 carbon atoms. This has been attributed to the negative contribution of head group to $\overline{V}_1$, or to the methylene group adjacent to the hydrophilic head, which is assumed to give a small contribution to $\overline{V}_1$.

It is generally accepted that, due to strong electrical interactions, counterions are adsorbed in the Stern layer, and are bound to the surfaces of the micelles(155). The electrostatic interactions between the charges on the micelles, covalent bonding, charge transfer and desolvation influence $\overline{V}_1$ and $\Delta\overline{V}_1$ (222).

Since the micelle includes the firmly attached counter-ions, and firmly attached water molecules(155,222), the observed partial molal volumes of the micelles are not true $\overline{V}_1$'s of the micelles(222). They include partial molal volumes of bound counter-ions and water molecules, which locate in the Stern layer around the kinetic micelle.

The effect of aliphatic alcohols on the volumetric properties of the micelles has also been examined. The addition of alcohol to the aqueous solutions of surfactant, changes the solvent-solute interactions in the system. The three component system consisting of an aqueous phase containing surfactant ions, additive molecules (alcohol), and a mixed micellar phase, composed of alkylamonium bromide ions (and counter ions + water + alcohol) has been treated as a two-phase system(223). The $\overline{V}_2$ value of alkylammonium bromide at different concentration of 25°C, has been calculated from density data using the following equation(223),

$$\overline{V}_2 = \frac{M}{p_1} - \frac{(n_0M_0 + nM + n_2M_2}{p_1^2} \left[\frac{\partial p_1}{\partial n_1}\right]_{p,T,n_0,n_2} \qquad \text{IV-11}$$

The same density data has been employed, (Tables II.I.3.A,B,C,D) in order to obtain the slope of the density-concentration curve, for dodecylammonium bromide containing alcohol molecule. (FigsIV.4,IV.4.A).

The $\overline{V}^o_2$ value of micelles has been derived by plotting $\overline{V}_2$ value against $C-C_o$, and extrapolation of the curve to $C = 0$, gives the $\overline{V}^o_2$ value of the mixed micelles. (FigsI V.5.,IV.5.A).

When one mole CH_3OH is added to the aqueous solution of alkylammonium bromide, the $\overline{V}^o_2$ value of micelles increases (285.90 ml/mole for C_{12}). The increase in $\overline{V}^o_2$, increases as the concentration of alcohol increases (Fig.IV.6). In the higher concentration studied (4M.CH_3OH), the $\overline{V}^o_2$ value is 310.04 ml/mole (Table IV.I.2).

On the other hand, the observation indicates that the $\overline{V}^o_2$ value increases as the chain length of alcohol increases. As can be seen in Fig.IV.6, the $\overline{V}^o_2$ value of the micelles of dodecyltrimethyammonium bromide containing 1M, and 2M alcohol from methanol to n-propanol increases. However on addition to 2M alcohol to the system, $\overline{V}^o_2$ decreases when n-propanol is added.

The addition of alcohol molecules to aqueous solution of alkylammonium bromides, as has been discussed in Chapter II.h2 causes a change in structure of solvent molecules, and solute solvent interactions. The aliphatic alcohols are usually structure promoting at low concentration(91,210). This behaviour tends to the opposite direction as the concentration increases.

Consequently this nature of the alcohol molecule affects the kinetic properties of micelles(155). The transfer of an alcohol molecule from a nonpolar environment to the aqueous region causes an increase in $\overline{V}_1$ of the alcohol molecule(211). Since the alcohol molecule behaves as a hydrocarbon due to its apolar group(91,97,210), it is reasonable to assume that the $\overline{V}^o_2$ value increases, when the molecule is transferred from an aqueous region to a nonpolar environment. The alcohols penetrate into the kinetic micelle through the Gouy-Chapman-Stern electrical double layer around the micelle(155). The volume change due to the penetration process of alcohol molecules into the micelle, contributes to the increase in $\overline{V}^o_2$ of the micelle, as can be seen in TableIV.I2the difference between $\overline{V}_1$ and $\overline{V}^o_2$ is 0.8 ml/mole for 1M CH_3OH. In the higher concentration (4M CH_3OH) $\Delta\overline{V}_2$ is 24.94 ml/mole.

It is apparent that the partial molal volume of the micelle increases with addition of alcohol molecules the increment $\Delta\overline{V}_2$ indicates that $\overline{V}^o_2$ is altered by the increase in alcohol concentration. (Fig.IV.7. Tables IV.I.2, A,B).

Since the decrease in volume for an homologous series of paraffins and alcohols during fusion is of the order of 10-20%, the higher $\overline{V}$ values below C_o and at the C_o compared to crystal molar volumes $\overline{V}_c$ of alkylammonium bromides are consistent with a partial melting process(224) (Table IV.I.1).

IV.Id - Conclusions.

The volumetric properties of alkylammonium bromides below the C.M.C and at the critical micelle concentration show that the partial molal volume of the surfactant, in both cases increases with increasing the chain length. This observation indicates that the micelle formation is accompanied by an increase in volume. This is due to the transfer of alkylammonium ions, from an aqueous environment to a nonpolar region, in terms of the limitation of interfacial energy with water molecules. The decrease in contact with polar molecules causes an increase in the partial molal volume of the micelles.

The addition of aliphatic alcohol to the system also contributes volume change, and an increase in the partial molal volume of the micelles. The influence of the alcohols to the volumetric properties of the micelles, can be discussed in terms of hydrophobic interactions, since they behave as hydrocarbons in aqueous solutions. The volume change in partial molal volume of the micelles, per $-CH_2-$ group of alcohol increases with increasing chain length. They penetrate into the interior of micelle and contribute positive partial molal volume increase, as the concentration of alcohol increases. The increment decreases at higher concentration due to the saturation effect on the interior of the kinetic micelle.

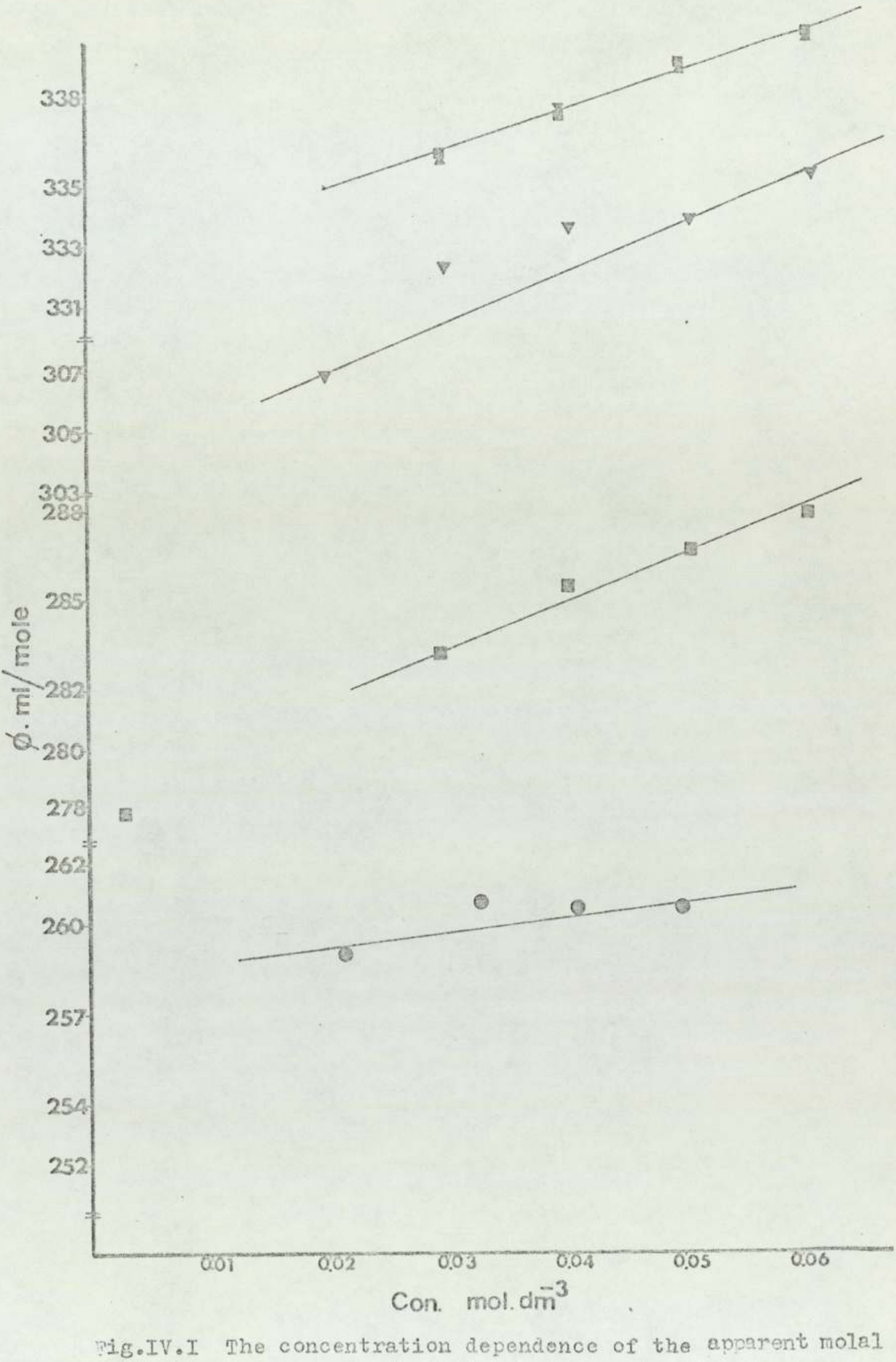


Fig.IV.I The concentration dependence of the apparent molal volumes of alkyltrimethyl ammonium bromides at 25° C; ● C_{10}, ■ C_{12}, ▼ C_{14}, and ▨ C_{16}

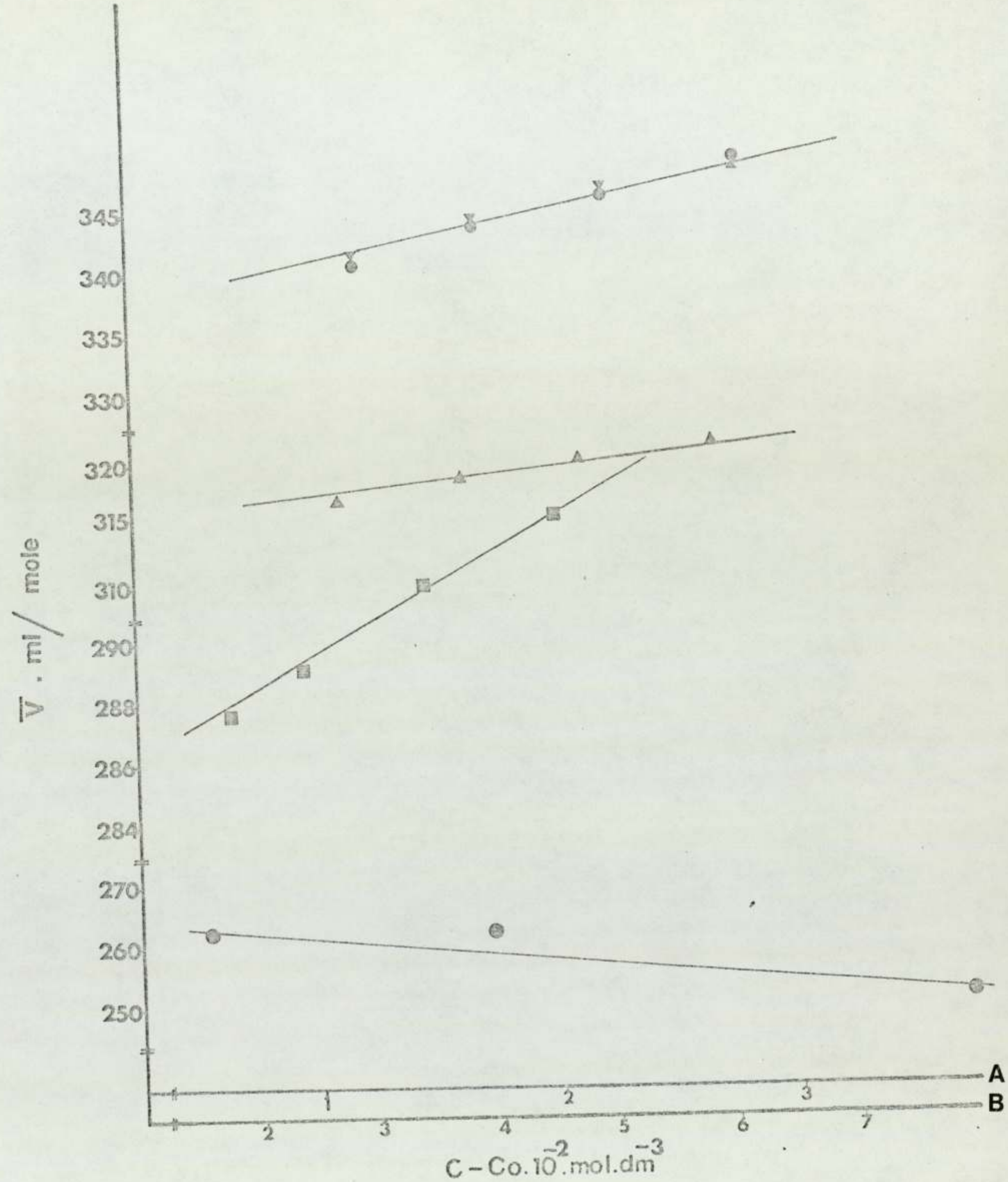


Fig.IV.2 The partial molal volumes versus concentration for the alkyltrimethyl ammonium bromides above the C.M.C at 25° C; ● C_{10}, ■ C_{12}, ▲ C_{14}, and ▼ C_{16} ; **A** C_{10}, **B** C_{12}, C_{14}, C_{16}

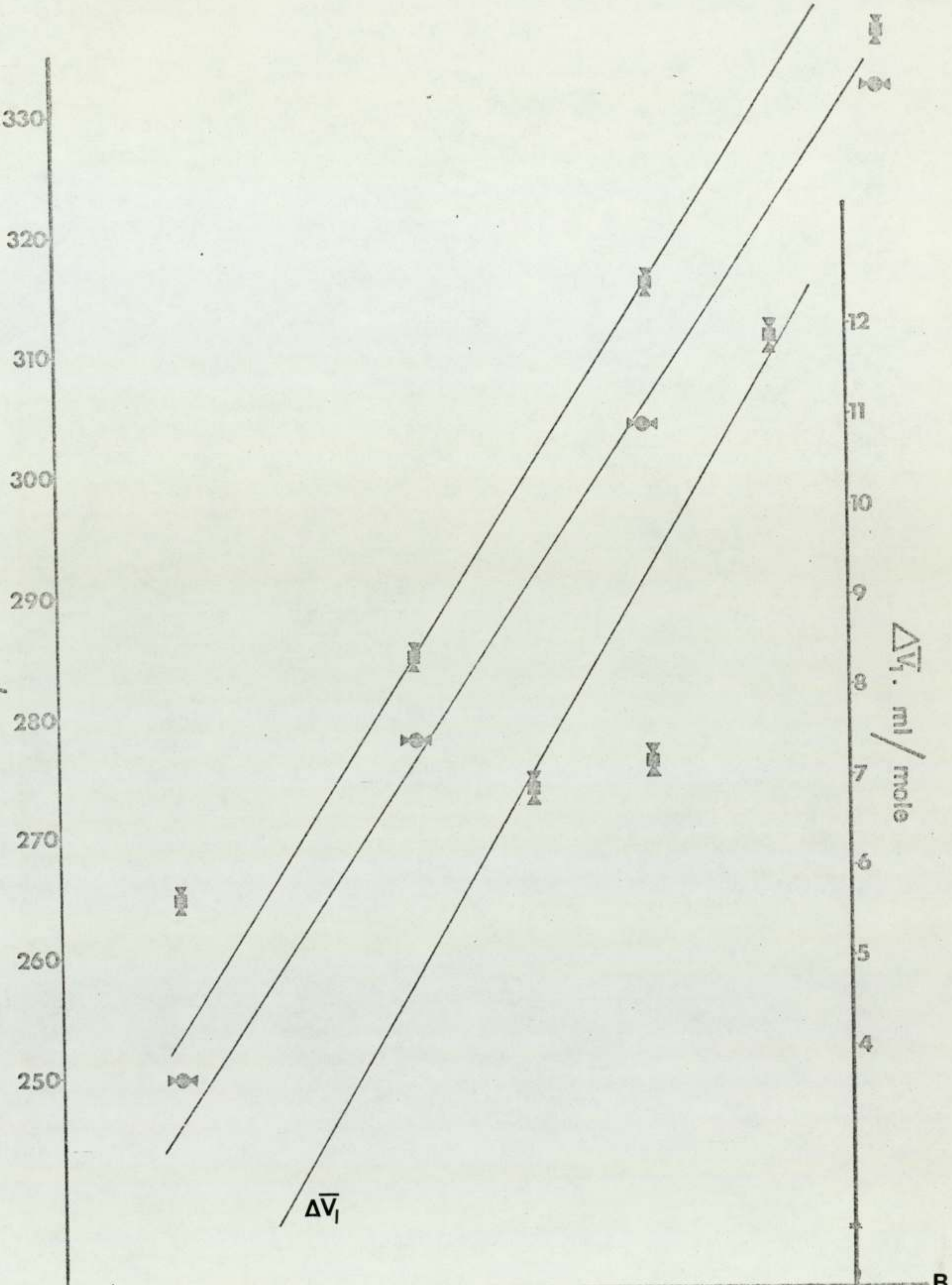


Fig. IV.3 **A**, The partial molal volumes of the alkyltrimethyl ammonium bromides below the Co, and above the Co, as a function of the hydrocarbon chain length; ⧓ below the Co, ⧗ above the Co. **B**, The behaviour of $\Delta\overline{V}_1$ as a function of the main alkyl chain length.

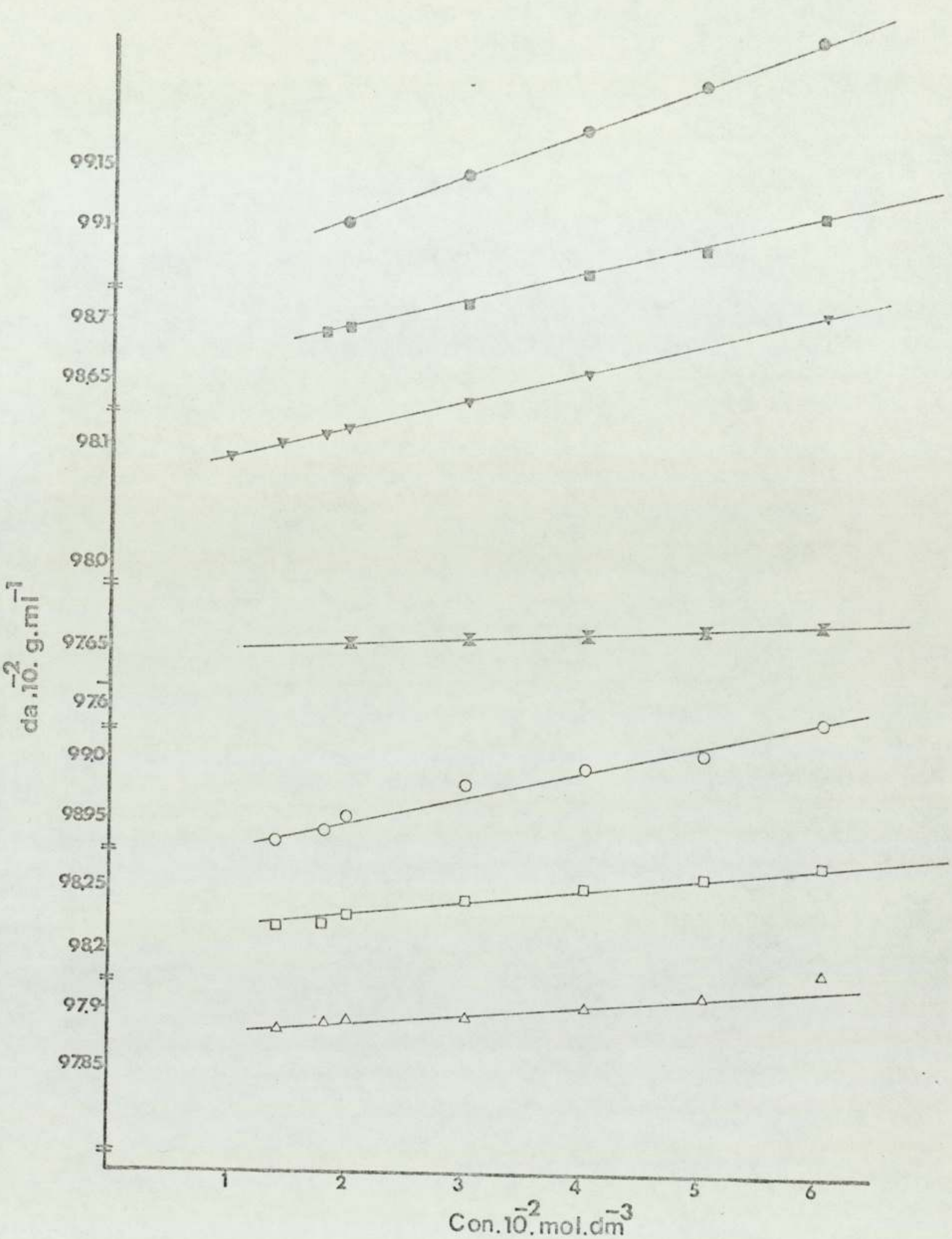


Fig. IV.4 Variation of the density of dodecyltrimethyl ammonium bromide with the various concentration of methanol and ethanol in water at 25° C; Me-OH: ● 1M, ■ 2M, ▲ 3M, and ⧗ 4 M; Et-OH: ○ 1 M, □ 2 M, and △ 2.5 M

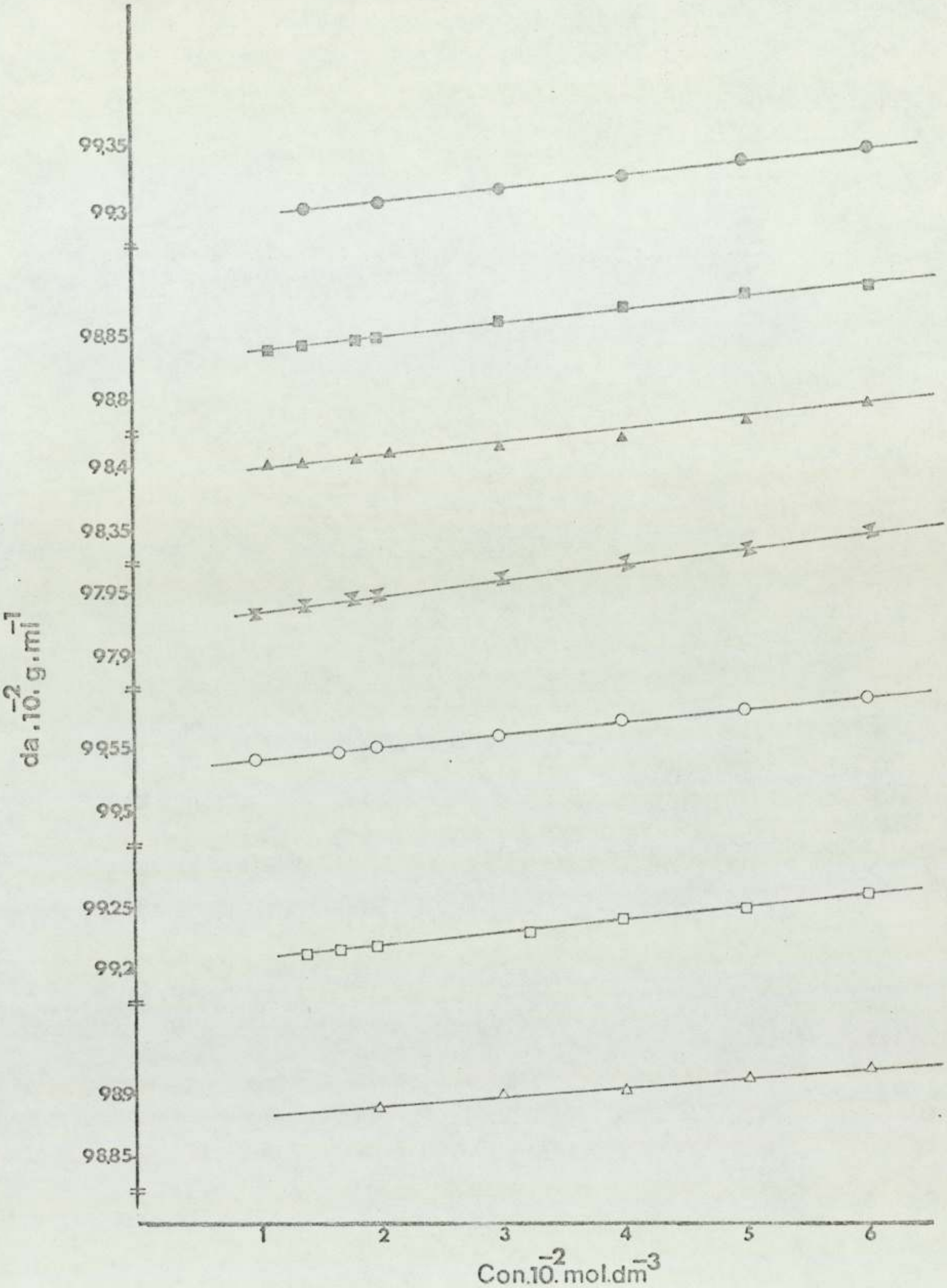


Fig. IV.4.A Variation of the density of dodecyltrimethyl ammonium bromide with the various concentration of propanol and butanol in water at 25° C; Pr–OH: ● 0.5 M, ■ 1 M, ▲ 1.5 M and ⧗ 2 M: Bt–OH: ○ 0.2 M, □ 0.5 M, and △ 0.8 M

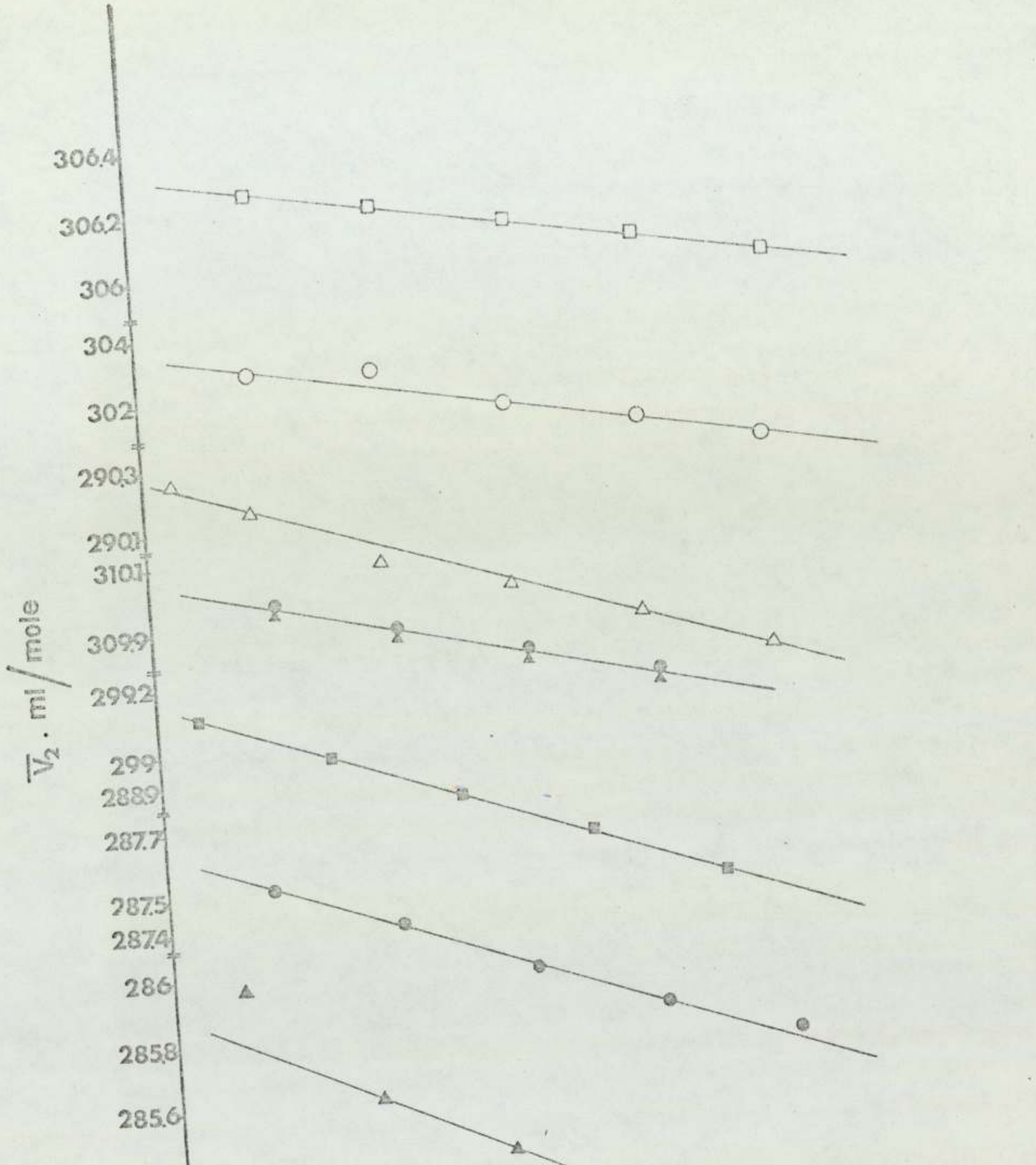


Fig.IV.5 The various methanol and ethanol concentration dependence of the partial molal volume of the dodecyltrimethyl ammonium bromide in water at 25° C; Me-OH: ▲ 1M, ● 2M, ▪ 3M, and ⧗ 4M ; Et-OH: △ 1M, ○ 2M, and □ 2.5M

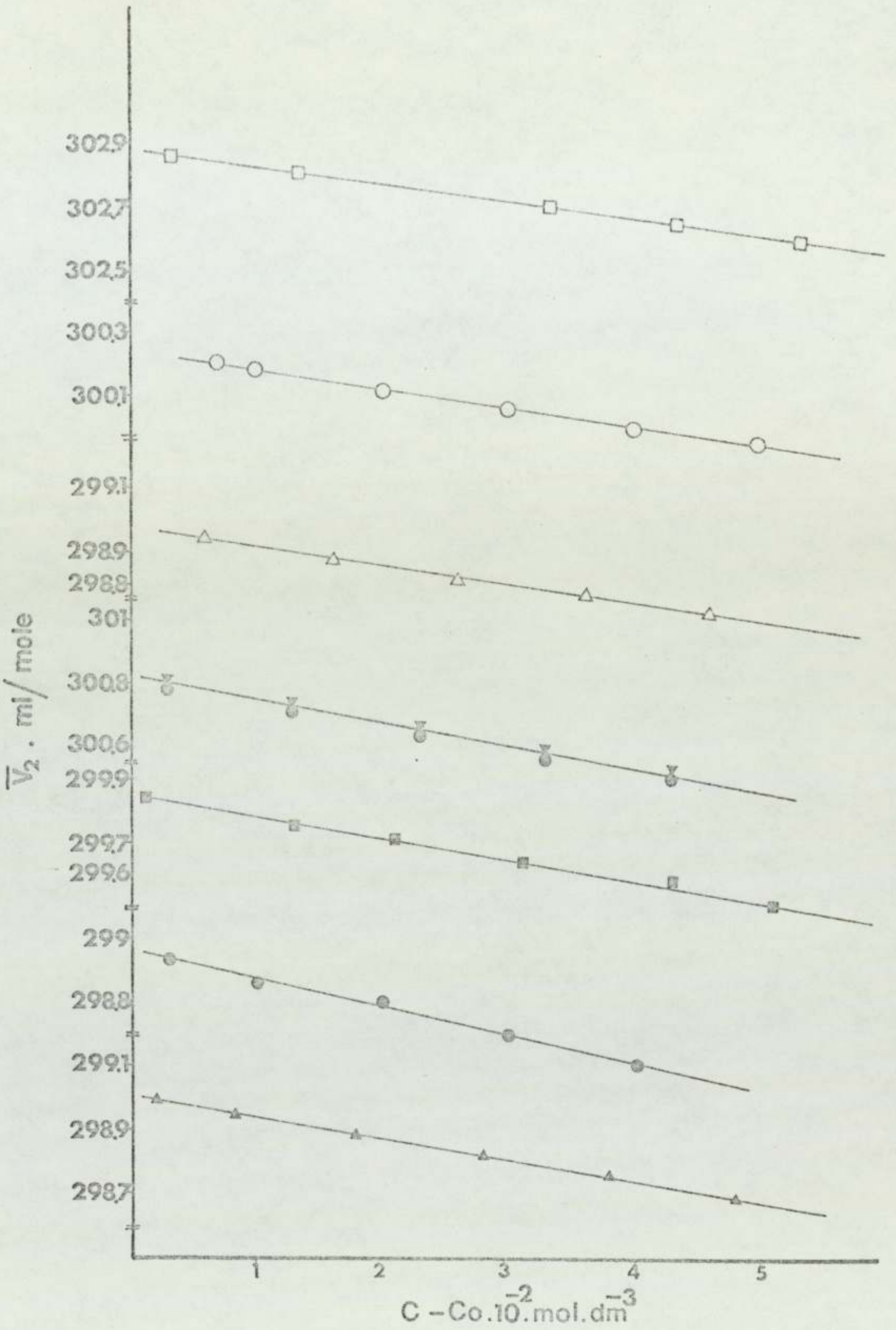


Fig. IV.5.A The various propanol and butanol concentration dependence of the partial molal volume of the dodecyltrimethyl ammonium bromide in water at 25° C; Pr-OH: ▲ 0.5 M, ● 1 M, ▣ 1.5M, and ☿ 2 M; Bt-OH: △ 0.2M, ○ 0.5M, and □ 0.8 M

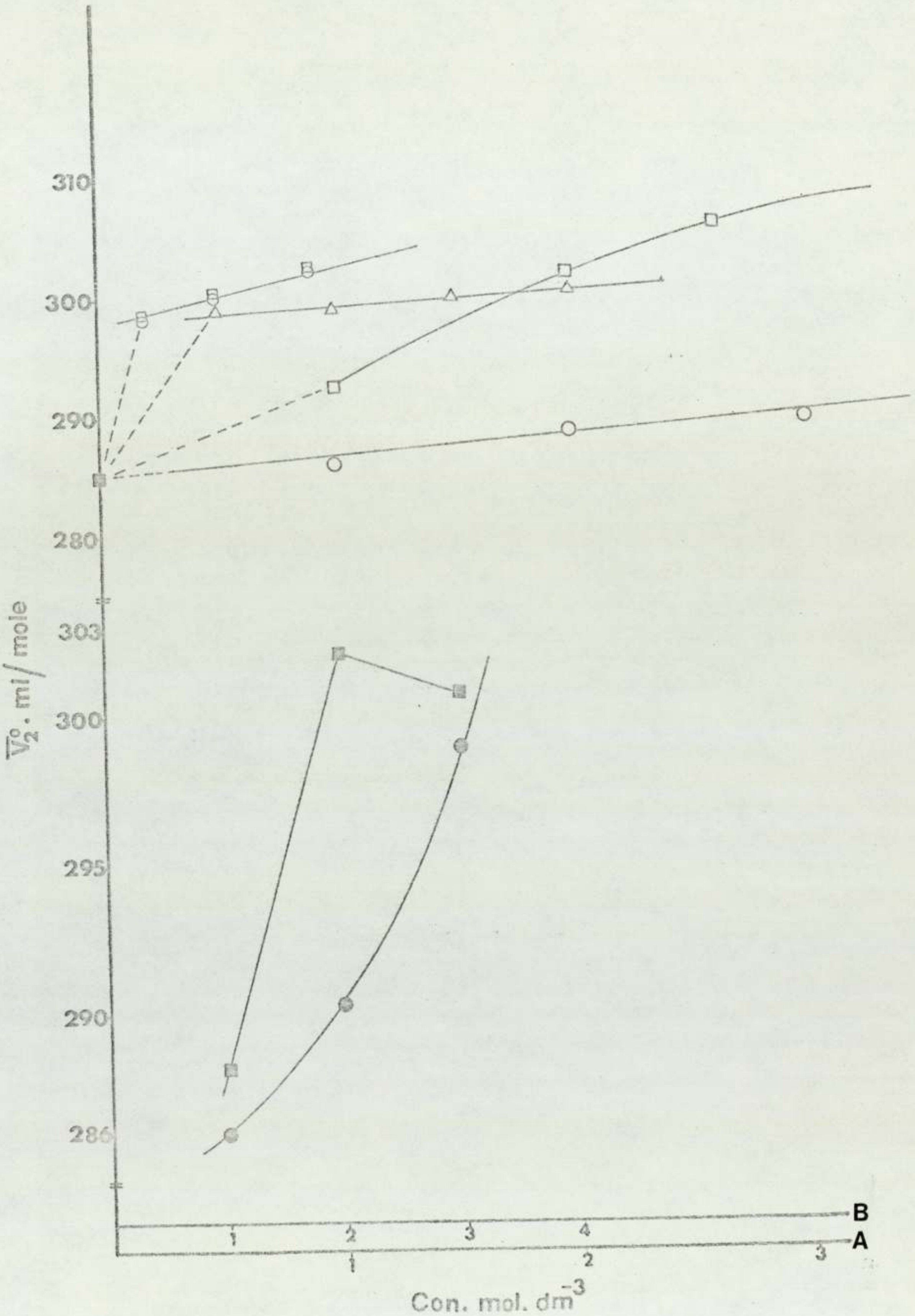


Fig. IV. 6 **A,** The partial molal volume of dodecyltrimethyl ammonium bromide at Co, as a function of the concentration of aliphatic alcohols; **B,** Dependence of the partial molal volume of Co on the alkyl chain length at 25° C; **A** ○ Me-OH, □ Et-O, △ Pr-OH ⊟ Bt-OH; **B** ● **IM**, ■ **2M** Alcohols

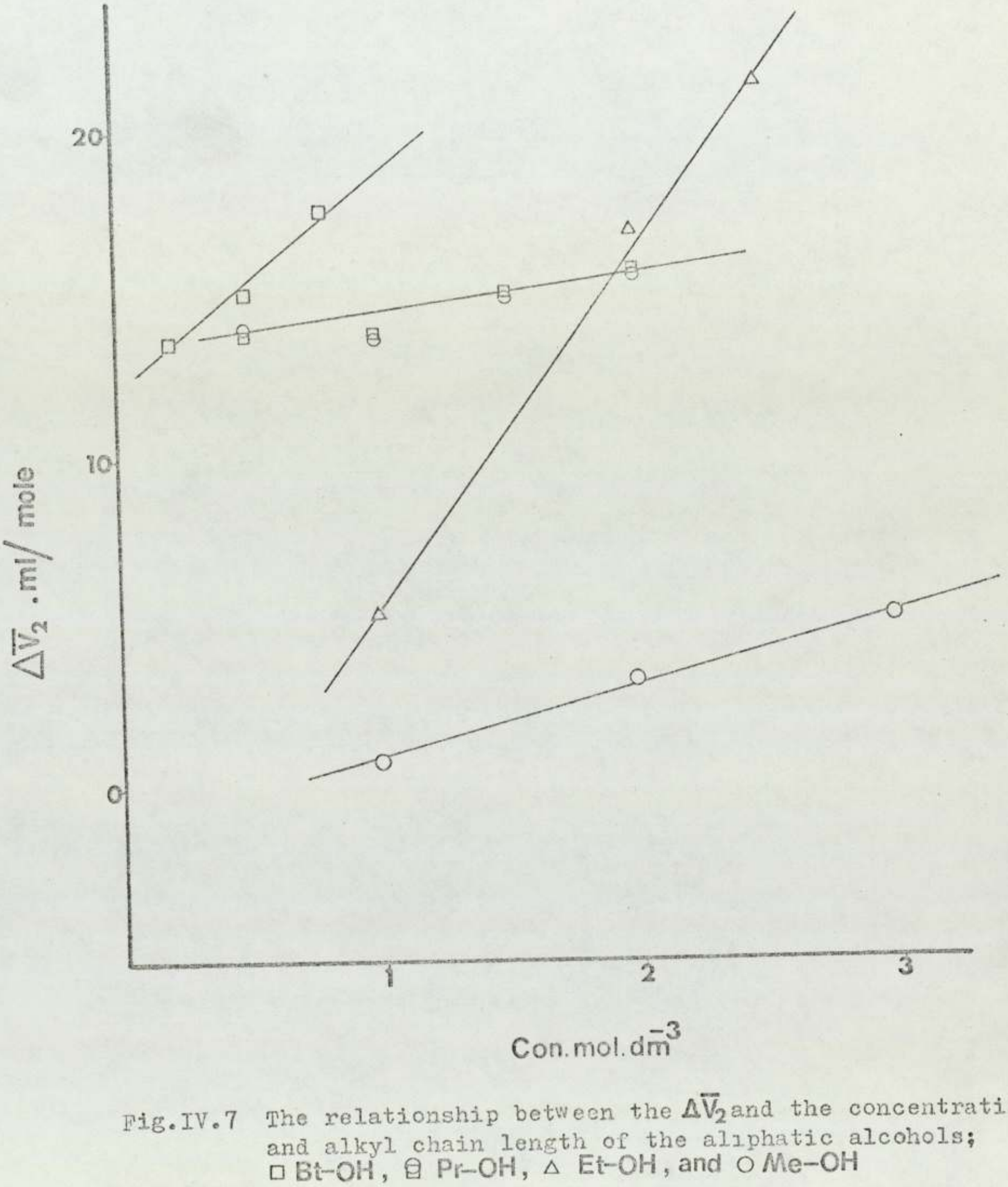


Fig.IV.7 The relationship between the $\Delta\overline{V}_2$ and the concentration and alkyl chain length of the aliphatic alcohols; □ Bt-OH, ⊖ Pr-OH, △ Et-OH, and ○ Me-OH

PARTIAL MOLAL VOLUMES OF ALKYL AMMONIUM BROMIDES

IN WATER AT 25° C

TABLE IV.I.1

C $mol.dm^{-3}$	Ø $ml.mole^{-1}$	$\overline{V}$ $ml.mole^{-1}$	$\overline{V}_o$ $ml.mole^{-1}$	$\overline{V}_1$ $ml.mole^{-1}$	$\overline{V}^o_{1A}$ $ml.mole^{-1}$	$\overline{V}^o_{1B}$	$\Delta\overline{V}_1$ $ml.mole^{-1}$	$\overline{V}_c$ $ml.mole^{-1}$	D_s $g.ml^{-1}$
C_{10}									
0.1	250.06	255.25	258.20	265.00	17	15.45	6.8	254.9	1.0996
0.08	258.32	262.5							
0.07	259.68	262.64							
0.06	265.27								
0.05	260.75								
0.04	260.71								
0.03	260.96								
0.02	258.90								
0.01	249.50								
C_{12}									
0.06	287.66	294.10	278.05	285.10			7.1	276.40	1.1155
0.05	286.59	291.90							
0.04	285.43	289.60							
0.03	283.03	286.22							
0.02	277.25	279.36							
C_{14}									
0.06	313.64	323.45	303.6	315.50			11.9	297.34	1.1314
0.05	312.3	320.44							
0.04	311.8	318.29							
0.03	310.66	315.52							
0.02	306.83								
C_{16}									
0.06	340.14	348.06	332.20	337			4.8	319.06	1.1423
0.05	339.24	345.82							
0.04	338.19	343.43							
0.03	336.09	340.20							

PARTIAL MOLAL VOLUME OF DODECYL TRIMETHLY AMMONIUM BROMIDE IN WATER CONTAINING ALIPHATIC ALCOHOLS AT 25°C

TABLE IV.I.2

C $mol.dm^{-3}$	$\overline{V}_2$ $ml.mole^{-1}$	$\overline{V}_2^o$ $ml.mole^{-1}$	S_{pv} $ml.g^{-1}$	$\Delta\overline{V}_2$ $ml.mole^{-1}$	$\left[\frac{\partial d}{\partial n}\right]_{p,t,n_o,n}$
1 M, Me-OH					
0.06 0.05 0.04 0.03 0.02 0.018	285.10 285.27 285.45 285.62 285.98 285.90	285.90	0.92704	0.8	0.0240
2 M					
0.06 0.05 0.04 0.03 0.02 0.016	287.02 287.13 287.25 287.40 287.53 287.58	288.33	0.93492	3.23	0.0227
3 M					
0.06 0.05 0.04 0.03 0.02	288.57 288.73 288.85 288.99 289.12	289.15	0.93758	4.05	0.0220
4 M					
0.06 0.05 0.04 0.03	309.71 309.78 309.86 309.97	310.04	1.00531	24.94	0.005
1 M, Et-OH					
0.06 0.05 0.04 0.03 0.02 0.014	289.69 289.83 289.91 289.99 290.16 290.26	290.26	0.94118	5.16	0.02
2 M					
0.06 0.05 0.04 0.03 0.02 0.01	301.83 301.90 301.95 302.03 302.09 302.15	302.15	0.97973	17.05	0.0104

TABLE IV.I.2.A

C $mol.dm^{-3}$	$\overline{V}_2$ $ml.mole^{-1}$	$\overline{V}_2^o$ $ml.mole^{-1}$	S_{pv} $ml.g^{-1}$	$\Delta\overline{V}_2$ $ml.mole^{-1}$	$\left[\frac{\partial d}{\partial n}\right]_{p,t,n_o,n}$
2.5M					
0.06	306.01	306.32	0.99325	21.22	0.0075
0.05	306.09				
0.04	306.15				
0.03	306.22				
0.02	306.26				
0.01	306.32				
0.5M, Pr-OH					
0.06	298.69	299.0	0.96984	14	0.011
0.05	298.76				
0.04	298.82				
0.03	298.90				
0.02	298.99				
0.014	299.03				
1M					
0.06	298.89	298.96	0.96939	13.86	0.012
0.05	298.60				
0.04	298.70				
0.03	298.80				
0.02	298.86				
0.01	298.94				
1.5M					
0.06	299.5	299.86	0.97231	14.76	0.012
0.05	299.58				
0.04	299.65				
0.03	299.71				
0.02	299.75				
0.01	299.85				
2M					
0.06	300.2	300.83	0.97545	15.73	0.012
0.05	300.52				
0.04	300.58				
0.03	300.66				
0.02	300.74				
0.01	300.82				

TABLE IV.I.2.B

C $mol.dm^{-3}$	$\overline{V}_2$ $ml.mole^{-1}$	$\overline{V}_2^o$ $ml.mole^{-1}$	S_{pv} $ml.g^{-1}$	$\Delta\overline{V}_2$ $ml.mole^{-1}$	$\left[\frac{\partial d}{\partial n}\right]_{p,t,n_o,n_2}$
0.2M, Bt-OH					
0.06	298.70	298.98	0.96945	13.88	0.0105
0.05	298.76				
0.04	298.81				
0.03	298.88				
0.02	298.94				
0.017	298.96				
0.5M					
0.06	299.95	300.20	0.97341	15.10	0.01
0.05	300.02				
0.04	300.08				
0.03	300.13				
0.02	300.19				
0.017	300.21				
0.8M					
0.06	302.59	302.88	0.98210	17.78	0.0083
0.05	302.64				
0.04	302.71				
0.02	302.82				
0.01	302.87				

CHAPTER V - The Effects of Various Additives on Conductance properties of micelles.

V.Ia - Conductivity of Electrolytes.

The conductivity or resistivity arises as a proportionality coefficient, in the relation between the resistance of a conductor R, its length L and cross-section S.

$$\frac{1}{R} = \frac{1}{Q} \frac{S}{L} = x \frac{S}{L} \qquad \text{V-1}$$

The electrolytic conductivity can be defined in terms of mobility, concentration, and charge of the ions$^{(225)}$.

$$x = \sum \frac{z_i^2 F^2}{RT} D_i c_i = \sum \left| z_i \right| F c_i U_i \qquad \text{V-2}$$

The above expression, if the solution contains a single strong electrolyte, can be related to a unit equivalent concentration by the equation

$$x = \frac{F c_{eq}}{1000} (U_+ + U_-) \qquad \text{V-3}$$

which is known as the equivalent conductivity. Its limiting value at infinite dilution is a constant for a given solution. The equation (V-2) can be rewritten in terms of the dissociation constant.

$$x = \alpha \frac{F c_{eq}}{1000} \left[U_+ + U_- \right] \qquad \text{V-4}$$

then the equivalent conductivity takes the form,

$$\Lambda = \frac{1000\, x}{C_{eq}} = F \left[U_+ + U_- \right] \qquad \text{V-5}$$

It is usually represented in Ω^{-1} cm^2 per 1 gram equivalent. In the case of strong and weak electrolytes, the equivalent conductivity at limiting dilution can be defined as(188,225)

$$\Lambda^\circ = F \left| U_+^\circ + U_-^\circ \right| = \lambda_+^\circ + \lambda_-^\circ \qquad \text{V-6}$$

This equation is valid in both cases, when the dissociation constant is equal to 1. According to Kohlrausch's law, which describes independent ionic conductivities for a solution containing S_1 ionic species equation (V-6) takes the form

$$\Lambda = \sum_{i=1}^{S_1} \lambda_i^\circ \qquad \text{V-7}$$

On the other hand, at low concentrations, the specific conductivity is directly proportional to concentration, while at higher concentration, it increases due to decrease in equivalent conductivity.

Kohlrausch has shown that the equivalent conductivity can be defined by the relation

$$\Lambda = \Lambda^\circ - k\sqrt{c} \qquad \text{V-8}$$

However, the limiting law which has been discussed by Onsager for a uni-univalent electrolyte, can be given by the equation(68,188,225)

$$\Lambda = \Lambda^\circ - \left[B_1\Lambda^\circ + B_2\right]\sqrt{\alpha c} \qquad \text{V-9}$$

It is apparent that equation (V-9) is identical with the Kohlrausch relation, where B_1 and B_2 are experimental constants. In view of expression (V-9), the Onsager limiting law for weak electrolytes has the form(68,188,225)

$$\Lambda = \alpha\left[\Lambda^\circ - \left[B_1\Lambda^\circ + B_2\right]\sqrt{\alpha c}\right] \qquad \text{V-10}$$

The ratio of equivalent conductivities to the limiting equivalent conductivity at a given and infinite dilution, is known as the conductivity coefficient(225)

$$\frac{\Lambda}{\Lambda^{o}} = q \qquad \text{V-11}$$

This ratio can be rewritten at a given concentration, in terms of the dissociation constant of the electrolyte

$$\frac{\Lambda}{\Lambda^{o}} = \alpha q \qquad \text{V-12}$$

V.Ib - The effect of aromatic alcohols and ureas on the micellar properties of alkylammonium bromides.

V.Ib1 - Aromatic alcohols.

The solute-solute and solvent solute interactions in aqueous solutions of alkylammonium bromides, has been examined by the addition of various concentration of aromatic solutes to the systems, at 25°C by using the conductivity method.

The observation indicates that the addition of 0.01M phenol to the aqueous system of C_{14} and C_{16} changes the micellar properties of surfactants.

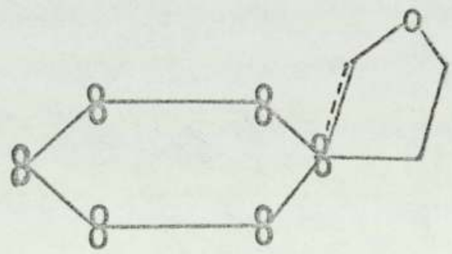
On the addition of 0.01M phenol to the system, as can be seen in Figs.V.1,V.2 and tables V.I.1,V.I.2, the C_o has increased from 3.7×10^{-3} mol.dm^{-3} and 1.08 mol dm^{-3} to 3.82×10^{-3} mol.dm^{-3} and 1.26×10^{-3} mol dm^{-3} for C_{14} and C_{16} respectively. When 0.02M phenol is added to the system, C_o has decreased. A similar effect has been observed in both systems. The decrement in C_o is 0.35×10^{-3} mol dm^{-3} and 0.14 mol dm^{-3} respectively. It is apparent that the effect of phenol on the micelles is not the same magnitude.

In view of this observation, one can postulate that the interactions between phenol and water clusters around the nonpolar group of the surfactant ion, and water molecules(5) decrease the structural order of water molecules more effectively in the aqueous solution of C_{14} than that of C_{16}. The penetration of phenol molecules into the core of the micelle, increases the molecular weight of the micelle, which has been observed in non-ionic surfactant aqueous system. The degree of penetration depends on the interaction between the benzene ring, and hydrocarbon chain length of the surfactant, and adsorption of the aromatic solutes in the Stern layer.

It is known(158) that hydrophobic interactions between nonpolar groups in the micellar core, restricts the penetration of additive molecules. On the other hand -OH groups in the Stern layer(155) associate with the hydrated polar head groups counter-ions and water molecules in terms of hydrophobic interactions.

The decreasing static dielectric constant of the Stern layer influences the dipole orientation of the counter ions, and adsorbed phenol and water molecules. The decrement in charge density of micelles due to the described effects, consequently the magnitude of the decrement in free energy, presumably influences more effectively the micelles of C_{14} than those of C_{16}.

It has been shown(226) that intramolecular hydrogen bonding occurs between the hydroxyl group, and π electrons at the 1-position of the aromatic nucleus of phenethyl alcohol in 0.5% CCl_4 such as



Brown-Brady have postulated(227) that an electrophilic atom, or group could be attracted by the electron cloud at the position of greatest density. According to their view the electron density is low near the centre of the ring, and high above and below the ring of carbon atoms.

Due to this fact, an electrophilic atom can move readily around the electron cloud. The formation of a covalent bond with one of carbon atom of the ring, in terms of π-electron clouds association, increases the electrophilic nature of the reagent.

The penetration and distortion of the π-electron cloud, involves the formation of complexes in the polar medium. Dewar has interpreted(228) that the positive ion is able to move over the π-electron layer of the aromatic molecule, due to electron deficiency of the cation, which interacts with the π electrons of aromatic molecule. Because of this fact the displacement of a hydrogen by cationic attack, induces the positive ion to take its place.

On the addition of an aromatic alcohol to the aqueous system, the dielectric constant of the solution decreases. Since the phenolic hydroxyl group is a stronger proton donor(229) than the aliphatic alcohol -OH group, it associates with water molecules in terms of hydrogen bonding. However, because of having a nonpolar side and polar group, aromatic alcohols influence the surfactant ion in the solution, an association occurs by means of interaction of the aromatic molecule with the nonpolar side of the monomer, due to the cationic effect of Br^- ion, on the π-electron cloud of aromatic molecule(228). The structural order of water molecules, and water networks is effectively influenced by this association(5). The structure breaking effect of the aromatic molecule increases with increasing concentration.

On the other hand, aromatic alcohols associate also with nonpolar groups of the surfactant ions, with their hydrophobic sides, in terms of hydrophobic hydration(5) (hydrophobic interaction). Owing to the hydrophilic nature of the medium, intramolecular hydrogen bonding can occur between the aromatic nucleus, and hydroxyl group(226).

This might have additional effect on the solution properties.

The effect of cations on the π-electron cloud of the aromatic molecule, and ionized Br^- ion in water, cause the hydrophobic association between aromatic alcohol, hydrocarbon chain, surfactant and water molecules.

It is apparent that these effects in the bulk solution, influence the micellar properties of the systems. As can be seen in Fig.V.3, and Table V.I.1. On the addition of 0.01M phenol to the aqueous solution of C_{14} and C_{16} the specific conductance (0.284 m ohm^{-1} cm^{-1}) of the micellar solution is lower than that of the aqueous solution (0.293m ohm^{-1} cm^{-1}). The conductance and specific conductance of the micelles, have been calculated from the recorded graph, in terms of the equations (V-15, V-16).

The equivalent conductance of micelles has been calculated by using equation (V-5). The decrement in specific conductance, decreases with the increasing concentration of phenol. However, the addition of 0.01M benzyl alcohol increases the specific conductance of the micelles (0.305 m ohm^{-1} cm^{-1}) (similar in C_{16}), then decreases with increasing concentration (Figs.V.3,V.4).

The increase in specific conductance on the addition of 0.01M aromatic alcohol to the system is presumably due to the structure maker character of the aromatic alcohol at low concentration. As is seen in Figs.V.3,V.4, the higher specific conductance is observed, when the hydrophobic surface of molecule is increased (0.305m ohm^{-1} cm^{-1} and 0.298m ohm^{-1} cm^{-1} for 0.01M benzyl alcohol and 0.01M DL-1-phenylethanol in aqueous solution of C_{14} respectively). The C_0 increases slightly as the $-CH_2$ group increases, on the alcohol side of the molecule (Fig.V.5). The reason could be attributed to the cooperative effect of the $-CH_2-OH$ group in low concentration in the aqueous solution. In the presence of phenyl-propanol, the specific conductance of the micelles falls between phenol and DL-1-phenylethanol. In both systems

(Fig.V.3,V.4). The equivalent conductance of the micelles except in the case of phenyl-propanol, decreases up to the certain concentration (0.04M in phenol = 73.00 cm^2 ohm^{-1} mol^{-1}, 0.06M in benzyl alcohol = 71.00 cm^2 ohm^{-1} mol^{-1}), then it increases as the concentration increases (Fig.V.6 and Table V.I.1).

In the case of phenyl-propanol the equivalent conductance increases nonlinearly with the increase in concentration (Fig.V.6). However the situation with C_{16} is different. The equivalent conductance increases with increasing alcohol concentration, but not with so great a magnitude (Fig.V.7 and Table V.I.2).

The factors involved for the conductance properties of the mixed micelles is not clearly known. But one can postulate that ion-pair formation(230), due to the low dielectric constant of solution, the anion size, the degree of dissociation of surfactant ion, the formation of ionic complex, and the effect of aromatic alcohol on the charge density of the micelles(158), influences the conductance properties of the micelles.

An increase in C_0 has been also observed up to a certain concentration, followed by a decrease in C_0 with the increasing concentration, for the addition of benzyl alcohol, and the other higher aromatic alcohols to the aqueous system of alkylammonium bromides.

The maximum increase in C_0 for all aromatic alcohols used, occurs on the addition of 0.01M alcohol to the system. On the addition of 0.02M alcohol to the aqueous solution of C_{14}, the observed C_0 except phenol, is higher than C_0 of the aqueous solution of C_{14} (3.79×10^{-3} mol.cm^{-3} for benzyl alcohol, and 3.79×10^{-3} mol.dm^{-3} for phenyl-propanol, Table V.I.1).

In the case of C_{16}, except with phenol, the C_0 increases also with the addition of 0.02M aromatic alcohol to the system (1.18×10^{-3} mol.dm^{-3} for benzyl alcohol, and 1.31×10^{-3} mol.dm^{-3}

for phenyl-ethanol Table V.I.2).

However in both cationic systems, the addition of 0.04M of any alcohol to the system, decreases the C_o (Figs.V.1,V.2 and Tables V.I.1, V.I.2) the decrement in C_o increases with the increasing concentration.

In the light of this observation, it is reasonable to assume the following reasons as possible driving force, to change the micellar properties of alkylammonium bromides, on the addition of aromatic alcohols.

It has been shown(231) that there is no high-field shift, in the low concentration of surfactant solution containing 2% phenol. When the concentration of surfactant is increased above 8%,a high chemical shift has been observed. The reason has been attributed to the effect of phenol, on the structure of water molecules.

The higher concentration of surfactant removes the phenol molecules from the aqueous region to the micellar pseudophase(231). It has been observed that the solubility of alcohols gradually decreases after 0.04M concentration. The decrement in solubility increases, as the chain length of the alcohol group increases. On the addition of 0.01M phenol to the aqueous system of C_{14} and C_{16}, the alcohol molecule penetrates into the micellar core, through the Gouy-Chapman-Stern electrical double layer around the micelle(155).

This process is favoured due to the described features of the structure of aromatic alcohols. They behave as structure makers at low concentration. Presumably the adsorption of aromatic solutes at low concentration, does not effectively influence the properties of the Stern layer. When the concentration of solute is increased, the effect of solute molecule on water structure, and water networks around the nonpolar groups increases. This increment breaks the cooperative effect of water molecules(5).

On the other hand, the aromatic molecule is forced by the penetration of the cation into the π-electron cloud, to associate with an anion(227,228). This association takes place with the formation of an ionic complex(227,228). The migration of an unassociated alcohol molecule, from the bulk solution to the electrical double layer of micelle, influences the micellar structure through the Stern layer, micellar core interface(155).

The molecular size of the aromatic solute also plays a unique role in solubilization. The solubility of alcohol in the interior of the micelle is influenced by hydrophobic interactions between aromatic ring and hydrophobic chain length in the micellar core. A saturation effect could occur due to the restriction in the penetration process.

However the increase in concentration, increases the effect aromatic solutes have on the electrokinetic properties of the Stern layer. Due to adsorption of aromatic alcohol in the Stern layer, the repulsion energy of the hydrated polar head group increases. The aromatic solute interacts with adsorbed counter ions, and bound water molecules, in terms of hydrophobic interactions and electrostatic forces. The charge transfer process causes reduction in the charge density of the micelle(158), consequently there is a decrease in C_0. It is believed also that the thermodynamic properties of the micelle would substantiate the above observations.

It is known that the increase in hydrophobicity affects the surface charge of the micelle, and decreases the charge density(158). The decrement in C_0 with the increasing concentration of aromatic alcohol, can be attributed to the described effects of the aromatic molecules.

V.Iba - Ureas and Urethane.

The mechanism of the action of urea on water structure and solute solvent interactions has not been discussed quantitatively. The addition of urea to an aqueous solution, causes a change in the structural order of water molecules and disordered water(232). It has been postulated that the urea can only mix into disordered water regions, by reason of geometry. This process lowers the chemical potential of unbonded water, and melts some clusters in order to re-establish the equilibrium.

Mukerjee et al.(233) have shown that urea at higher concentrations reduces the cooperative structure of water, due to its ability to increase the dielectric constant, and surface tension of water. According to this view urea affects the entropy change on micellization, rather than enthalpy change, in terms of the weakening of hydrophobic bonding.

It has also been shown(155) that the urea decreases the repulsive forces between the ionic heads of the monomers, and at 25°C breaks up the micelles. The hydrophobic character of urea is increased with increasing the hydrophobic surface, which is believed to increase the order of demicellizing effectiveness and weakening of the hydrophobic bonding(179).

Jones has also postulated(234) that the breaking down of water structure, due to the presence of urea in aqueous solution, decreases the cooperative nature of the water molecules.

A similar conclusion such as urea reduces the strength of hydrophobic bonding, has been introduced by Schick(235). Wetlaufer et al.(236) have suggested that the increase in solubility of hydrocarbons in aqueous solution, is due to the solvation of the hydrocarbon by water in the presence of urea, or to the urea molecules which have also taken an active part in the solvation of hydrocarbon. On the other hand, it has been shown(237) that hydrogen bonding contributes denaturating effectiveness of DNA, due to hydrogen bonding between urea and DNA. Herskovits et al.(238) have concluded that hydrophobic forces contribute to the stability of native DNA(238).

The other approach is(239) that the aqueous urea solutions are able to accommodate nonpolar amino acid sides better than water can. The stabilization of the polar side chain of asparagine, has been interpreted in terms of urea contribution to the stability.

A different view indicates that the effect of alkyl urea, or the increased hydrophobic surface of substituted urea, decreases the denaturating effectiveness(240). However it is known that urea in aqueous solution, takes an active part in the cooperative effect of water molecules (formation of clusters). Due to this fact, urea contributes to the open structure by the same mechanism as water molecule(241).

Since the hydrogen bonded solutes or groups such as (OH. NH_2 or NH_3) do not effectively alter water structure, it has been discussed that urea participates in cluster formation in aqueous solution. Further evidence shows that urea is extremely soluble in water, and its partial molal heat capacity at infinite dilution is very close to that of the solid. It is known that urea in the solid state is hydrogen bonded(241). In the light of this observation, it has been concluded that urea must be hydrogen bonded in water.

Beside these facts, the B coefficient of urea in water also supports the idea that urea behaves as a structure maker rather than breaker.

It has been observed that the addition of ureas to an aqueous solution of alkyl ammonium bromides, influenced the micellar properties. As can be seen in Fig.V.8, the C_o increases with increasing concentration of additive. On the addition of 1M urea to the aqueous solution of C_{14} C_o is increased up to $4.72 \cdot 10^{-3}$ mol.dm^{-3}.

When 0.5M urethane, ethylurea or dimethylurea is added to the system (C_{14}), the C_0 has markedly increased, compared with the urea (4.8×10^{-3} mol.dm^{-3}, 5.2×10^{-3} mol.dm^{-3} and 5.22×10^{-3} mol.dm^{-3} respectively. Table V.I.3.)

The effect of urethane on C_0 is more pronounced compared with urea and ethylurea. On the addition of 2M solute to the aqueous system of C_{14},C_0 is increased (7.86×10^{-3} mol.dm^{-3}, 5.38×10^{-3} mol.dm^{-3} and 7.6×10^{-3} mol.dm^{-3} for urethane, urea and ethylurea respectively), it would be assumed that the observed higher specific conductance, and marked increase in C_0 for urethane, arises from the mutual orientation of the urethane in aqueous solution. It has a more effective polar side than ureas, which associate strongly with water molecules by means of hydrophobic bonding. This polar group increases the structure forming character of the molecule, because of its tendency for hydrogen bonding$^{(116)}$.

Urethane differs only from ethylurea, by having one more "O" atom instead of 'N' atom. It is apparent that the structure promoting effect of the molecule arises from the replacement of the N atome by 'O', which gives a polar character to the group, or molecule. In view of this fact the higher specific conductance of C_0 can be attributed to the cooperative nature of the molecule. However the power of raising C_0 for dimethylurea is higher compared with the other ureas and urethane (Fig.V.8, Table V.I.3).

The addition of the same solutes to the aqueous solution of C_{16} showed results of a similar pattern (Fig.V.8, Table V.I.4). The increase in C_0 for the systems studied, could be interpreted in terms of the cooperative nature of the ureas and urethane in aqueous solution.

Urea has great ability to participate in hydrogen bonding with water molecules, in terms of having three potential bonding centres(233,241), and it also affects the polarity of water. Since it participates in cluster formation, it is expected that the hydrocarbon solutes would also dissolve in aqueous urea solutions.

On the other hand urea forms clathrates in the solid state. This association might take place in aqueous urea solution(241). The cooperative effect of urea increases the solubility of the hydrocarbons in water urea solution, and increases the dielectric constant of water(179,233). This evidence supports the idea that urea actively participates in the formation of mixed clusters in aqueous urea solutions(241).

The increase in C_0 with the addition of various ureas, could be attributed to those described effects. However the equivalent conductance of C_0 in both systems, decreases as the hydrophobic surface of the molecule increases (Fig.V.9). The C_0 increases also as the concentration of solute increases (Tabs.V.I.3, V.I.4). On the addition of 1M urea to the aqueous solution of C_{14}, the observed equivalent conductance of C_0 is high compared with the ureas and urethane (77.542 $cm^2\ ohm^{-1}\ mol^{-1}$, 73.333 $cm^2\ ohm^{-1}\ mol^{-1}$ and 59.0 $cm^2 ohm^{-1}\ mol^{-1}$ for urea, urethane and ethylurea respectively) (Table V.I.3).

As is seen in Fig.V.9, on the addition of any solute, at any concentration, the obtained equivalent conductance of C_{14} is lower than in aqueous solution. This confirms also that they behave as structure promoting in aqueous solution.

In the aqueous solution of C_{16}, the equivalent conductance of C_0 is higher, compared with C_0 in aqueous solution, when 0.5M urea is added (80.34 $cm^2\ ohm^{-1}\ mol^{-1}$ and 73.61 $cm^2\ ohm^{-1}\ mol^{-1}$ in urea and H_2O respectively. Fig.V.9). Similar behaviour has been observed on the addition of 0.5M ethylurea. The reason for the increase in equivalent conductance at C_0 is not known.

The decrement in equivalent conductance at C_0 indicates that the hydrophobic behaviour of the molecules increases with increasing hydrophobicity. The participation in mixed cluster formation increases the solubility of the hydrocarbon molecule. Hydrophobic association of ureas with water molecules, the effect of hydrocarbon chain length and the increment in dielectric constant induce the formation of suitable cavities to accommodate hydrocarbons or hydrophobic groups, which is easier than in pure water, due to the formation of large cavities.

This process might also cause an increase in specific conductance, due to the increase in cooperative character of the medium(241). In this work, it is assumed that ureas and urethane increase the structural order of water molecules, in terms of hydrophobic bonding, taking an active part in mixed cluster formation around nonpolar moeities(241). Herskovits(242) concluded that the hydrophobic influence of the solute on water molecules contributes to the viscosity increment of aqueous solutions. He found that the B coefficient of ureas increases with increasing hydrophobic surface (0.035, 0.155 and 0.265 for urea, ethylurea and 1.3 dimethylurea respectively). If water molecules hydrogen bonded to urea do not participate in hydrogen bonding with neighbouring molecules, this should reflect in the B coefficient of the solute, in terms of the Dole-Jones(192) relationship. It has been shown that structure breaker ions have negative B coefficients, because of their disturbing effect on water structure(69,194). In view of this fact one can say that ureas and urethane do not behave as structure breaker in aqueous solution.

V.Ic - Experimental Procedure

V.Ic1 - Materials

V.Ic1A- Aromatic alcohols

Benzyl alcohol, DL-1-phenylethanol were BDH L.R.material. 3-phenylpropyl alcohol was obtained from Pfaltz and Bauer Inc. as L.R. grade and phenol was Fisons A.R. material.

V.I.c1B- Ureas and Urethane.

Urea (BDH A.R. grade), N-ethylurea (Koch-light pure grade), and dimethylurea (Sigma L.R. material) were recrystallized(179) several times from hot ethanol, and dried under vacuum. Potassium-chloride (BDH L.R.grade) was dried in a vacuum oven at approximately 80 to 100°C, before using for redetermination ofthe conductivity cell constant. Water used for preparation of dilute solutions was double distilled water ($\Delta w < 1 \times 10^{-6}$ ohm^{-1} cm^{-1}).

The preparative procedures for surface active agents used in this work have been described in Chapter II.

V.Ic2 - Measurement and Instrumentation.

The conductivities of aqueous alkylammonium bromides solutions and containing aromatic alcohols and ureas were measured using a continuous infusion technique(243).

V.Ic2A - Setting and Calibration.

The conductivity bridge (Wayne Kerr Universal Bridge B.642) was trimmed, and calibrated according to the instrument(244) manual. The chart recorder which was connected to the bridge was also checked, to obtain accurate chart speed and linearity, and that was adjusted to the bridge reading in order to get zero reading.

The zero conductivity reading was considered as the base line, and any increase in conductivity due to conductance of electrolyte in solution was recorded by corresponding pen movement.

The automatic motorized infusion apparatus (unita continuous infusion apparatus, B.Braun Melsungen) used consists of a calibrated glass barrel, and a steel plunger fitted with a rubber gasket. The accuracy of the volume infused from the syringe was checked by two methods(243) and was found to be 20 ml.

a) The volume infused into the calibrated volumetric flask of suitable volume at time (t), was in good agreement with the volume corresponding to the time given by manufacturer.

b) In the second method, the double distilled water, of a known volume, was titrated by the KCl solution of a known concentration, by using the calibrated conductivity bridge, chart recorded and checked conductivity cell. The increase in conductance, corresponding to the rate of KCl added, was recorded with the chart recorder of known speed. The obtained specific conductivity of KCl by this experiment, for a known concentration was compared with the corresponding values given in literature $K = 0.012856\ ohm^{-1}\ cm^{-1}$ and $0.0014087\ ohm^{-1}\ cm^{-1}$ at 25°C for 10^{-1} molar and 10^{-2} molar KCl respectively(68). The value of specific conductance of 0.1 M. KCl derived ($0.012875\ ohm^{-1}\ cm^{-1}$) is in good agreement with the above value.

The concentration of the solution can be obtained by the equation.

$$C_t = \frac{V_t}{V_i' + V_t} C_a \qquad \text{V-13}$$

The volume infused by the syringe at time (t) can be calculated from the following equation

$$V_t = \frac{\Delta D \times \Delta F}{C_{sp}} \qquad \text{V-14}$$

At any instant of the titration, the specific conductivity can be obtained from the following relationship.

$$\Lambda_{sp} = (\Lambda_i + \Lambda_t)pt \ k_{cell} \qquad \text{V-15}$$

where

$$pt = \frac{V_i' + V_t}{V_i} \qquad \text{V-16}$$

at time (t).

V.Ic2B - Determination of the C_0 of Alkylammonium bromides in water and mixed solutions.

In order to obtain a sharper end point where the conductivity slope changes, and minimize the dilution effect, the higher concentration of surfactant solution was employed, as the concentration of titrant. Before using the bridge the described procedure for calibration was applied to the bridge, then set to the conductivity of the doubled distilled water (Λw (1×10^{-6} ohm^{-1} cm^{-1}).

Following this procedure, the double distilled water of known volume (50 ml) was pipetted into a thermostated cleaned and dried beaker, then the dip-type conductivity cell (Philips) of known cell constant (which was redetermined by using standard KCl solutions (k_{cell} = 1.42), and the bridge was set for the determining of C_0's of surfactants. A standard solution of 0.1 mol dm^{-3} of C_{14} was placed in 20 ml syringe, so that no air bubbles would be injected from the syringe into the titration beaker. The syringe was then mounted onto the unita infusion apparatus, with its tip submerged in the solution in the titration beaker. The rate of flow and the chart recorder was set to the position (Rate 8 = 66.1/60 ml/min.) and (50 secs/cm. = 0.833 min/cm) respectively. After the equilibrium of distilled water with temperature 25°C, setting the sensitivity of bridge to the position (2), the chart recorder was started at a speed mentioned above, then the motor was driven to infuse the aqueous solution of C_{14} into the titration beaker. The addition of the titrant was continued well above the C_0, in order to obtain the slope of the conductivity at the below and above C_o.

Studies of the effect of aromatic alcohols and ureas on the C_o of alkylammonium bromides were carried out in a similar manner. The standard solutions of various additives in different concentration were titrated, instead of 50 ml double distilled water, with the surfactant solution containing the respective additive of known concentration. In the case of C_{16} the concentration of titrant used was 0.02M.

The C_o of alkylammonium bromides was determined from the recorded conductivity graph, by obtaining the point of critical conductivity change on the graph, and calculating the corresponding concentration C_o by using equations (V-13 and V-14). The obtained C_o values of alkylammonium bromides were 3.7×10^{-3} mol.dm^{-3}, and 1.08×10^{-3} mol.dm^{-3} for C_{14} and C_{16} respectively.

V.Id - Conclusions.

The effect of aromatic alcohols, ureas and urethane on micellar properties of alkylammonium bromides in aqueous solution, has been examined by a conductivity method. It has been observed that all aromatic alcohols, increase the C_0 of the systems examined, when 0.01M additive is added to the aqueous solution, then it decreases as the concentration increases. The reason for this has been discussed in terms of hydrophobic interactions, structure maker effects of the aromatic molecules at low concentration, and the influence of alcohols on the electrical double layer properties of micelles.

The addition of ureas and urethane has markedly changed the micellar properties of studied systems. The C_0 is increased as the concentration of urea or urethane increases,the mechanism of action of these solutes on micellar properties has also been examined by means of hydrophobic association of these molecules. The increase in specific conductance with the addition of additive, has been attributed to the cooperative effect of the solute on water structure. It is further assumed that ureas and urethane behave as structure promoters, and take active part in the formation of mixed icebergs in the aqueous solution in terms of hydrophobic interactions.

The conductance properties also support the idea that these solutes behave as structure promoters, in terms of active participation in hydrophobic interactions, and in formation of water networks around the nonpolar groups.

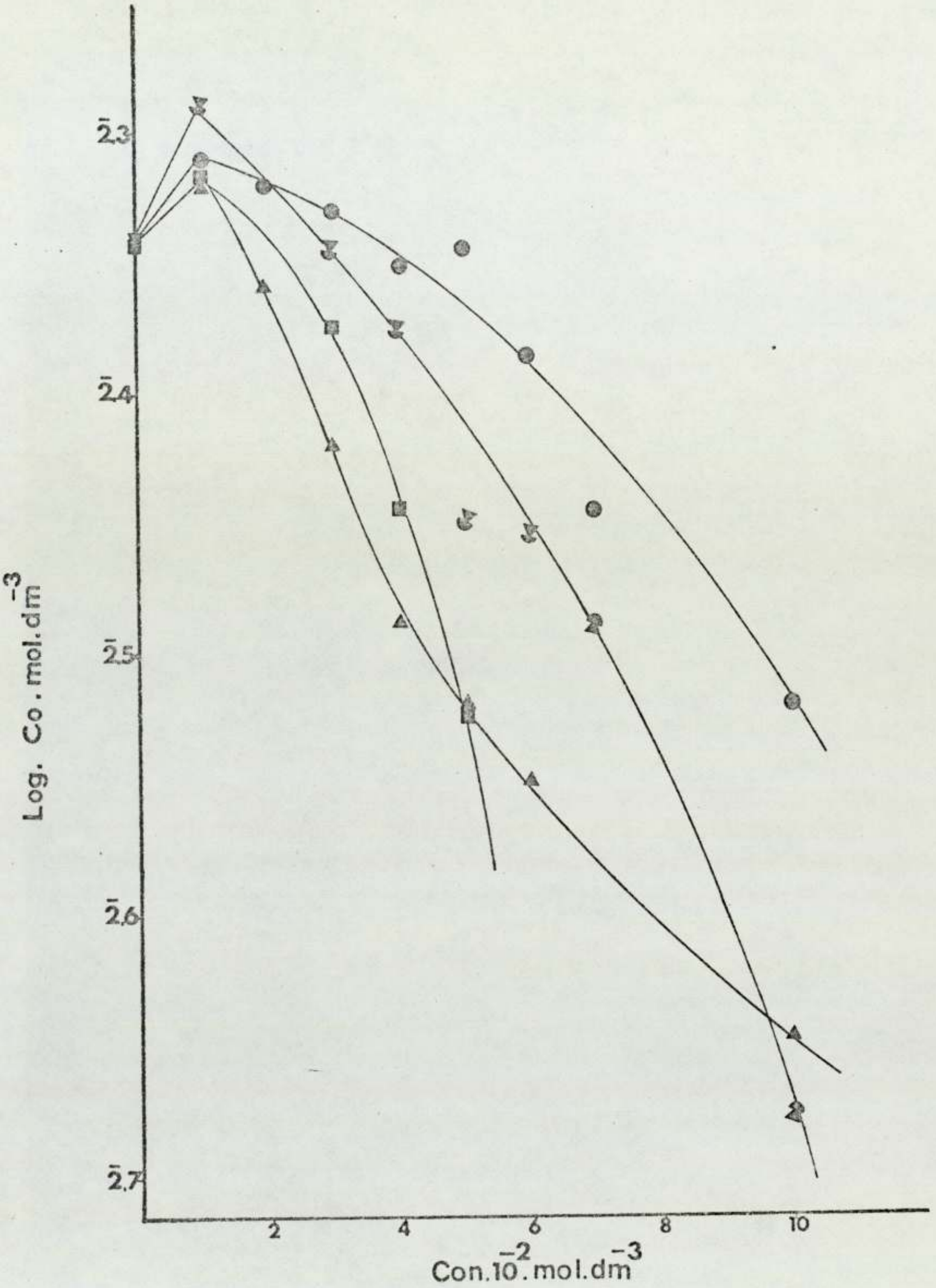


Fig.V.I Dependence of log Co of the tetradecyl trimethyl ammonium bromide on the various concentration of the aromatic alcohols in water at 25° C; ▲ Phenol, ● Benzylalcohol, ⧗ Phenylethanol, and ■ Phenylpropanol

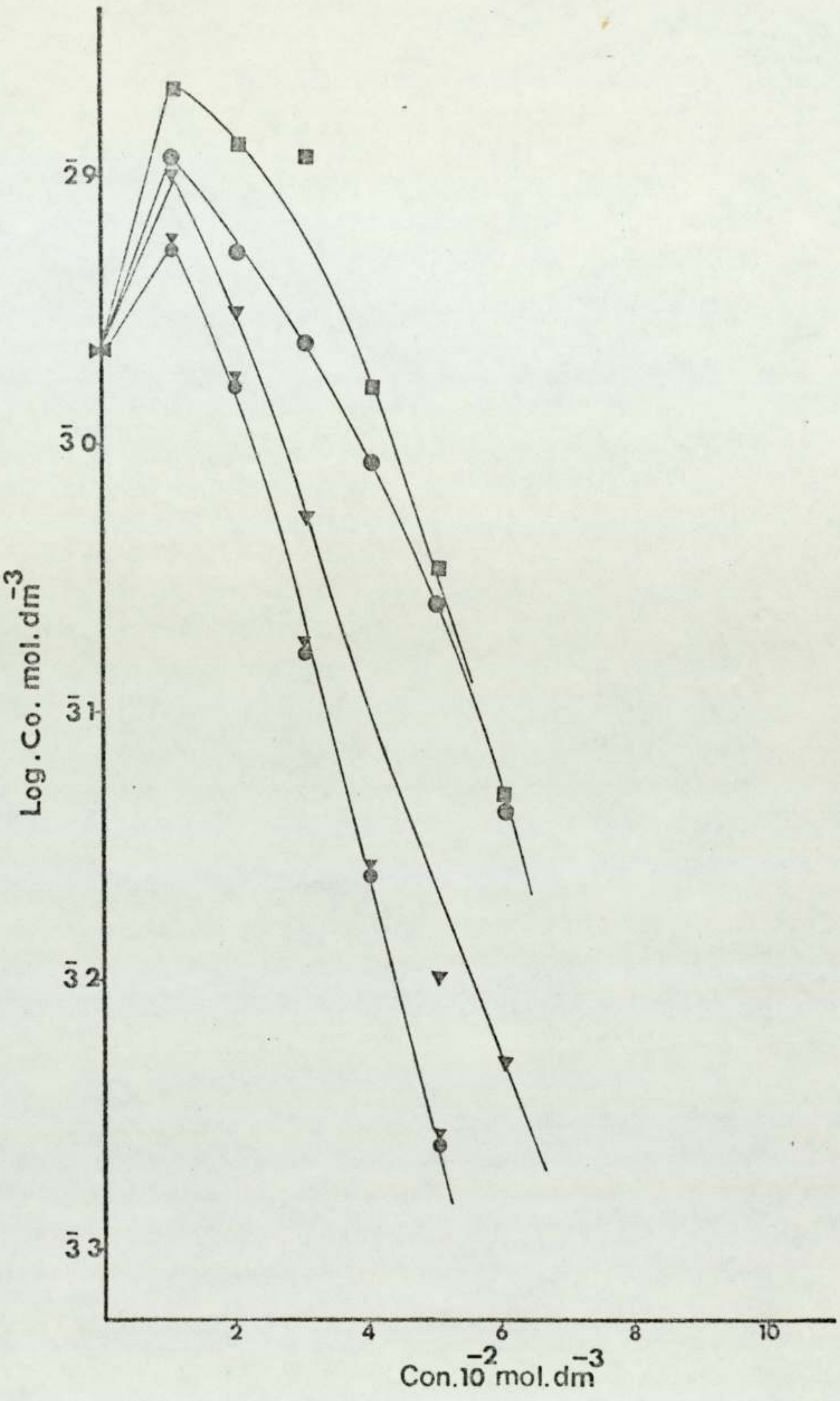


Fig.V.2 Dependence of Log Co of the Cethyltrimethyl ammonium bromide on the various concentration of the aromatic alcohols in Water at 25° C; ▲ Phenol, ● Benzylalcohol, ■ Phenylethanol, and ⧗ Phenylpropanol

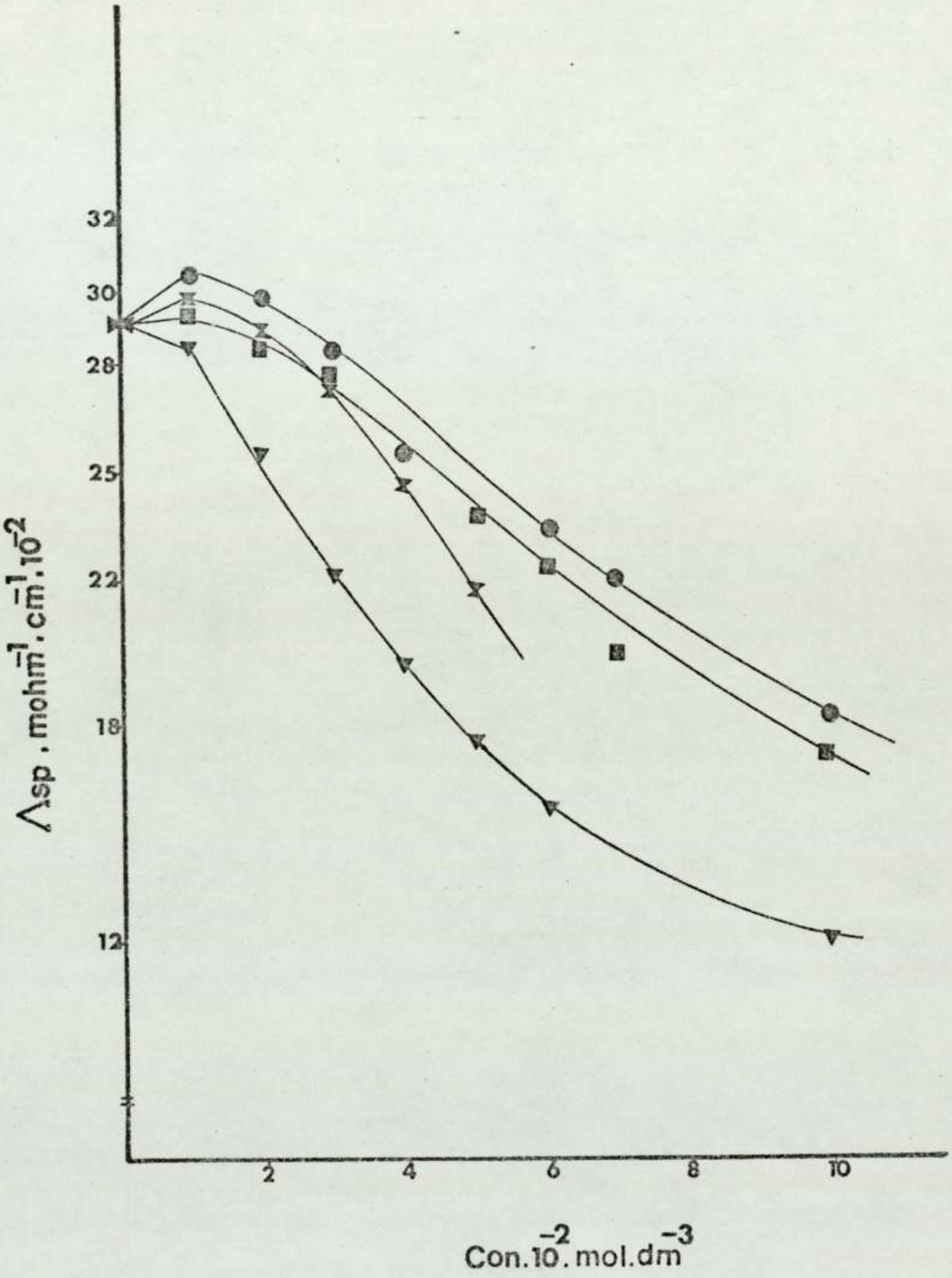


Fig.V.3 The relationship between specific conductivity of the tetradecyl trimethyl ammonium bromide at Co and the concentration of aromatic alcohols in water at 25° C; ▲ Phenol, ● Benzylalcohol, ■ Phenylethanol, and Ɪ Phenylpropanol

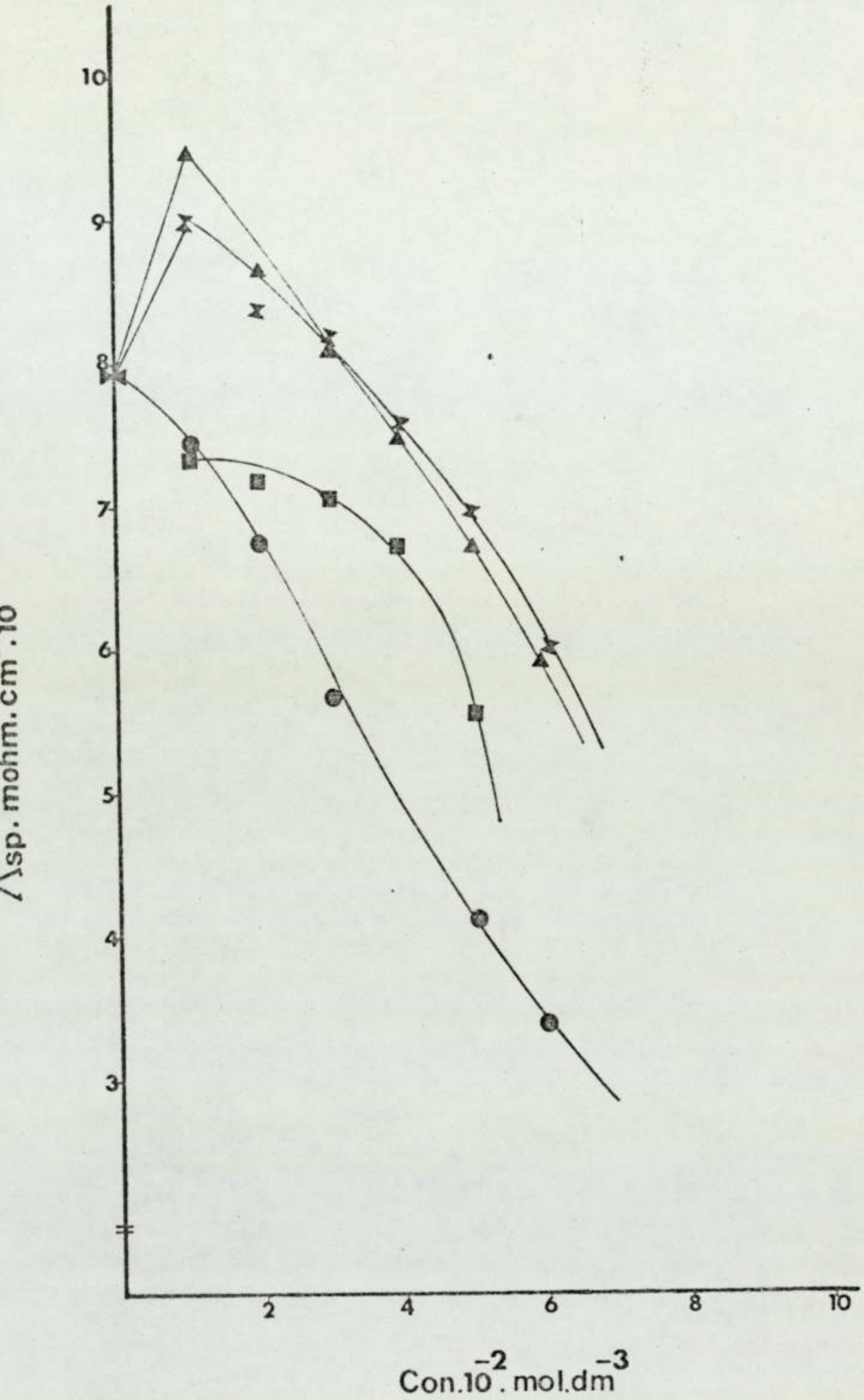


Fig.V.4 The relationship between specific conductivity of the cethyl trimethyl ammonium bromide at Co. and the concentration of aromatic alcohols in water at 25° C; ● Phenol, ▲ Benzylalcohol, ⧗ Phenylethanol, and ■ Phenylpropanol

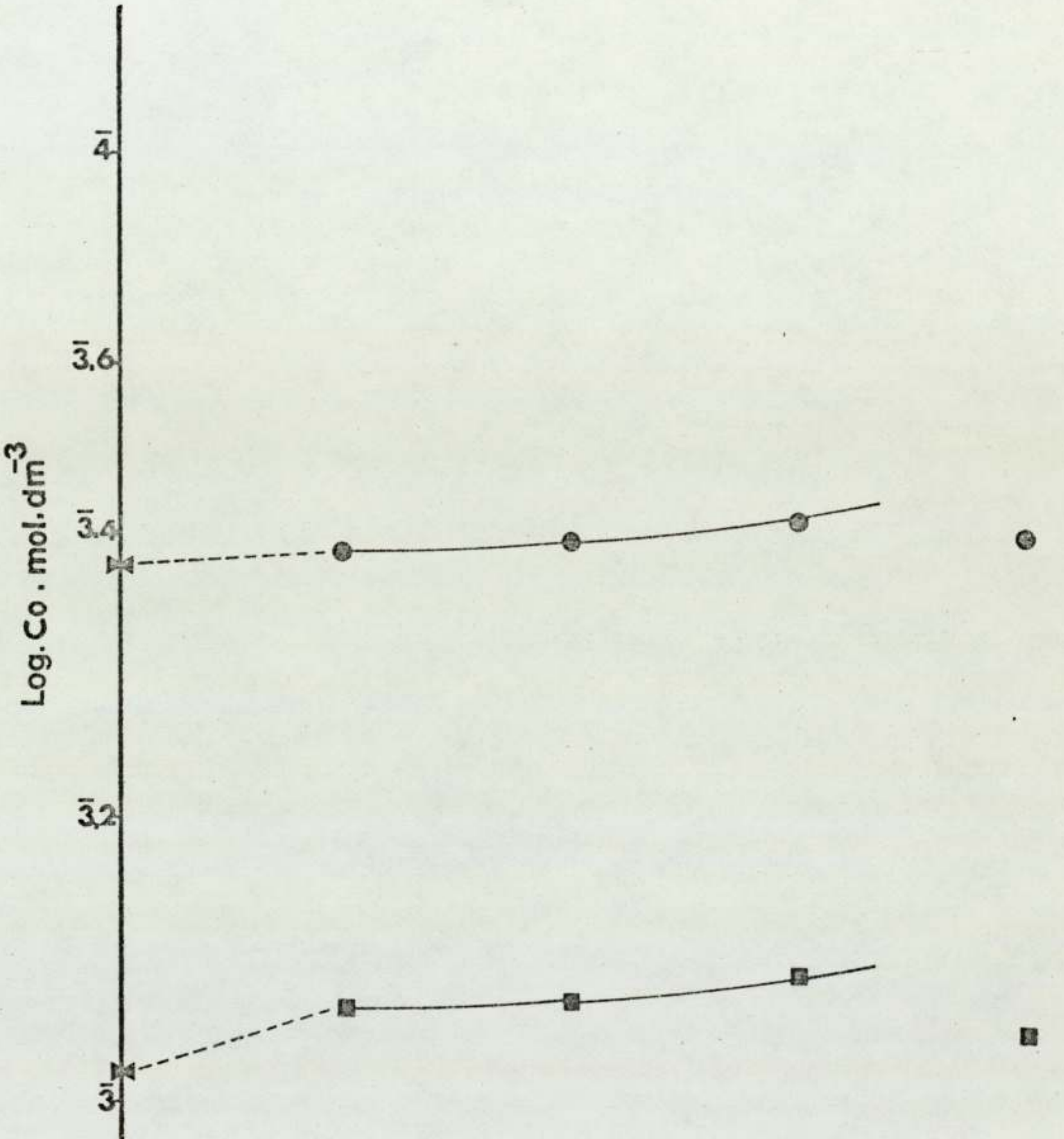


Fig.V.5 Log Co of C_{14}, and C_{16} as afunction of the alkyl chain length of the aromatic alcohol; ● C_{14} , ■ C_{16}

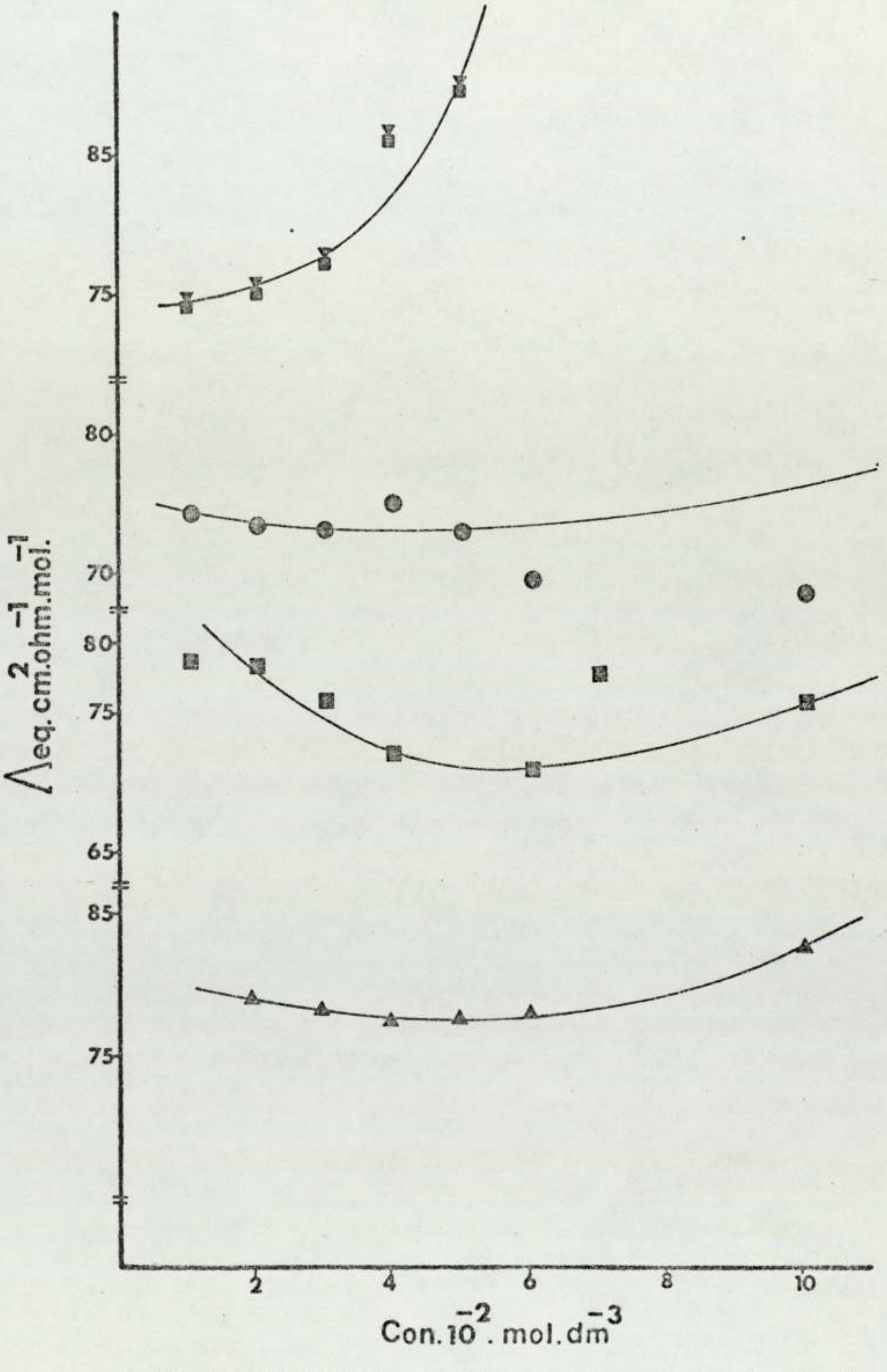


Fig.V.6 Variation of the equivalent conductivity of the tetradecyl trimethyl ammonium bromide at Co with the various concentration of aromatic alcohols in Water at 25° C; ● Phenol, ■ Benzylalcohol, ▲ Phenylethanol, ⧗ Phenylpropanol

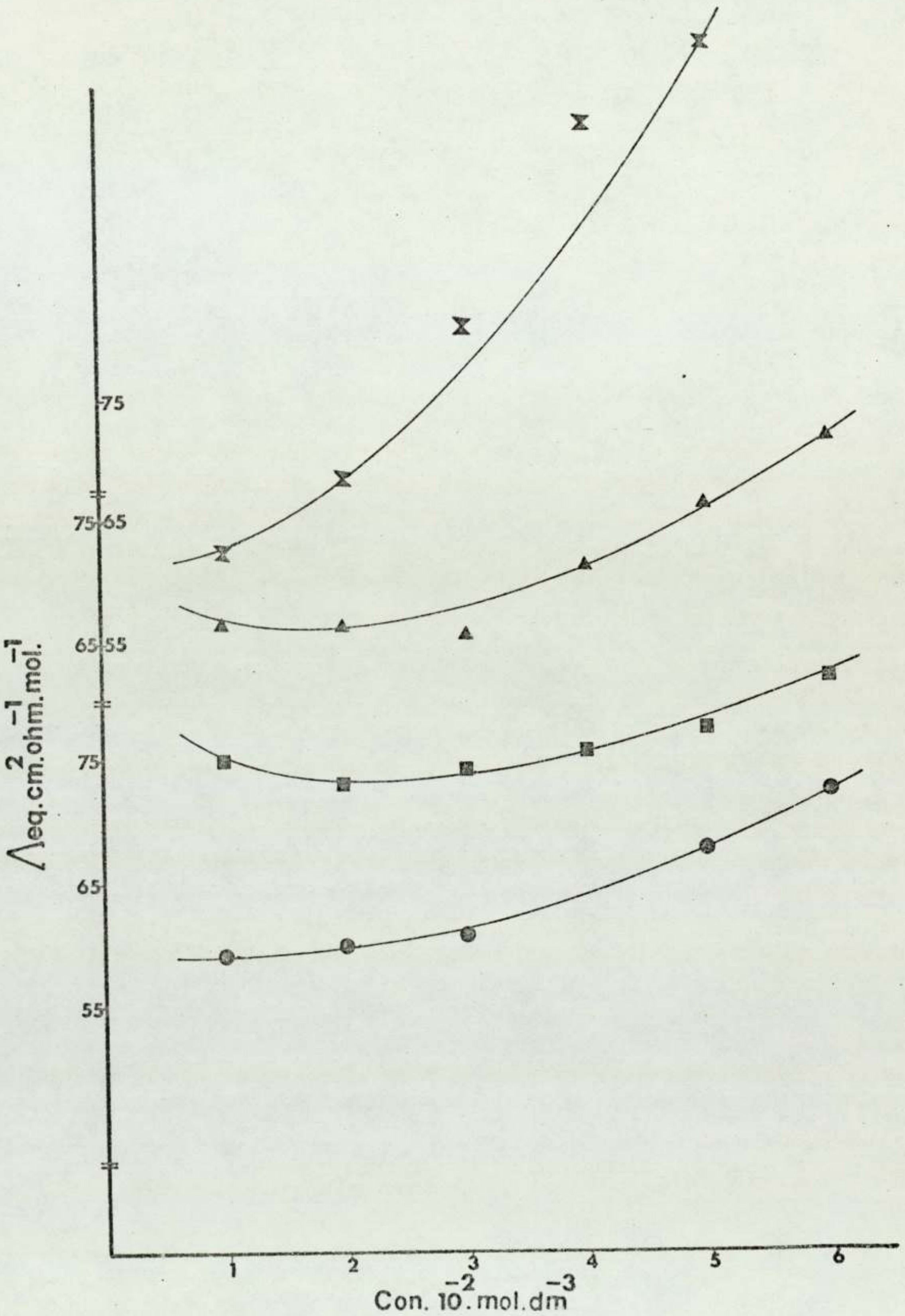


Fig.V.7 Variation of the equivalent conductivity of the cethyltrimethyl ammonium bromide at Co with the various concentration of aromatic alcohols in Water at 25° C; ● Phenol, ■ Benzylalcohol, ▲ Phenylethanol, and X Phenylpropanol

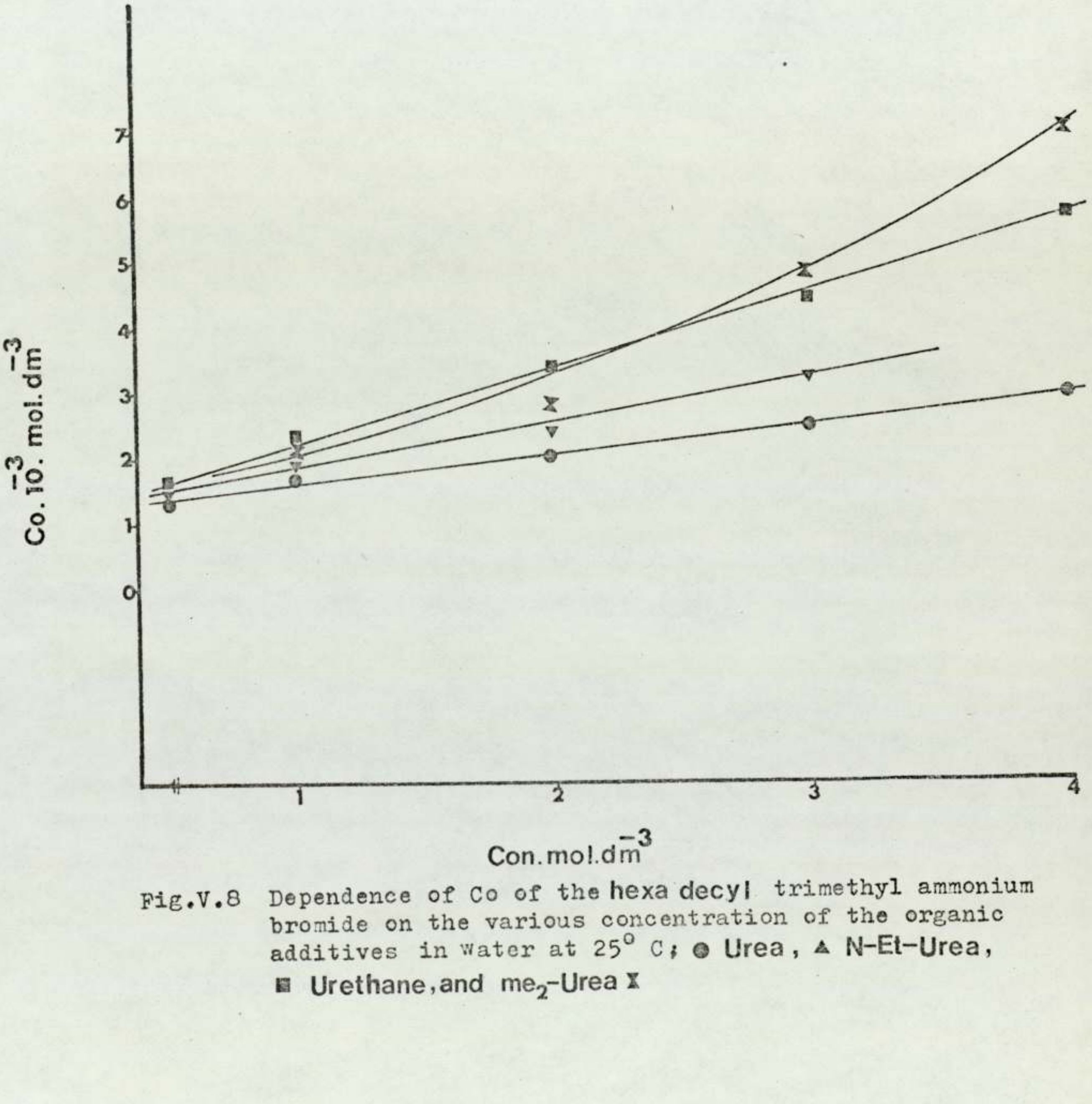


Fig.V.8 Dependence of Co of the hexa decyl trimethyl ammonium bromide on the various concentration of the organic additives in water at 25° C; ● Urea, ▲ N-Et-Urea, ■ Urethane, and me_2-Urea ⧗

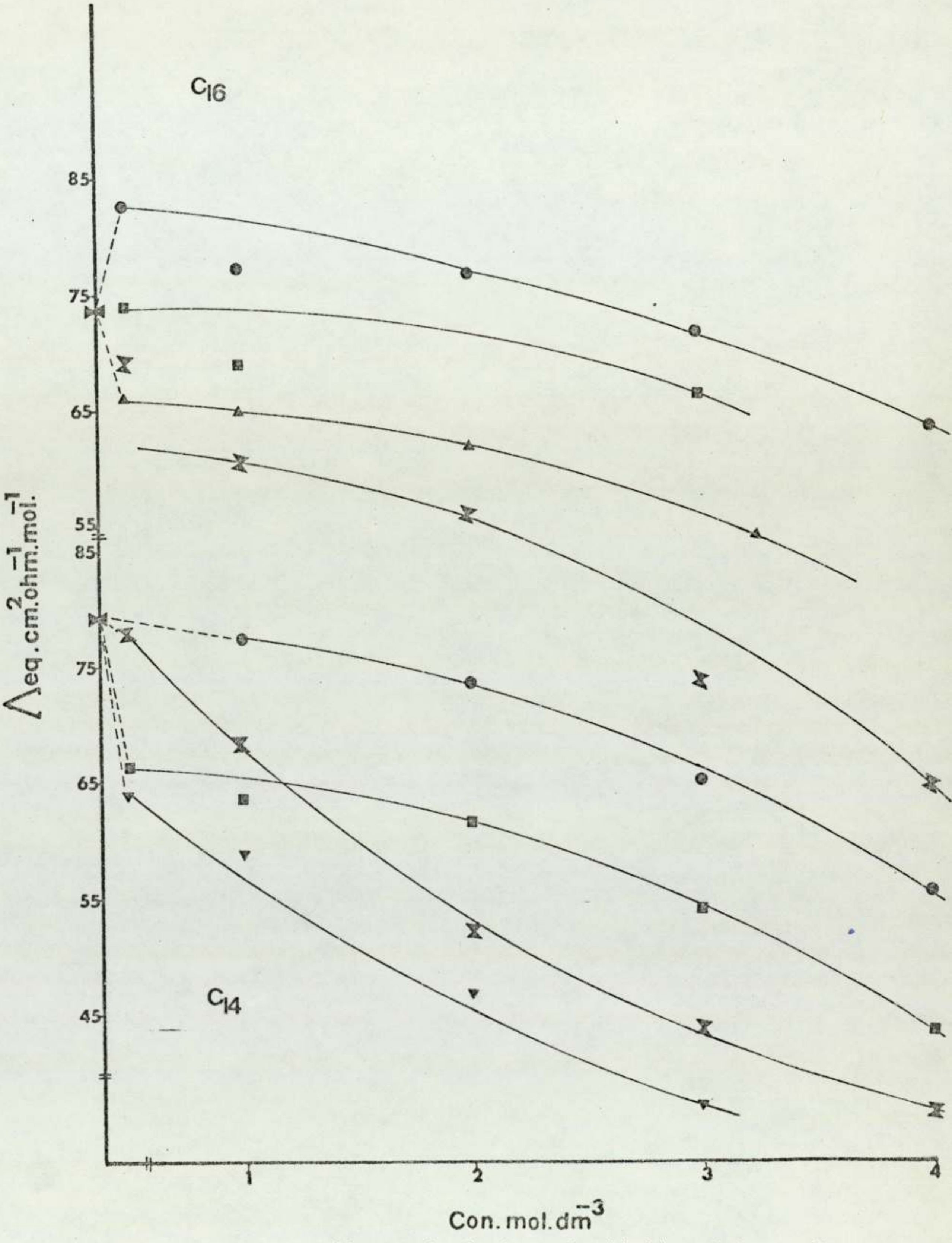


Fig.V.9 Plots of the equivalent conductivity of C_{14} and C_{16} at Co versus concentration of the organic additive in water at 25° C; C_{14} : ● Urea, ■ Urethane, ⧗ me_2-Urea, and ▲ N-Et-Urea; C_{16} : ● Urea, ■ N-Et-Urea, ▲ Urethane, and ⧗ me_2-Urea

CONDUCTANCE PROPERTIES OF THE MYRISTYL AMMONIUM BROMIDE IN WATER AND CONTAINING AROMATIC ALCOHOLS AT 25° C

TABLE V.I.1

C mol.dm^{-3}	Λc mohm^{-1}.cm^{-1}	Λsp mohm^{-1}.cm^{-1}	Λeq cm^2.ohm^{-1}.mol^{-1}	Co mol.dm^{-3}
C_{14} H_2O	0.206	0.293	78.975	3.7 x10^{-3}
Phenol				
0.01	0.200	0.284	74.736	3.82x10^{-3}
0.02	0.180	0.256	73.775	3.47x10^{-3}
0.03	0.155	0.220	73.333	3.0 x10^{-3}
0.04	0.138	0.196	75.384	2.6 x10^{-3}
0.05	0.124	0.176	73.333	2.4 x10^{-3}
0.06	0.110	0.156	69.643	2.24x10^{-3}
0.10	0.085	0.121	67.222	1.8 x10^{-3}
Benzylalcohol				
0.01	0.215	0.305	78.608	3.88x10^{-3}
0.02	0.210	0.298	78.627	3.79x10^{-3}
0.03	0.200	0.284	75.936	3.74x10^{-3}
0.04	0.180	0.255	72.034	3.54x10^{-3}
0.06	0.165	0.234	71.341	3.28x10^{-3}
0.07	0.155	0.220	77.193	2.85x10^{-3}
0.1	0.128	0.182	75.833	2.4 x10^{-3}
Ph. ethanol				
0.01	0.210	0.298	73.039	4.08x10^{-3}
0.02	0.20	0.284	79.552	3.57x10^{-3}
0.03	0.195	0.277	78.248	3.54x10^{-3}
0.04	0.180	0.256	77.576	3.3 x10^{-3}
0.05	0.168	0.238	77.780	3.06x10^{-3}
0.06	0.158	0.224	78.596	2.85x10^{-3}
0.10	0.10	0.142	83.041	1.71x10^{-3}
Ph.propanol				
0.01	0.2085	0.296	74.747	3.96x10^{-3}
0.02	0.203	0.288	75.989	3.79x10^{-3}
0.03	0.186	0.264	78.338	3.37x10^{-3}
0.04	0.173	0.245	87.500	2.8 x10^{-3}
0.05	0.153	0.217	90.416	2.4 x10^{-3}

CONDUCTANCE PROPERTIES OF THE CETHLY AMMONIUM BROMIDE

IN WATER AND CONTAINING AROMATIC ALCOHOLS AT 25° C

TABLE V.I.2

C mol.dm^{-3}	Λc mohm^{-1}.cm^{-1}	Λsp mohm^{-1}.cm^{-1}	Λeq cm^{2}.ohm^{-1}.mol^{-1}	Co mol.dm^{-3}
C_{16} H_2O	0.056	0.0795	73.61	1.08x10^{-3}
Phenol				
0.01	0.0525	0.0745	59.127	1.26x10^{-3}
0.02	0.0475	0.0675	60.267	1.12x10^{-3}
0.03	0.0400	0.0568	60.425	9.4 x10^{-4}
0.05	0.0300	0.0426	67.619	6.3 x10^{-4}
0.06	0.0240	0.0341	72.553	4.7 x10^{-4}
Benzylalcohol				
0.01	0.0670	0.0952	74.961	1.27x10^{-3}
0.02	0.0610	0.0866	73.389	1.18x10^{-3}
0.03	0.0570	0.081	74.380	1.089x10^{-3}
0.04	0.0530	0.0753	76.680	9.82x10^{-4}
0.05	0.0475	0.0675	77.231	8.74x10^{-4}
0.06	0.0420	0.0596	81.644	7.3 x10^{-4}
Ph.ethanol				
0.01	0.0635	0.0902	66.406	1.36x10^{-3}
0.02	0.0610	0.0866	66.106	1.31x10^{-3}
0.03	0.0585	0.0831	65.433	1.27x10^{-3}
0.04	0.053	0.0753	71.714	1.05x10^{-3}
0.05	0.049	0.0696	76.567	9.09x10^{-4}
0.06	0.042	0.0596	81.643	7.3 x10^{-4}
Ph.propanol				
0.01	0.052	0.074	62.712	1.18x10^{-3}
0.02	0.051	0.072	68.571	1.05x10^{-3}
0.03	0.050	0.071	81.328	8.73x10^{-4}
0.04	0.0475	0.0675	97.543	6.92x10^{-4}
0.05	0.040	0.0568	103.839	5.47x10^{-4}

THE EFFECT OF UREAS AND URETHANE ON THE CONDUCTIMETRIC BEHAVIOUR OF MYRISTYL AMMONIUM BROMIDE IN WATER AT 25° C

TABLE V.I.3

C mol.dm^{-3}	Λc mohm^{-1}.cm^{-1}	Λsp mohm^{-1}. cm^{-1}	Λeq cm^{2}.ohm^{-1} mol^{-1}	Co mol.dm^{-3}
Urea	C_{14}			
1.0	0.258	0.366	77.542	4.72x10^{-3}
2.0	0.28	0.397	73.792	5.38x10^{-3}
3.0	0.31	0.440	65.088	6.76x10^{-3}
4.0	0.35	0.497	55.592	8.94x10^{-3}
Urethane				
0.5	0.255	0.362	75.416	4.80x10^{-3}
1.0	0.260	0.369	73.333	5.4 x10^{-3}
2.0	0.325	0.462	58.778	7.86x10^{-3}
3.0	0.290	0.412	47.302	8.71x10^{-3}
4.0	0.310	0.440	40.741	1.08x10^{-2}
N-Et-Urea				
0.1	0.230	0.326	70.869	4.6 x10^{-3}
0.5	0.235	0.334	64.231	5.2 x10^{-3}
1.0	0.240	0.354	59.000	6.0 x10^{-3}
2.0	0.253	0.359	47.236	7.6 x10^{-3}
3.0	0.266	0.378	37.425	1.01x10^{-2}
me_2-Urea				
0.5	0.285	0.405	77.885	5.22x10^{-3}
1.0	0.310	0.440	68.750	6.4 x10^{-3}
2.0	0.350	0.497	52.315	9.5 x10^{-3}
3.0	0.38	0.539	44.180	1.22x10^{-2}
4.0	0.44	0.625	36.764	1.7 x10^{-2}

THE EFFECT OF UREAS AND URETHANE ON THE CONDUCTIMERIC

BEHAVIOUR OF CETHYL AMMONIUM BROMIDE IN WATER AT 25° C

TABLE V.I.4

C $mol.dm^{-3}$	Λc $mohm^{-1}\ cm^{-1}$	Λsp $mohm^{-1}.cm^{-1}$	Λeq $cm^{2}.ohm^{-1}\ mol^{-1}$	C_o $mol.dm^{-3}$
Urea	C_{16}			
0.5	0.066	0.094	80.34	1.17×10^{-3}
1.0	0.073	0.104	77.037	1.35×10^{-3}
2.0	0.081	0.115	76.666	1.5×10^{-3}
3.0	0.086	0.122	71.764	1.7×10^{-3}
4.0	0.089	0.126	63.959	1.97×10^{-3}
Urethane				
0.5	0.0735	0.104	66.242	1.57×10^{-3}
1.0	0.101	0.143	65.000	2.2×10^{-3}
2.0	0.140	0.199	62.187	3.2×10^{-3}
3.0	0.160	0.227	54.047	4.2×10^{-3}
4.0	0.175	0.248	43.510	5.7×10^{-3}
N-Et-Urea				
0.5	0.074	0.105	74.285	1.4×10^{-3}
1.0	0.087	0.123	68.333	1.8×10^{-3}
2.0	0.115	0.163	75.814	2.15×10^{-3}
3.0	0.145	0.206	66.452	3.1×10^{-3}
me_2-Urea				
0.5	0.078	0.111	69.375	1.6×10^{-3}
1.0	0.098	0.139	60.434	2.3×10^{-3}
2.0	0.11	0.156	55.714	2.8×10^{-3}
3.0	0.14	0.199	41.458	4.8×10^{-3}
4.0	0.16	0.227	32.428	7.0×10^{-3}

CHAPTER VI - Light Scattering and Micellar Structure of Alkylammonium bromides.

VI-Ia - Theory of Light Scattering by Solutions.

According to Debye$^{(245)}$, scattering is due to non-homogeneous molecular structure. In his theory, in order to explain the increase in scattered intensity when a solvent is made inhomogeneous by the addition of a solute, and to derive appropriate conclusions about the number of solute particles in the medium, from the measurement of the light scattered at different angles of observation, he has taken the following considerations into account.

In order to derive the loss of light energy due to its radiation, the particle in the medium was treated as having an electromagnetic field around itself, and fluctuations of the concentration and density has been considered. In this approach the solvent is considered as perfectly homogeneous and its dielectric constant is given by the relation,

$$\epsilon_o = \mu_o^2 \qquad \text{VI-1}$$

When this medium is influenced by a homogeneous electric field of intensity F, the electric moment of medium (for 1 cm^3 volume) is given by the expression

$$(\epsilon_o - 1)\ \frac{F}{4\pi} \qquad \text{IV-2}$$

Since the homogeneous field is disturbed by the presence of the particles, the effect of the particles on the homogeneous field has been observed at a point which is at a larger distance from the particle.

In this treatment it has been assumed that (m) and (F) have the same direction. If a volume of solution contains (n) particles per cm^3, its total electric moment in the direction of F, is defined by the expression

$$V\left[\ (\epsilon_o - 1)\ \frac{F}{4\pi} + nm\ \right] \qquad \text{VI-3}$$

In view of this expression the dielectric constant of the solution takes the form

$$\epsilon - \epsilon_0 = 4\pi m \frac{m}{F} \qquad \text{VI-4}$$

In order to derive the radiation field surrounding the particle at large distance, it has been treated in a way that at small distance its electrostatic field is equal to the dipole m vibrating with the frequency of the light.

The electric intensity E, and the magnetic intensity H at a large distance r (large compared with the wave length) are given by the following expressions

$$E = mk_0^2 \quad \frac{\sin v}{r} \; \mathrm{Cos}(\omega t - n_0 k_0 r)$$

$$H = \mu_0 \, E \qquad \text{VI-5}$$

where $k_0 = \frac{\omega}{\nu_1} = \frac{2\pi}{\lambda_0}$.

The energy radiated per second through 1 cm^2 of the sphere is given in terms of the time average Poynling's vector.

$$\frac{\nu_1}{8\pi} \mu_0 m^2 k_0^4 \quad \frac{\mathrm{Sin} 2v}{r^2} \qquad \text{VI-6}$$

and the total energy loss per second per particle is defined by the relation

$$\frac{1}{3} \; \frac{\nu_1}{\mu_0} \mu_0^2 \; m^2 \; k_0^4 \qquad \text{VI-7}$$

However he has shown that if a light beam, its intensity equal to the energy carried through 1 cm^2 per second, goes through a solution

$$I = \frac{\nu_1 \; \mu_0^2 F^2}{\mu_0 \; 8\pi} \qquad \text{VI-8}$$

it loses its intensity according to the relation

$$-\frac{dI}{dx} = n\ \frac{1}{3}\ \frac{\nu_1}{\mu_0}\ \mu_0^2 m^2 k_0^4 = \left(\frac{8\pi\ nk_0^4 m^2}{3F^2}\right) I \qquad \text{VI-9}$$

in the direction of propagation. From the above equation the turbidity is given by the expression

$$\tau = \frac{8\pi}{3}\ nk_0^4\ \frac{m^2}{F^2} \qquad \text{VI-10}$$

As can be seen, the turbidity is proportional to the number of particles per unit volume, and with the square of m/F. It is apparent from the above equation that the turbidity measures energy losses and intensities. The substitution of equation (VI-4) into (VI-10) gives the following relation,

$$\tau = \frac{32\pi^3}{3}\ \frac{\mu_0^2 (n_s - n_o)^2}{\lambda^4}\ \frac{1}{n} \qquad \text{VI-11}$$

then it takes the form

$$\frac{\tau}{c} = HM \qquad \text{VI-12}$$

where H is the optical constant which is defined by the expression

$$H = \frac{32\pi^3}{3}\ \frac{n_o^2}{N\ \lambda^4}\ \left(\frac{n_s - n_o}{c}\right)^2 \qquad \text{VI-13}$$

Since in dilute solution $\mu - \mu_0$ is directly proportional to the concentration, the equation can be rewritten as follows

$$H\ \frac{c}{\tau} = \frac{\partial}{\partial c}\left(\frac{p}{RT}\right) \qquad \text{VI-14}$$

where

$$\frac{p}{RT} = \frac{C}{M} + Bc^2$$

then the following relation is obtained

$$H\ \frac{c}{\tau} = \frac{1}{M} + 2\ Bc \qquad \text{VI-15}$$

VI.Ib - Scattering due to density and concentration fluctuations.

The fluctuation in density arises from related fluctuation in the polarizability a' of a volume element ∂V(246). The fluctuation behaves as a region of excess polarizability $\delta a'$. The relation between the excess polarizability, and volume element and the turbidity is given by the equation

$$\tau = \frac{128\pi^5}{3\lambda^4}\left[\frac{(\delta a')^2}{\delta V}\right] \tag{VI-16}$$

where $(\delta a')^2$ is the mean square of the excess polarizability corresponding to the volume element δV. The relation of $\delta a'$ with the average dielectric constant of the medium, and the dielectric constant of region exhibiting the fluctuation, can be defined by the expression in terms of δV.

$$\delta a' = \frac{3}{4\pi}\left|\frac{\varepsilon'-\varepsilon}{\varepsilon'+2\varepsilon}\right|\delta V \tag{VI-17}$$

It it is assumed that the fluctuation in region ε' is small, then the above expression takes the form

$$\delta a' = \frac{\delta V\delta\varepsilon}{4\pi\varepsilon} \tag{VI-18}$$

this expression can be related to the turbidity as follows,

$$\tau = \left|\frac{8\pi^3(\delta\varepsilon)^2}{3\lambda^4\varepsilon^2}\right|\delta V \tag{VI-13}$$

This turbidity expression with respect to the dielectric constant (ε) of the medium, where the function of density has been introduced in terms of the temperature and density

$$\tau = \frac{8\pi^3\delta V}{3\lambda_0^4}\left[d\left(\frac{\partial\varepsilon}{\partial d}\right)_T\right]\frac{(\delta d)^2}{d^2} \tag{VI-20}$$

where $(\delta d)^2$ is the mean square fluctuation in density, which occurs in the volume element δV. By several computing processes, $(\delta d)^2$ has been evaluated with respect to the thermodynamic relations by the expression,

$$(\delta d)^2 = kT/\beta s \ \delta V \qquad \text{VI-21}$$

The turbidity of the solution can be defined by means of density and concentration fluctuations

$$\tau = \tau d + \tau E \qquad \text{VI-22}$$

The distribution of molecules between the volume elements, and the evaluation of average distribution values gives the magnitude of concentration fluctuations in the volume element. The relation between turbidity and the mean square fluctuation of solute molecule, has been derived in the same way taking into account temperature and density

$$\tau = \frac{8\pi^3}{3\lambda_o} \delta V \left(\frac{\partial \varepsilon}{\partial m}\right)^2_{T,d} (\delta m)^2 \qquad \text{VI-23}$$

VI-Ic - Charge effects in light scattering by colloidal systems.

The scattering of light by small particles is effected by local inhomogenieties of refractive index(245,247), which arise from the fluctuation of density, or concentration which are due to the random thermal motion of solute(247).

The fluctuation in concentration contributes to light scattering proportionally to the magnitude of fluctuation which results in the refractive index. When a colloid particle having charge is treated as a light scattering species, it affects the extent of fluctuations in terms of the requirement of electroneutrality(248). In the case of added gegenions to the system, donnan equilibrium between the fluctuating volume and the bulk solution is established(248,249).

It has been postulated that the turbidity of pure colloidal electrolyte is reduced (p+1) times, when the colloid charge is p. It is apparent that the micelle of ionic surfactant is charged in the aqueous solution and in the presence of ions(248).

In view of the fluctuations theory of light scattering, it has been discussed that the extent of fluctuations is affected by the charge of micelle(248). The presence of monomeric ion reduces the optical efficiency of fluctuations. Consequently the concentration of monomer beyond the critical micelle concentration C_o, is influenced by the equilibrium between monomeric ions and charged micelle(248).

The turbidity of solution is due to the fluctuations in the concentration of solute(245,247,250). As a result of this fact one can assume that the refractive index fluctuates proportionately. In the case of pure association colloid, each mole of micelle is optically equivalent to the degree of association of monomer(248).

Hence, the optical effectiveness of fluctuations of micelles is reduced by a factor of $(1-p/2Nc)$ from Nc to $(Nc-p/2)$(248). Since the turbidity involves intensities rather than amplitudes of vibrations, it has been concluded that it is affected by the square of refractive index increment $\left(\frac{dn}{dc}\right)^2$. Due to this fact, the turbidity of the solution is reduced by $(1-p/2Nc)^2$ (248), and the micellar molecular weight calculated by the Debye method(245) is smaller than the real value.

In the light of this observation, the degree of association has been given by the equation in terms of the Debye relation

$$\frac{1}{M'} = \frac{1}{NA\ M_1} = A \qquad \text{VI-24}$$

The above expression takes the form for the corrected micellar moleculear weight (M)

$$\frac{1}{M} = \frac{1}{NcM_1} = A\left(1 - \frac{p}{2Nc}\right)^2 \qquad \text{VI-25}$$

It has also been given by the following equations for corrected aggregation number, and corrected charge of the micelles(251)

$$Nc = \frac{1}{AM_1} + \frac{2C_oBM_1 + 4\sqrt{2C_oBM_1} - AM_1\sqrt{2C_oBM_1}}{4AM_1 - 2A^2M_1^2} \qquad \text{IV-26}$$

and

$$p = \frac{2\sqrt{2C_oBM_1} + 2C_oBM_1}{2AM_1 - A^2M_1^2} \qquad \text{VI-27}$$

respectively. The uncorrected charge of micelle can be defined by the equation, in terms of the corrected charge and the aggregation number(248)

$$p' = \frac{p(2Nc-p)}{2Nc} \qquad \text{VI-28}$$

VI-Id - Experimental Procedure.

VI-Id$_1$- Materials

The preparation of surface active agents, and purification of aliphatic alcohols which were used in this work has been described in Chapter II. KCl (BDH L.R.grade) was dried in a vacuum oven at about 80-100°C. Double distilled water ($\Lambda w < 1\times10^{-6}$ ohm^{-1} cm^{-1} at 25°C) was filtered several times, through a Millipore filter disc, mean pore size 0.2μ, before using for the preparation of dilute solutions. The solutions were prepared on the molal basis.

VI-Id$_2$-Instrumentation and Measurement.

The refractive index increment (dn/dc) of the solutions was measured by using a differential refractometer. (The Brice-Phoenix, Model BP-2000-V). The instrument was calibrated according to the instrument manual(252).

VI-Id$_2$.A - Calibration.

The calibration of the instrument was made by using a reference solution, whose refractive index difference between solution and solvent is known. As a reference solution, various concentrations of KCl solution were used. Following procedure was employed to calibrate the instrument by using 546 mμ wave length at 25°C.

First both compartments of the differential cell were filled with water, and the glass cover was placed on the cell, then the handle of the rotatable cell holder was turned against the top so that it pointed towards the lamp.

The microscope was focussed on the narrow slit image and the iris diaphram of the projector was set to f:11 (position), then by means of the micrometer drum, the cross hair was set within the eyepiece so that it was aligned with the centre of the slit image. The reading was obtained from the eyepiece scale and the micrometer drum. The process was repeated several times, average (d_1^a) was taken. After that the handle of the cell holder was turned 180° towards the observer, the microscope was refocussed, and the above operation was repeated to obtain the reading at this position (d_2^a).

In order to calculate the solvent zero reading, the average reading (d_1^a) was subtracted from the average (d_2^a). The obtained solvent (water) zero reading (0.0058) is in good agreement with the value (0.006) given by the manufacturer[(252)].

Following this procedure, the solution compartment was filled with 1 ml calibration solution (KCl), covered with the glass cover, time was allowed for the temperature equilibrium of the solution (15 min.) and its solvent within the cell. After that the cell holder handle was turned towards the lamp housing, and the average reading (d_1) of the solution was recorded. Following this procedure, the cell handle was turned 180° towards observer, and the reading d_2 was determined. The reading for solution (d_2-d_1) was derived by subtracting the average reading for d_1 from the average reading for d_2.

The value of total displacement Δd, corrected for the solvent zero reading was calculated by the equation

$$\Delta d = (d_2 - d_1) - (d_2{}^a - d_1{}^a) \qquad \text{IV-29}$$

the refractive index difference is given by the following relationship

$$\Delta n = Ck.\Delta d \qquad \text{VI-30}$$

By using experimental Δd value 0.8054 (for 0.5964 g/dl standard KCl solution at 25°), and related refractive index difference between standard KCl solution and solvent (e.g.8.17×10^{-4})(252), the calibration constant ($Ck = 1.014 \times 10^{-3}$) was determined for the selected wave length (546 mμ).

VI.Id$_2$.B - Light scattering measurements were made by using a Photo Gonio Diffusometer (Model 4200)(253). The instrument was set and calibrated according to the instrument manual(253).

Initially electrical, optical and mechanical conditions were checked, then the glass scattering standard was placed in the central hole of the rotating plate. After that it was connected with general supply so that the pilot light was on, then the lamp water cooling circuit tap was opened. After a few seconds the high voltage mechanism put into the operation.

The measuring meter needle was set to zero, then was adjusted by using the highest sensitivity position. Following this process finally the needle position was set to the zero reading. The instrument was allowed about 20 minutes for warming up, then was set to the measure position, and the value of the photo tube dark current was checked. After adjusting the zero reading position, the lamp was put into operation. The measuring meter was adjusted for the maximum variation selecting related sensitivity, so that the measuring photo tube was set for maximum sensitivity.

The intensity scattered at 90° by the scattering glass standard is ranging about the intensity scattered by dust free pure benzene. In order to work with a sensitivity corresponding to 50 divisions for the intensity scattered by benzene, the sensitivity position being on I position, the measuring meter was adjusted so that the reading on the division corresponded to the value ($50 \times 0.92 = 46$). The ratio of the intensity scattered by the glass standard, to the intensity scattered by pure benzene is 0.92 (standard glass constant).

The turbidity of cleaned double distilled water ($\Lambda w < 1 \times 10^{-6}$ ohm^{-1} cm^{-1}) was determined (1.8×10^{-5} cm^{-1}), and compared with the value given in literature(254) (1.83×10^{-5} cm^{-1}) for the wave length used (546 mμ).

VI.Ida.B1 - Cleaning the measuring cell and solutions.

All glassware and the measuring cell were filled with a sulfochromic mixture and allowed to stand for about 24 hours. They were then rinsed with dust free distilled water several times. Following this procedure the measuring cell and all glassware were further cleaned using acetone vapour.

Great care was taken in the process of cleaning the prepared dilute solutions. The solution was pipetted into a cleaned glass cylinder, which was fitted with a cleaned filter disc of mean pore size 0.2μ, in the sterilized air condition, then the solution was filtered through the millipore filter under pressure. The process of cleaning the solutions was checked by measuring the dissymmetry of solution.

V.Ida.B2 - Checking the Dissymmetry.

After the calibration of instrument, the scattering glass standard was taken out, and the measuring cell containing the solution was set in its place. Then the intensities scattered by the solution at 60° and 120° angle were measured. The ratio of intensity scattered at 60° to the intensity scattered at 120° by the solution was compared with the standard dissymmetry (1.010) to check the degree of dedusting of the solution.

After the filtration, the concentration of solution was checked by using the differential refractometer. The measured adsorption of material on glassware and millipore used was negligible.

VI.Ie - Light scattering by alkylammonium bromides in water and solutions containing various additives.

VI.Ie1- Light Scattering by the aqueous surfactant solutions.

Light scattering in colloidal solutions depends primarily on the interference effect, which occurs due to dispersed particles(250). If the particle is small compared with the wavelength, each colloidal particle behaves as a light scatter species. As has been discussed, the turbidity of a solution depends on the homogenity of the solution, which is influenced by the fluctuations in concentration and density(245).

Light scattering measurements were made on solutions of the alkylammonium bromides in water, and solutions containing aliphatic alcohols, by using the Photo Gonio Diffusometer(253) at 25°C. The procedure of measurement was performed as described in this Chapter VI.Id. The scattered intensities of solutions was measured at 90° angle, and the Rayleigh ratios for the solutions was calculated, in terms of the scattering glass standard, and the Rayleigh ratio for standard benzene.

The C_o's of systems studied has been determined by plotting S_{90} against concentration ($mol.dm^{-3}$) (Figs.VI.1,3,4). The obtained C_o value for C_{10} is 6.5×10^{-2} mol dm^{-3}, which is in good agreement with the value obtained from viscosity, and surface tension measurement (6.5×10^{-2} mol.dm^{-3} and 6.0×10^{-2} mol.dm^{-3} respectively).

The C_0 values for C_{12}, C_{14} and C_{16} also agree well with the values obtained from the other methods (Tables VI.I.1, II.I.1,II.I.1.A). The micellar molecular weights of the surfactants in aqueous solution and containing various additives can be derived in terms of the Debye equation (VI-15), which can be rewritten(250) by the relation as follows,

$$\frac{H(C-C_0)}{\tau-\tau_0} = \frac{1}{M}+2B(C-C_0) \qquad \text{VI-31}$$

In order to obtain the apparent molecular weights (AMW) of the micelles, the left side of the above equation was plotted as a linear function of $C-C_0$, and the extrapolation of the obtained curve to $C-C_0 = 0$ gives the intercept, which is equal to $\frac{1}{M}$ according to the Debye relation (Figs.VI.2,VI.5).

Since unassociated surfactant contributes a negligible amount to the total turbidity of a micellar solution, τ_0 is assumed to be equal to the turbidity of solvent. The turbidity of solutions have been evaluated by the equation(246),

$$\tau = \frac{16\pi}{3} \times S_{90} \qquad \text{VI-32}$$

The light scattering measurements of alkylammonium bromides show that the micelles of these surfactants increase in size (molecular weight) (Fig.VI-6, Table VI.I.1.A). The micellar properties of alkylammonium bromides from hydrodynamic data has been discussed in Chapter II. It is concluded that the micelles of surfactants studied in aqueous solutions are spherical, hydrated and small. The increment in micellar molecular weight (AMW) increases as the chain length increases(250) (1.0101×10^4 and 1.5384×10^4 for C_{10} and C_{12} respectively Table VI.I.1.A).

The size of the micelles can be calculated from the micellar density in terms of partial molal volumes, and partial specific volume of the micelles.

The radius of the micelle can be derived by the expression(42)

$$RL = \sqrt[3]{3M/4\pi\ Nd} \qquad VI-33$$

However the obtained density values from partial specific volume of the micelles, has been used to calculate radius of the micelles. In order to derive also the radius of micelle from hydrodynamic data the following equation has been applied(174)

$$Rh = (3/4\pi)^{\frac{1}{3}}\ (Vh)^{\frac{1}{3}} \qquad VI-34$$

The calculated value of radius of micelle for C_{10} by the equation (VI-33), from light scattering data considering (AMW), is lower compared with the radius calculated from hydrodynamic data (16 Å and 21 Å respectively). However the obtained R^c value for C_{10}, taking into account the corrected miceller molecular weight (18 Å) agrees reasonably with the R^o value (Table II.I.4). The difference between the radii obtained by two methods for the other surfactants increases as the chain length increases.

The corrected and uncorrected degree of association of micelles, the effective charge and uncorrected charge has been derived by the equations (VI-26,VI-24,VI-27 and VI-28). It can be seen (Table VI.I.1.A) that the effective charge increases with increasing chain length (14 and 15 for C_{10} and C_{12} respectively), and the difference between uncorrected and the effective charge is 2 for both C_{10} and C_{12}.

As has been discussed in Section (VI.Ib, VI.Ic) in this Chapter, the turbidity of solution is due to inhomogeneties in the refractive index of region, which arise from the fluctuations in concentration and density(245,246,250). The degree of fluctuation is influenced by the charge of micelle(248). As a result of this fact, the optical effectiveness of the micelle is reduced, which affects the turbidity of the solution. The actual value of turbidity of the colloidal solution is effected by the factor of (p+1)(248), when the quantity of micellar charge is equal to p.

The effective charge refers to the equivalent charge under ideal conditions(251). Its value is lower than the true value at the shear surface, which is derived from electrophoretic mobility measurements. The degree of dissociation of micellar charge given by the ratio of micellar charge to the number of monomers, decreases with increasing true number of monomers corresponding to the chain length of surfactant. (Table VI.I.1A, 0.280 and 0.238 for C_{10} and C_{12} respectively). The obtained values corrected for the number of monomers, for the true micellar molcular weights of surfactants (50 and 63 for C_{10} and C_{12}) are slightly higher than the values given in literature (46 and 61.5 for C_{10} and C_{12} respectively)(248).

VI.Ie2 - Light scattering by surfactant solutions containing various aliphatic alcohols.

On the addition of aliphatic alcohols to the system, the micellar properties show deviation from the observed features in aqueous solutions. As has been discussed in Chapter II, the intrinsic viscosity of the micelles increases with increasing chain length. However it decreases for a particular alcohol, when the concentration increases. The increase in viscosity and intrinsic viscosity $[\eta]$ has been discussed in terms of hydrophobic interactions, hydration and electroviscous effect.

As can be seen (Fig.VI.5, Table VI.1.3) on the addition of 1 M C_2H_5OH and 0.5M C_3H_7OH to the aqueous solution of C_{12}, the AMW has considerably increased (5.263×10^4 and 4.0×10^4 respectively) compared with the AMW of C_{12} in aqueous solution (1.5384×10^4). The addition of 0.5M C_4H_9OH shows a similar pattern. However, on the addition of higher concentrations different behaviour has been observed. The AMW decreases when 2M C_2H_5OH, and 1 M C_3H_7OH is added to the aqueous solution (4.167×10^4 and 2.8×10^4 respectively Table VI.I.3)
It is known that the micellar molecular weight increases, when low molecular weight inorganic electrolyte is added to the colloidal system.

The effect of ions on the micellar properties have been extensively examined(150,151,255). The known fact is that the added ion increases the size of micelle and changes the shape of it. Since the physico-chemical nature of alcohol is different than inorganic electrolytes, (e.g. NaCl, NaBr) it does not appear probable that the similar approach could be used for alcoholic solutions of surfactants. As has been discussed, the alcohols penetrates into the micelle through the Stern layer around the kinetic micelle. They decrease the dielectric constant of bulk solution, and Stern layer(179). This effect increases with increasing apolar chain length of the alcohol molecule.

On the other hand alcohols behave as structure promoters at low concentration. However this behaviour tends to the opposite direction, as the concentration increases. The increment towards the alcohol-rich solution state breaks the micelles. It has been definitely established that the aliphatic alcohols enter into the oriented structure of micelles(179,186). Apart from this fact one can conclude that on the addition of alcohol to the system, due to the penetration of alcohol molecule, micellar molecular weight will be increased depending on the degree of solubilization.

The added alcohol decreases the head group repulsion in the micelle because the alcohol molecules orientate themselves between the monomers(186). As the molecules are brought together in the micelles, short range repulsive forces come into operation and corresponding repulsive energy increases.

The decrement in AMW after certain concentration (Table VI.I.3, Fig.VI.6) could be attributed to the solubilization degree of alcohol in the interior of micelle, the dielectric effect of alcohol on Stern layer, the dipole orientations in bulk solution, and hydrophobic interactions between possible orientations in the Stern layer, and in the interior of micelle between hydrocarbon groups.

However the penetration of alcohol into the micelle changes the structure and shape of micelle. The change in $[\eta]$ of micelles confirms also the idea that the micelle shape is changed by the addition of solute to the system.

On the addition of alcohol to the system, the $[\eta]$ deviates from the value (0.025 g/dl) given by Einstein for rigid spherical uncharged particles(126,127). The obtained $[\eta]$ for a micelle on the addition of 1 M C_2H_5OH is lower (0.044g.dl^{-1}) compared with the value from aqueous solution (0.069 g.dl^{-1}). It decreases with increasing concentration. The observed lower values of $[\eta]$ for micelles is due to the decrease in hydration and electroviscous effects. The addition of C_3H_7OH and C_4H_9OH shows a similar behaviour.

Hence on the addition of alcohols, the deviation from (0.025 g.dl^{-1}) could be attributed to the change in axial ratios of the micelles. It is a known fact that the increase in axial ratio of the particle, increases the intrinsic viscosity(169,256). The axial ratio of micelles decreases as the alcohol concentration increases (4.1 and 3.3 for 1 M C_2H_5OH and 2M C_2H_5OH respectively). The semi axis of revolution A_b and equatorial radius A_a of the micelles has been calculated taking into account the density of micelle and micellar molecular weight (AMW).

Since the axial ratios of the micelles, compared with the values given by Mehl et al.(169) and Scheraga(170) in terms of the shape function, and light scattering and viscosity data support the assumption of prolate type of micelle, it has been concluded that the micelles are rod (prolate) type rather the other shapes. On the addition of 1 M C_2H_5OH to the aqueous solution, the dimensions of the micelles have changed considerably (70Å and 17 Å for A_a and A_b

respectively, Table II.I.5).

The dissymmetry measurements (at 60° and 120°) indicate also that the slight deviation from standard dissymmetry (1.01) is due to the increase in molecular size and shape (1.04 and 1.054 for 1 M C_2H_5OH, and 2 M C_2H_5OH respectively. Table VI.I.2.A).

On the addition of alcohols to the system (Figs.VI.3, VI.4, Tables VI.I.2,A,B,C) the Rayleigh ratio and turbidity decreases as the concentration of alcohol increases (0.842×10^{-5} cm^{-1} and 1.4101×10^{-4} cm^{-1} for 4×10^{-2} mol dm^{-3} containing 1 M C_2H_5OH compared with 1.0385×10^{-5} cm^{-1} and 1.7391×10^{-4} cm^{-1} in aqueous solution of 4×10^{-2} mol.dm^{-3} surfactant respectively).

The effect of a second solvent on the light scattering properties, has been examined in terms of the density and concentration fluctuations, and the adsorption of low molecular weight species on the solute(257,258).

The parameter which measures the change in composition of the mixture surrounding the particles due to the selective adsorption has been discussed by Ewart et al.(257). This view has been employed by Parfitt-Wood(259,260) to methanol-water and ethanol-water mixed systems. They have concluded that if the optical efficiency of the fluctuations of the second solvent, related to the concentration fluctuation Rayleigh ratio of the liquid mixture is small, then its extra term on the fluctuations could be neglected.

According to their view the optical effect of concentration fluctuations of the secondary solvent on the micelles may be neglected. They have examined the effect of methanol as secondary solvent, on light scattering properties of SDS by adding 0.06-0.27 mole fraction alcohol to the system. They have observed that in a methanol-water mixture of mole fraction of methanol 0.12, the micellar molecular weight (AMW) decreases(260). The decrement increases with increasing mole fraction of alcohol, and they have also discussed the absence of micelle at 0.27 mol fraction of alcohol(260). Hermann-Benjamin(261) found similar behaviour on the addition of ethanol to a non-ionic system. The observed decrement in turbidity is due to the change in mean square density and concentration fluctuations in the refractive index increment. Since the alcohols behave as structure making at low concentration due to the apolar side of molecule(97), it is reasonable to assume that, even if they decrease the dielectric constant of solution, they will behave in the same manner in the Stern layer.

The optical efficiency of fluctuations of the secondary solvent on micelles contributes also to the change in the Rayleigh ratio, and decrement in the turbidity. On the other hand the effect of adsorbed solutes also plays a unique role in the changing light scattering properties of surfactant solutions.

As has been observed by Parfitt-Wood(260), in high concentration alcohols behave as structure breakers then, due to this fact, they destroy the micelles, consequently as concentration of alcohol is increased no critical change is observed in the turbidity-concentration curve.

However, in the mixed systems, the corrected micellar number, and the effective charge has also been calculated (33 and 28 (corrected) and 30.3 and 25.6 (uncorrected) for 1 M C_2H_5OH and 2M C_2H_5OH respectively) (Table VI.I.3).

The increase in effective charge could be attributed to the increase in molecular size, and the effect of alcohols on the hydration of micelles. The decrement in hydration of micelles and increment in repulsive energy(186) due to the penetration of alcohol into the micelle, could cause more adsorption of the counter ions in the Stern layer. This effect could also be taken as a possible reason for increase in the effective charge, because of an increase in the concentration of counter ions in the Stern layer. The difference between effective charge and uncorrected charge (8 and 2.7 for 0.5 M C_3H_7OH and 1 M C_3H_7OH respectively) arises from the fluctuations in the solution$^{(248,251)}$. The degree of dissociation of the micellar charge decreases as the concentration increases (0.296 and 0.220 for 0.5 M C_3H_7OH and 1 M C_3H_7OH respectively Table VI.I.3).

As it can be seen, the addition of aliphatic alcohols to the aqueous solution of C_{12} has changed the light scattering properties of the micelles. The main effect arises from the change in the density and concentration fluctuations. The effect of alcohol as a secondary solvent on those fluctuations, and the optical efficiency of micelles plays also an important role in the observed features of micelles.

VI.If - Conclusions.

The light scattering by alkylammonium bromides in water, and solutions containing various aliphatic alcohols has been examined at 25°C. The observations indicate that the micellar molecular weight increases, as the hydrocarbon chain length increases. Since fluctuations in density, in concentration and charge on the micelle effect the optical efficiency of micelles and the turbidity of the solution, in view of these facts the true micellar number and the effective charge of the micelles, has been observed.

Secondly the effect of aliphatic alcohols on the micelles has been studied, by adding various concentration to the aqueous system. The addition of alcohols first increased (AMW) then it decreased (AMW) with increasing concentration. In addition to this behaviour, they affected the turbidity of the solution in terms of changing the fluctuations in the bulk solution, and the kinetic properties of micelles. The effective charge has also increased, then it decreased with increasing concentration of alcohol. The change in micellar properties is presumably due to the interference effect of alcohol on fluctuations, and electrokinetic properties of micelles in terms of structure promoting and breaking behaviour.

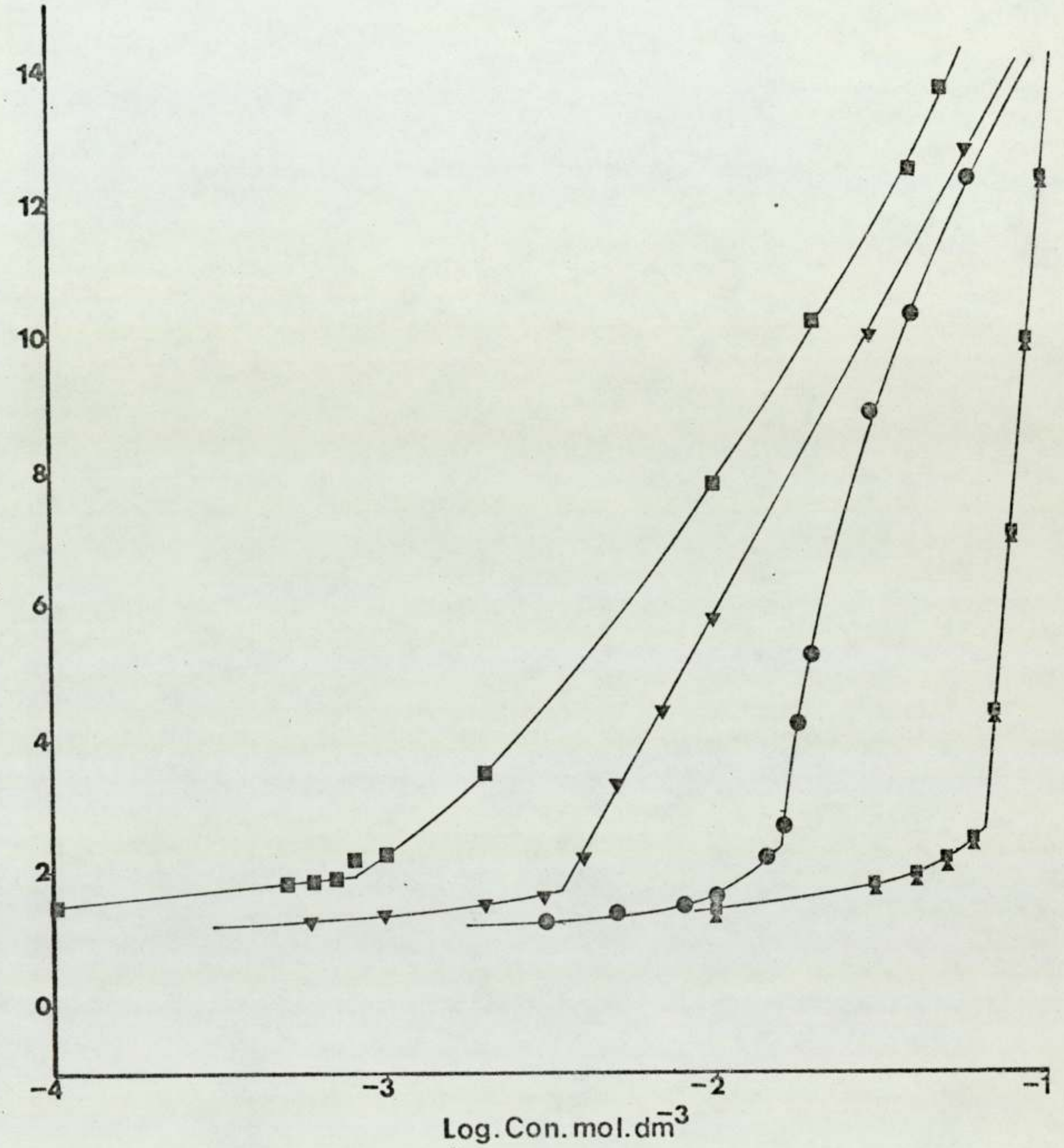


Fig.VI.I Scattering at 90° by aqueous solutions of the alkyltrimethyl ammonium bromides at 25° C; ▲ C_{10}, ● C_{12}, ▼ C_{14}, and ■ C_{16}

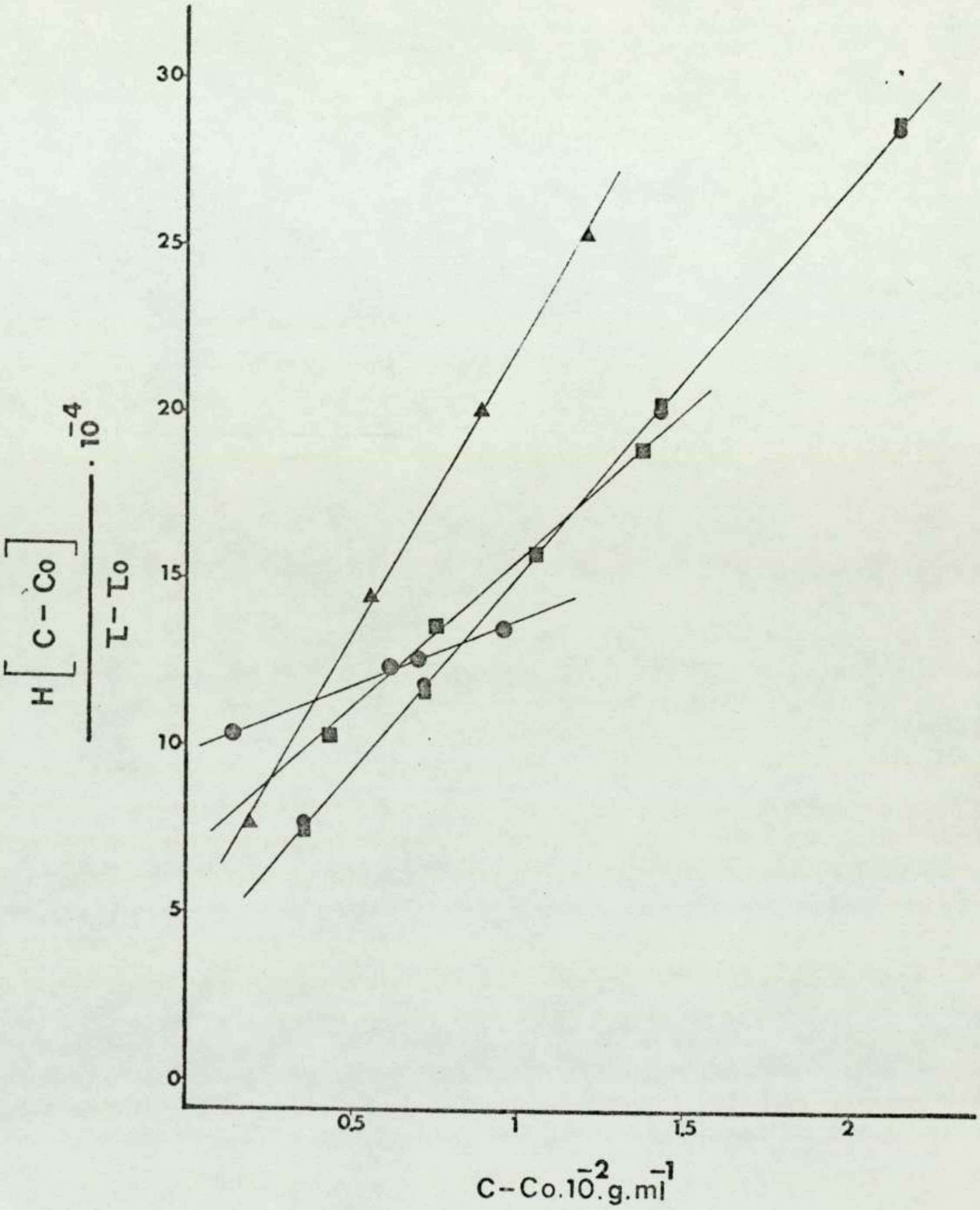


Fig.VI.2 Debye plots of the alkyltrimethyl ammonium bromides in water as a function of C-Co at 25° C; ● C_{10}, ■ C_{12}, ▲ C_{14}, and ▼ C_{16}

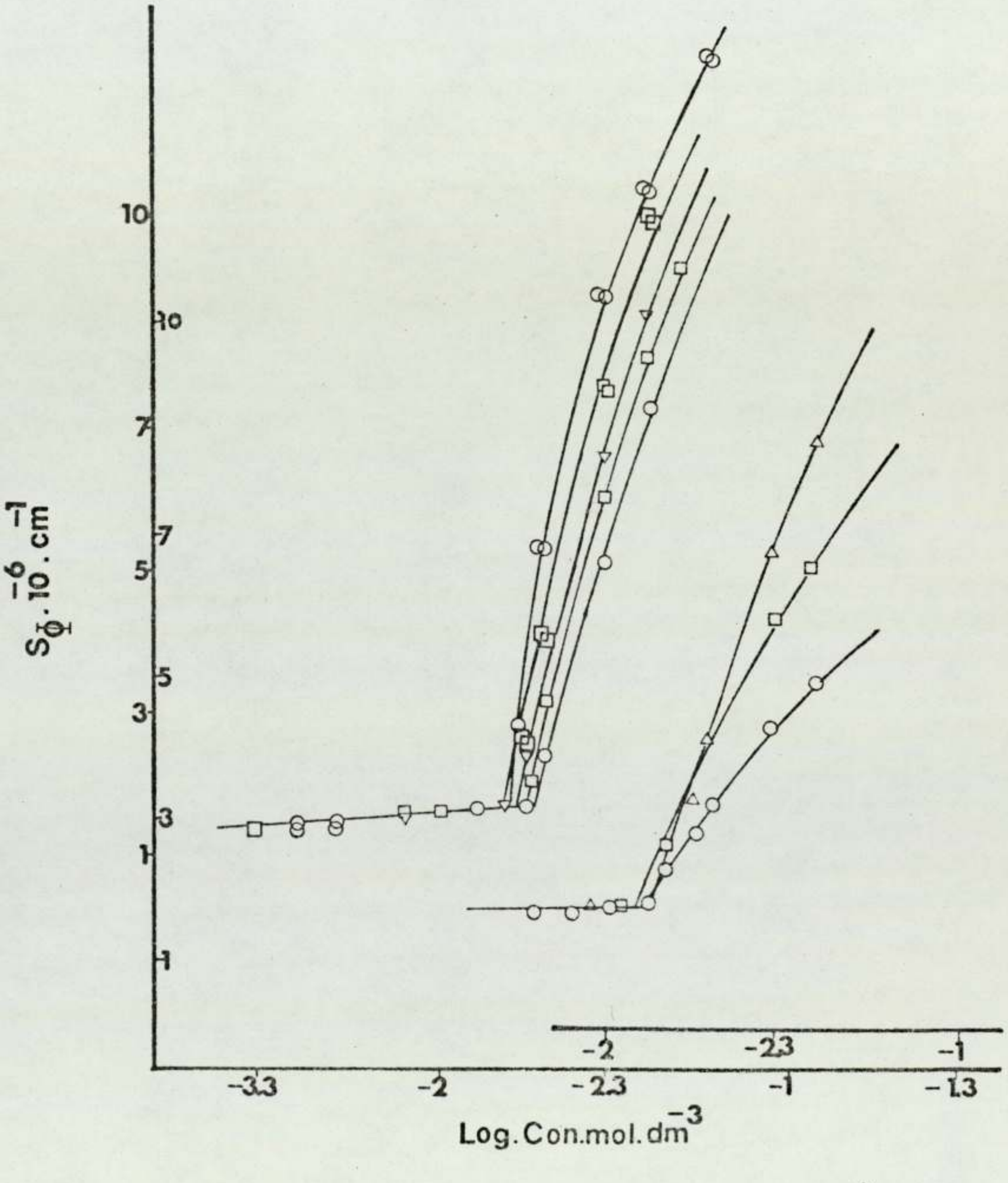


Fig.VI.3 Dependence of the scattering at 90° by dodecyltrimetyl ammonium bromides on the various concentration of methanol and ethanol in water at 25° C; Me-OH: ○○ H_2O. ⧉ 1M, ▽ 2M, □ 3M, and ○ 4M; Et-OH: △ 1M, □ 2M, and ○ 2.8M

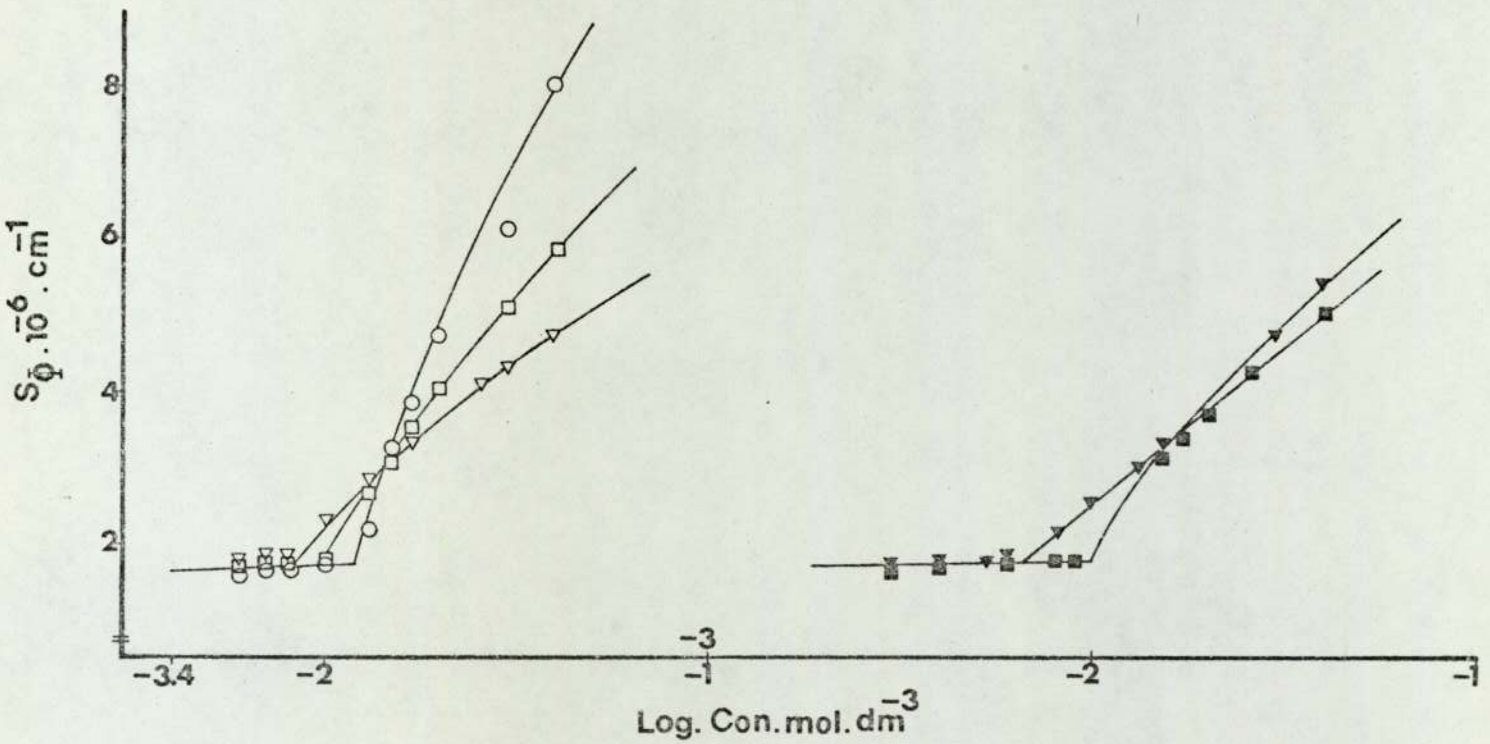


Fig. VI.4 Dependence of the scattering at 90° by dodecyltrimethyl ammonium bromides on the various concentration of propanol and butanol in water at 25° C; Pr-OH: ○ 0.5M, □ 1M, and △ 1.5M ; Bt-OH: ▲ 0.5M, ■ 1M

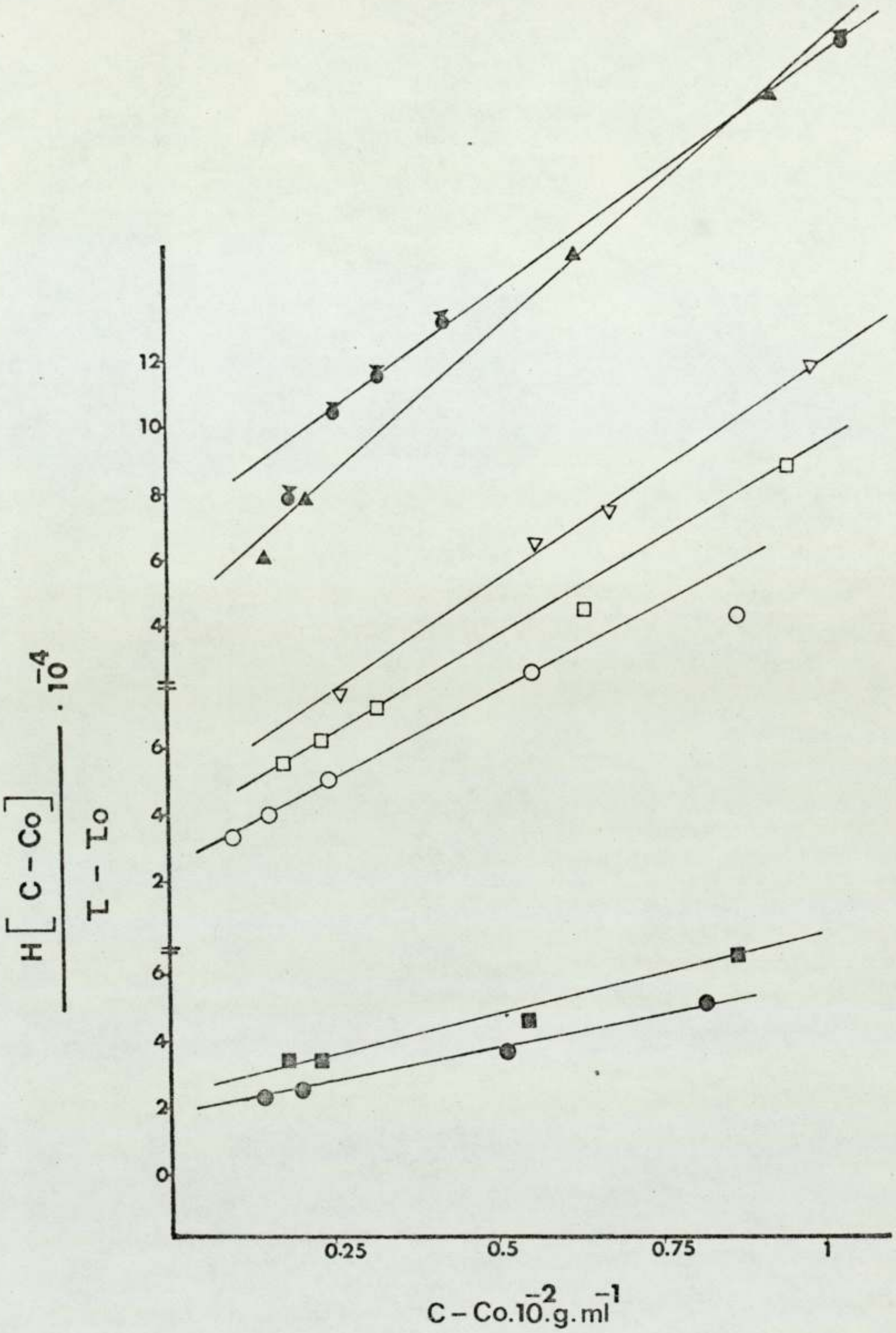


Fig.VI.5 Debye plots of the dodecyltrimethyl ammonium bromidecontaining various concentration of the aliphatic alcohols in water as a function of C-Co at 25° C; Et-OH: ● 1M, ■ 2M; Pr-OH: ○ 0.5M, □ 1M, and △ 1.5M; Bt-OH: ▲ 0.5M, ⧗ 1M

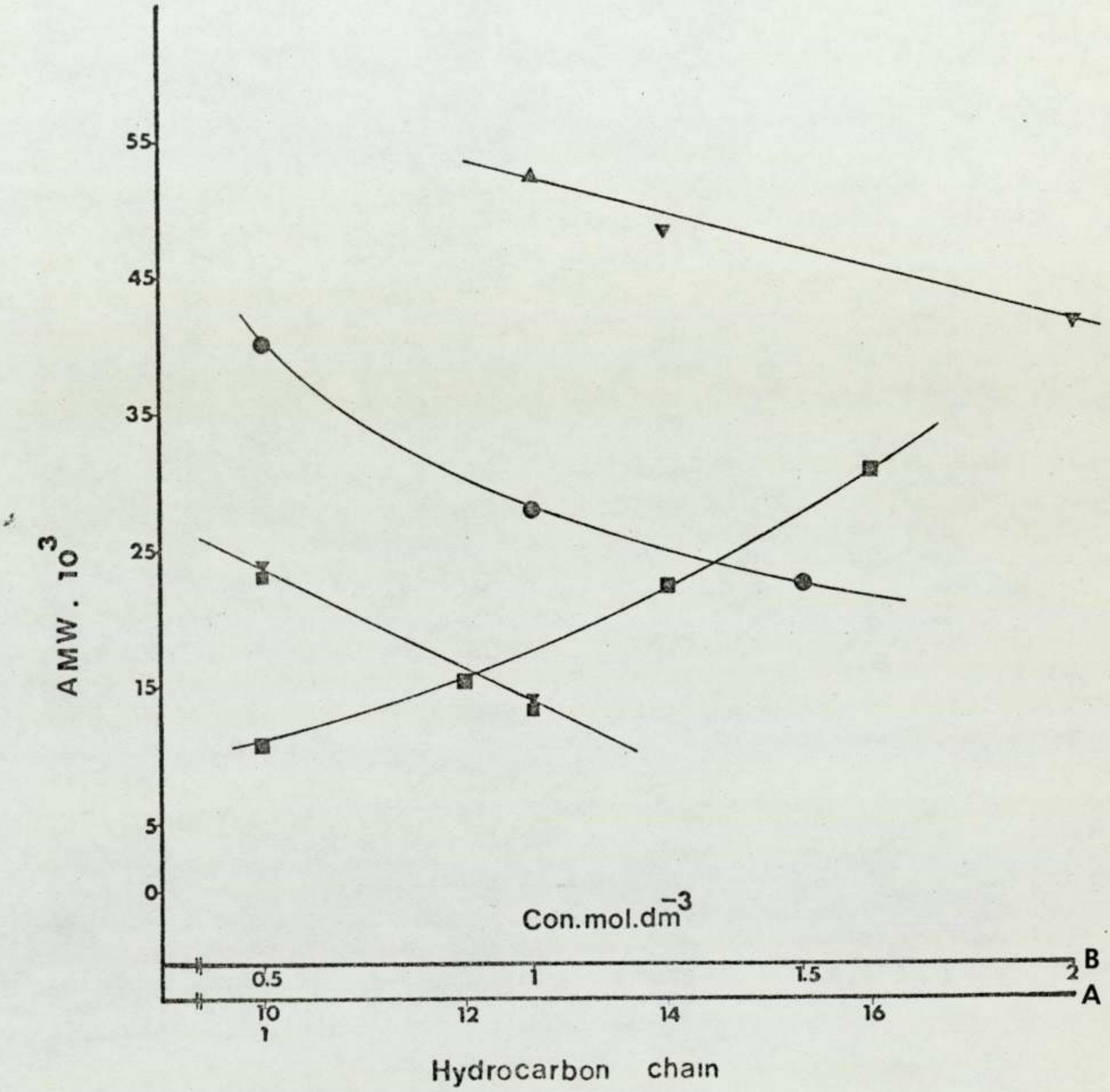


Fig.VI.6 **A**,The relationship between AMW and the alkylchain length;**B**,Variation of AMW of the dodecyltrimethyl ammonium bromide with various concentrations of the aliphatic alcohols at 25° C;**B** ▲ Et-OH , ● Pr-OH, and ⧗ Bt-OH ; **A** ■ AMW

LIHGT SCATTERING BY ALKYLAMMONIUM BROMIDES

IN AQUEOUS SOLUTIONS AT 25° C

TABLE VI.I.1

C mol.dm^{-3}	$S_{\emptyset}$ .10^{-5}.cm^{-1}	τ .10^{-4}.cm^{-1}	D_R	ΔI ml . g^{-1}	H	C_o mol.dm^{-3}
			C_{10}			
1×10^{-1}	1.2420	2.0799	1.02	0.152	2.52	6.5×10^{-2}
9×10^{-2}	1.0122	1.6951				
8×10^{-2}	0.7130	1.1940				
7×10^{-2}	0.4451	0.7454				
6×10^{-2}	0.2532	0.4241				
5×10^{-2}	0.2147	0.3595				
4×10^{-2}	0.1962	0.3285				
3×10^{-2}	0.1869	0.3130				
1×10^{-2}	0.1526	0.2555				
			C_{12}			
6×10^{-2}	1.2372	2.0720	1.02	0.155	2.63	1.55×10^{-2}
5×10^{-2}	1.150	1.9258				
4×10^{-2}	1.0385	1.7391				
3×10^{-2}	0.8964	1.5012				
2×10^{-2}	0.5343	0.8950				
1.8×10^{-2}	0.4200	0.7034				
1.6×10^{-2}	0.2691	0.4510				
1.4×10^{-2}	0.2268	0.3798				
1×10^{-2}	0.1613	0.2701				
8×10^{-3}	0.1461	0.2450				
5×10^{-3}	0.1384	0.2320				
3×10^{-3}	0.136	0.2277				
			C_{14}			
6×10^{-2}	1.249	2.0922	1.03	0.157	2.72	8×10^{-4}
5×10^{-2}	1.0848	1.8166				
4×10^{-2}	0.9164	1.5346				
3×10^{-2}	0.7664	1.2835				
2×10^{-2}	0.7183	1.2030				
7×10^{-3}	0.4498	0.7533				

5×10^{-3}	0.3407	0.5710				
4×10^{-3}	0.2249	0.3766				
3×10^{-3}	0.1662	0.2783				
2×10^{-3}	0.1499	0.2510				
1×10^{-3}	0.143	0.2395				
C_{16}						
6×10^{-2}	1.3713	2.2965	1.03	0.157	2.72	8×10^{-4}
5×10^{-2}	1.1662	1.9530				
4×10^{-2}	1.2530	2.0984				
3×10^{-2}	0.7992	1.3384				
2×10^{-3}	0.3566	0.5972				
1×10^{-3}	0.2339	0.392				
8×10^{-4}	0.239	0.4003				
6×10^{-4}	0.175	0.2931				
5×10^{-4}	0.1813	0.3036				

MICELLAR DIMENSIONS OF THE ALKYLAMMONIUM BROMIDES IN WATER

FROM LIGHT SCATTERING MEASUREMENT

TABLE VI.I.1.A

S·A·A	A	B g.ml	AMW	N_A	N_c	p	$\frac{p}{N_1}$	p'
C_{10}	9.9 x10^{-5}	4 x10^{-3}	10101	36	50	14	0.280	12
C_{12}	6.5 x10^{-5}	8.5x10^{-3}	15384	50	63	15	0.238	13.2
C_{14}	4.42x10^{-5}	1.7x10^{-2}	22624	67	82	16	0.195	14.4
C_{16}	3.2 x10^{-5}	1.2x10^{-2}	31250	86	93	8	0.086	7.6

LIGHT SCATTERING DATA FOR THE DODECYL TRIMETHYL AMMONIUM BROMIDE IN WATER CONTAINING ALIPHATIC ALCOHOLS AT 25° C

TABLE VI.I.2

C $mol.dm^{-3}$	$S_{Ø}$ $\cdot 10^{-5}\ cm^{-1}$	τ $\cdot 10^{-4}\ cm^{-1}$	D_R	C_o $mol.dm^{-3}$
1M, Me-OH				
4.0×10^{-2}	1.0033	1.6802	1.04	1.5×10^{-2}
3.0×10^{-2}	0.7599	1.2730		
2.0×10^{-2}	0.4116	0.6893		
1.7×10^{-2}	0.2604	0.4361		
1.5×10^{-2}	0.1779	0.2979		
1.3×10^{-2}	0.1726	0.2891		
1.0×10^{-2}	0.1652	0.2766		
8.0×10^{-3}	0.1642	0.2749		
4.0×10^{-3}	0.1544	0.9586		
2M				
4.0×10^{-2}	0.8646	1.4479	1.04	1.67×10^{-2}
3.0×10^{-2}	0.6584	1.1030		
2.0×10^{-2}	0.3321	0.5562		
1.8×10^{-2}	0.2491	0.4172		
1.6×10^{-2}	0.1952	0.3269		
1.4×10^{-2}	0.1683	0.2820		
1.0×10^{-2}	0.1653	0.2768		
7.0×10^{-3}	0.1660	0.2780		
5.0×10^{-3}	0.1483	0.2484		
3M				
4.0×10^{-2}	0.8054	1.3487	1.05	1.8×10^{-2}
3.0×10^{-2}	0.6038	1.0142		
2.0×10^{-2}	0.2881	0.4825		
1.8×10^{-2}	0.2126	0.3560		
1.6×10^{-2}	0.1781	0.2983		
1.3×10^{-2}	0.1639	0.2745		
1.0×10^{-2}	0.1618	0.2710		
8.0×10^{-3}	0.1625	0.2721		
6.0×10^{-3}	0.1529	0.2561		

TABLE VI.I.2.A

C mol.dm^{-3}	S_{ϕ} .10^{-5}.cm^{-1}	τ .10^{-4}.cm^{-1}	D_R	ΔI ml.g^{-1}	H	C_o mol.dm^{-3}
			4M			
4.0×10^{-2}	0.7362	1.2330	1.04	0.035	0.135	1.8×10^{-2}
3.0×10^{-2}	0.5107	0.8553				
2.0×10^{-2}	0.2480	0.4153				
1.7×10^{-2}	0.1807	0.3030				
1.5×10^{-2}	0.1660	0.2780				
1.3×10^{-2}	0.1550	0.2596				
9.0×10^{-3}	0.1550	0.2596				
4.0×10^{-3}	0.1581	0.2647				
			1M, Et-OH			
4.0×10^{-2}	0.8420	0.4101	1.04	0.0794	0.693	1.35×10^{-2}
3.0×10^{-2}	0.6811	1.141				
2.0×10^{-2}	0.4198	0.7030				
1.8×10^{-2}	0.3320	0.5559				
1.5×10^{-2}	0.2157	0.3612				
1.3×10^{-2}	0.1813	0.3040				
1.0×10^{-2}	0.1881	0.3150				
8.0×10^{-3}	0.1757	0.2942				
5.0×10^{-3}	0.1673	0.2802				
			2M			
4.0×10^{-2}	0.6640	1.1120	1.054	0.077	0.65	1.2×10^{-2}
3.0×10^{-2}	0.5951	0.9966				
2.0×10^{-2}	0.3669	0.6144				
1.8×10^{-2}	0.3101	0.5193				
1.5×10^{-2}	0.2750	0.4610				
1.3×10^{-2}	0.1764	0.2954				
1.0×10^{-2}	0.1800	0.3014				
8.0×10^{-3}	0.1800	0.3014				
4.0×10^{-3}	0.1800	0.3014				

TABLE VI.I.2.B

C mol.dm^{-3}	$S_{\emptyset}$ $.10^{-5}.cm^{-1}$	T $.10^{-4}.cm^{-1}$	D_R	ΔI ml.g^{-1}	H	Co mol.dm^{-3}
			2.8 M			
4.2×10^{-2}	0.4472	0.7489	1.05	-	-	1.3×10^{-2}
3.0×10^{-2}	0.4353	0.7289				
2.0×10^{-2}	0.3181	0.5330				
1.8×10^{-2}	0.2816	0.4720				
1.5×10^{-2}	0.2116	0.3543				
1.3×10^{-2}	0.1850	0.3098				
1.0×10^{-2}	0.1832	0.3070				
8×10^{-3}	0.1756	0.2941				
5×10^{-3}	0.1672	0.280				
			0.5M, Pr-OH			
4×10^{-2}	0.8007	1.3410	1.02	0.107	1.24	1.2×10^{-2}
3×10^{-2}	0.6142	1.0286				
2×10^{-2}	0.4794	0.8030				
1.7×10^{-2}	0.3887	0.6510				
1.5×10^{-2}	0.3146	0.5268				
1.3×10^{-2}	0.2258	0.3781				
1×10^{-2}	0.1812	0.3034				
8×10^{-3}	0.1763	0.2952				
4×10^{-3}	0.1675	0.2810				
			1 M			
4×10^{-2}	0.5822	0.9750	1.06	0.102	1.13	9.5×10^{-3}
3×10^{-2}	0.5100	0.8541				
2×10^{-2}	0.4056	0.6792				
1.7×10^{-2}	0.3516	0.5888				
1.5×10^{-2}	0.3101	0.5193				
1.3×10^{-2}	0.2798	0.4685				
1×10^{-2}	0.1823	0.3053				
8×10^{-3}	0.1772	0.2967				
4×10^{-3}	0.1683	0.282				

TABLE VI.I.2.C

C $mol.dm^{-3}$	$S_ø$ $.10^{-5}.cm^{-1}$	L $.10^{-4}.cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H	C_o $mol.dm^{-3}$
1.5M						
4×10^{-2}	0.47340	0.7930	1.02	0.098	1.085	8.25×10^{-3}
2.6×10^{-2}	0.4073	0.6821				
1.3×10^{-2}	0.2812	0.4710				
1×10^{-2}	0.2312	0.3872				
9×10^{-3}	0.1921	0.3220				
7×10^{-3}	0.1732	0.2901				
5×10^{-3}	0.1701	0.285				
0.5M, Bt-OH						
4×10^{-2}	0.5412	0.9063	1.03	0.120	1.48	1.0×10^{-2}
3.8×10^{-2}	0.4735	0.7930				
2.6×10^{-2}	0.4300	0.7201				
1.7×10^{-2}	0.3450	0.5777				
1.5×10^{-2}	0.3320	0.5559				
1.3×10^{-2}	0.2910	0.4873				
1.0×10^{-2}	0.20	0.3350				
9×10^{-3}	0.1801	0.3020				
6×10^{-3}	0.1751	0.2932				
5×10^{-3}	0.1742	0.292				
1M						
4×10^{-2}	0.515	0.8624	1.02	0.112	1.37	6.6×10^{-3}
2×10^{-2}	0.369	0.6180				
1.7×10^{-2}	0.337	0.5644				
1.5×10^{-2}	0.316	0.5292				
1.3×10^{-2}	0.312	0.5225				
1×10^{-2}	0.256	0.4287				
8×10^{-3}	0.2234	0.3741				
6×10^{-3}	0.1802	0.3020				
4×10^{-3}	0.1723	0.2885				
2×10^{-3}	0.1651	0.2765				

MICELLAR DIMENSIONS OF THE DODECLYTRIMETHYL AMMONIUM BROMIDE IN WATER CONTAINING ALCOHOLS FROM LIGHT SCATTERING MEASUREMENT

TABLE VI.I.3

A	B g.ml	AMW	N_A	N_C	p'	p	$\frac{p}{N}$	C mol.dm^{-3}
Et-OH								
$1.9\text{x}10^{-5}$	$3.75\text{x}10^{-3}$	52630	170	202	30.3	33	0.163	1 M
$2.4\text{x}10^{-5}$	$5.0\text{x}10^{-3}$	41670	135	162	25.6	28	0.173	2 M
Pr-OH								
$2.5\text{x}10^{-5}$	$1.06\text{x}10^{-2}$	40000	130	179	45	53	0.296	0.5 M
$3.6\text{x}10^{-5}$	$1.1\text{x}10^{-2}$	28000	91	114	22.3	25	0.220	1 M
$4.4\text{x}10^{-5}$	$1.3\text{x}10^{-2}$	22730	74	94	18.80	21	0.223	1.5 M
Bt-OH								
$4.2\text{x}10^{-5}$	$1.73\text{x}10^{-2}$	23800	77	104	25	29	0.278	0.5 M
$7.0\text{x}10^{-5}$	$1.33\text{x}10^{-2}$	14280	46	58	10.57	12	0.207	1 M

CHAPTER VII - Micellar Properties of Polyoxyethylene Monohexadecyl ethers in aqueous solution and containing additives.

VII.Ia - Viscometric measurements on dilute aqueous solutions of n-alkylpolyoxyethylene surfactants.

The micellar structure of non-ionic surfactants has not been extensively examined, in contrast to the investigations on the micellar structure of ionic surfactants. Kushner-Hubbard(262) have discussed the negative solubility coefficients of non-ionic surfactants in aqueous solution, in terms of the interactions of surfactant with solvent molecules. However the deviation of $[\eta]$ of the micelles from the Einstein value ($0.025\ g.dl^{-1}$) has been interpreted by means of the change in micellar shape, and the solvent effect on the surfactant molecules.

Due to this fact, the solubility of the surfactant molecules in water have been attributed to the hydration phenomenon, which occurs due to the affinity of the oxyethylene chain to water molecules.

The effect of the hydrophilic group of the surfactant molecule on the stability of non-ionic surfactants in solution has been studied by Reich(263). According to his view, the cross-sectional area of the hydrophilic group of a non-ionic surfactant plays an important role preventing the association of individual molecules. However, this view has been strengthened(188) by including the heat of hydration, and the configurational entropy terms of the flexible hydrophilic chain.

The factors which are involved in non-ionic micelle formation in aqueous solution have been also investiged by Schick et al.(172). Their observations indicate that the degree of association of the monomers depends on the length of both hydrophilic, and hydrophobic groups. They have also concluded that the aggregation number of non-ionic micelles decreases as the ethylene oxide chain length increases.

On the other hand, the extent of hydration of non-ionic surfactants in aqueous solutions has been examined by Schott(176), taking into account its role in the stability of their aqueous solutions.

The study of dilute aqueous solution of non-ionic surfactants was carried out by measuring the absolute viscosities of the surfactants at 25°C, using a U-tube viscometer and the C_o in aqueous surfactant solution was determined as described in Chapter II. As can be seen in Fig.VII.1, the relative viscosity increases with increasing EO chain length (1.0059 and 1.0083 for 5×10^{-4} mol.dm^{-3} of $C_{16}E_{10}$, and $C_{16}E_{18}$ respectively Table VII.I.1). The increase in relative viscosities of the cationic surfactants in aqueous solutions, and containing various additives has been discussed (Chapter II) in terms of hydration, electroviscous effect, particle shape and hydrophobic interactions.

In aqueous solution of non-ionic surfactants, since there are not the electrical forces involved in the molecular interactions of the non-ionic surfactant with water molecules, the increase in viscosity can be attributed to the possible hydration of molecules, change in particle shape, and the hydrophobic interactions of ethylene-oxide chain length, and hydrophobic group with water molecules(172,176,262) This long range interaction increases water structure around the non-polar and polar groups. The aggregation of monomers due to these interactions moves the nonpolar part of the molecule to the thermodynamically favourable to nonpolar region, reducing hydrocarbon water interface, and the release of energy involved in this process causes a physico-chemical change at certain concentration of the aqueous surfactant solution, which is C_o (5.6×10^{-5} mol.dm^{-3} and 1.4×10^{-5} mol.dm^{-3} for $C_{16}E_{10}$, and $C_{16}E_{60}$ respectively Tables VII.I.1, VII.I.1.A).

The C_o decreases as the EO chain length increases (Figs.VII.2, VII.5). The discrepancies in C_o values between this work and the literature values will be discussed in one of the sections of this chapter. The intrinsic viscosity of the micelles was determined in the same way as described in Chapter II. As can be seen in Fig.VII.8 (Table VII.I.1.B) the $[\eta]$ increases as the EO chain length increases (0.039 g.dl^{-1} and 0.117 g.dl^{-1} for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively).

The increment in $[\eta]$ is due to the hydration, the change in the shape, and size of the micelles(172,176). No clear picture has yet been obtained of how the hydration is affected by the ethylene oxide chain length. Elworthy-Macfarlane(264) have discussed that the hydration of non-ionic surfactants is due to a trapping of water molecule in the mesh of oxyethylene chain length. According to their view the hydration of the micelles depends on the length of the hydrophilic group, its degree of contraction , and on the geometry of the micelle.

The obtained higher intercepts on $\frac{\eta_{sp}}{\phi}$ versus ϕ curve have been discussed in terms of micellar asymmetry, the increase in temperature effects and the radial length of the micelle occupied by the polyoxyethylene chain. This increase induces the trapping of water molecules, in the mesh of polyoxyethylene chains. It has been also shown(265) that the micellar asymmetry develops at a higher temperature, and the higher Huggins constant, and the negative second virial coefficient B have been used as an indication of the asymmetry of the micelles.

However, the hydration of polyoxyethylene surfactant has been determined in terms of crystal density and specific volume of anhydrous non-ionic surfactants(175). The calculated g. water/g surfactant decreases with increasing ethylene oxide chain length (1.152 g /g.surfactant, 0.38 g /g.sur.for $C_{16}E_{10}$,$C_{16}E_{60}$ respectively, Table VII.I.6). These results are contrary to the values given by El Eini et al.(266).

On the other hand, the Huggins constants of the surfactant molecules in aqueous solution were calculated as described in Chapter II. The Huggins constant ($\simeq$ 2.0) is given by Tanford(327) and Schott(176) as an indication of sphericity of the uncharged rigid particles. In view of this observation the calculated Huggins constant are 5.84, 4.98 and 4.63 for $C_{16}E_{10}$, $C_{16}E_{18}$ and $E_{16}E_{60}$ respectively (Table VII.I.1.B).

As can be seen, there is considerable deviation from the value $\simeq 2.0$. Since the electrical forces and surface charge do not exist in the systems used, this deviation and high $[\eta]$ values of micelles can be attributed to the change in micellar shape, size, hydrophobic interactions and the hydration. In the light of this consideration, this view can be expanded to investigate the above properties of micelles in aqueous solution.

The intrinsic viscosity $[\eta]$ of micelles of $C_{16}E_{10}$ is 0.039 $g.dl^{-1}$ (Table VII.I.1.B). This value of $[\eta]$ is less compared with $[\eta]$ of the spherical micelles of C_{10} (cationic surfactant, 0.06 $g.dl^{-1}$, Table II.I.1). The increase in $[\eta]$ in ionic surfactant solutions has the contributions from electroviscous effect, hydration and shape of the micelles. If it is assumed that the increment in $[\eta]$ due to electroviscous effect is not significant, then one can conclude that the hydration of the micelles is the dominant factor beside the shape of the micelle.

In view of this assumption,when the $[\eta]$ value of micelles of C_{16} is compared with the $[\eta]$ of the micelles of $C_{16}E_{60}$, as can be seen (Tables VII.I.1.B, II.I.1.A) the difference is 0.021 $g.dl^{-1}$. If the micelles of both surfactants are spherical, and only the hydration effect is a major factor, with the size of micelles for increase in $[\eta]$, then one can say considering Einstein's theory that the increase in $[\eta]$ of micelles of polyoxyethylene monohexadecyl ethers should be higher compared with the small spherical micelles of ionic surfactants, since the hydration is a function of the polyoxyethcylene chain length,as this part of micelles is involved in the trapping of water molecule(264).

It is apparent that even though the non-ionic surfactant ($C_{16}E_{60}$) has the same hydrophobic surface area compared with the cationic surfactant (C_{16}TAB), and a long oxyethelere chain the increase in $[\eta]$ is not significant (0.096 g.dl^{-1} and 0.117 g.dl^{-1} for C_{16} and $C_{16}E_{60}$ respectively). In the light of this approach we can examine the possible shape of the micelles. When the oxyethylene chain length is increased, while the hydrocarbon surface is constant, it causes an increase in penetration, and greater density in the packing of the polyoxyethylene chains in the outer shell(176). This tighter network holds less water molecules than the more open network of shorter chains. The long chain length promotes the water of hydration of micelles to be squeezed out(176). However the hydration of micelles has also been discussed in view of the geometry of micelle, and the length of the hydrophilic group(264).

It has been concluded that since the hydrocarbon chain lengths are parallel to one another along the long axis of the rod type of micelle, the volume per monomer in which water molecules are trapped is smaller than in the spherical case. On the other hand, on the assumption of the state of very closely packed hydrophilic groups, which are very close to the hydrocarbon region (micellar core), water molecules may come into contact with the hydrocarbon region. This contact could increase the interfacial tension on the hydrocarbon-polyoxyethylene interface, causing the change in the micellar shape and size(265) (elongation).

In view of these facts, the shape of the micelles was examined in terms of hydrodynamic, and light scattering data and the approach was based on the elongated type of micelle. The shape function of the micelles of the non-ionic surfactants was calculated using equation (II-44), taking into account the specific volume of the monomer at C_0, which was calculted from corresponding partial molal volumes of the micelles. The calculated shape function of the micelles are (4.3) and (14.57) for $C_{16}E_{10}$ and $C_{16}E_{60}$ (Table VII.I.6).

These results also confirm that the deviation from the Einstein value for spherical particles 0.025 g.dl^{-1} is due to one of these facts, which is the change in micellar shape. These obtained results were compared with the table given by Mehl et al.(169) and Scheraga(170). In those tables this shape function (4.152) corresponds to the axial ratio (3.5) for prolate, while (4.382 corresponds to the axial ratio (4.5) for oblate. In view of these reported values for prolate and oblate particles, the obtained shape functions were substituted into equation (II-45,II-46), in order to derive the axial ratio of the semi axis of revolution to equatorial radius of the micelles.

The observation in this work indicates that the axial ratios of the micelles fit well to the prolate type shape. The axial ratio (3.7) for $C_{16}E_{10}$ corresponds the shape function (4.3) which is very close to the shape function for prolate given by Mehl et al.(169) and Scheraga (170).

On the other hand the higher axial ratio of the prolate micelles of $C_{16}E_{60}$ (10.4) corresponds to the shape function of the micelles (14.57) agreeing well with the value of axial ratio of the prolate particles (10.0) corresponding to the shape function (13.634), which is very close to the shape function determined for $C_{16}E_{60}$.

In the case of oblate obcets, the shape function 14.80 corresponds to an axial ratio 20 which is considerably higher than the observed value. The dimensions of the micelles were calculated in terms of the density of micelles, and micellar molecular weight (from light scattering data). The obtained partial specific volumes of the monomers from corresponding partial molal volumes are 0.91361 ml/g and 0.8020 ml/g at 25°C for $C_{16}E_{10}$, and $C_{16}E_{60}$ respectively (Table VII.I.2).

From this observation, it is apparent that the density of micelles are higher than the density of liquid hexadecane at 25°C at constant pressure. But the pressure in the interior of the micelle is not known. It is reasonable to assume that the core of micelles has some amount of water molecules. Similar type of results were obtained for the density of the cationic micelles from the partial molal volumes of the corresponding micelles. The view of the interior of micelles containing water molecules has also been confirmed by some investigators(162,163,164,165).

However, the observed micellar dimensions are 130 Å and 35 Å for Aa, and Ab of $C_{16}E_{10}$ (Table VII.I.6), and the equatorial radius of micelles increases as the EO increases, while the semiaxis of revolution decreases (198 Å and 19 Å for Aa, and Ab of $C_{16}E_{60}$. The obtained shape function, and partial specific volume were used to calculate the hydrated volume of the micelles, in terms of the equation (II-36) (0.642×10^{-18} ml and 0.295×10^{-18} ml for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively, Table VII.I.6).

As can be seen, the hydrated volume of micelles decreases as the EO chain length increases. This observation confirms also that the hydration of non-ionics, decreases as the hydrophilic chain length increases. This is due to the change in configurational orientation of the polyoxyethylene group. These experimental results are contrary to the hydration phenomenon, which have been observed by several investigators(172,176,263,264,265) in aqueous non-ionic systems. The observed dehydration of micelles (decrement in hydration) can be discussed in terms of the prolate shape of the micelles, which are less hydrated than the spherical micelles, and very close packing of the long ethylene oxide chains near the hydrocarbon region (micellar core) which squeezes water molecules out from the outer shell of the micelles.

VII.Ib - Partial Molal volumes of Polyoxyethylene Monohexadecyl ethers in aqueous solution.

The volumetric properties of short chain alcohols have been investigated by Friedman-Scheraga(211), in terms of the environmental effects on the partial molal volumes of the alchols, as the alcohols transfer from a hydrocarbon environment to an aqueous region. On the other hand Corkill et al.(217) have determined the partial molal volume properties of ionic, and non-ionic surfactants below the C_o, and above the C_o considering molecular structure of surfactants. They have concluded that the methyl group remote from the hydrophilic group contributes to an increase of P.M.V, while the additional methylene group which is close to a hydrophilic centre gives a negative contribution to P.M.V.

However, in aqueous systems the involved volume change due to the alkyl chain length has been interpreted by Nemethy and Scheraga(5), in terms of the pertubation of water molecules by alkyl chain length, introducing negative volume change.

When $\partial\overline{V}_2^E/\partial X_2$ passes through a minimum for a given solute at a given concentration, and at low temperature becomes negative(80), this behaviour can be attributed to the decrement effect per mole of solute to the total volume of the system, as the concentration of solute increases. It is apparent that the solute-solute effects play an important role even in very dilute solution. However it has been shown that the slope of the curve $\overline{V}_2(X_2)$ depends on the ratio of polar to nonpolar groups in the solute molecule(213).

This observation indicates that the negative slope of curve $\overline{V}_2(X_2)$ decreases in magnitude as the polar group increases. However in the case of a very polar solute, the slope of the curve is near to zero. In the light of this work one can say that as the nonpolar nature of the solute decreases, its ability to influence water structure at long range decreases(213).

However in the case of alcohols in water $\partial\overline{V}_2^E/\partial X_2$ becomes more negative moving to lower X_2, as the nonpolar group of alcohol increases in size. This behaviour is maximum in t-butyl group which is of a size that is more favourable to clathrate-type structure stabilization(116).

The structuring effects of mixed solutes can be examined considering another aspect of their volumetric behaviour, which is their ability to shift the temperature of maximum density of water. The observed positive temperature of maximum density of water in lower alcohols, ethers, and ketones supports the idea that positive $\Delta\theta$ corresponds to a stabilization of the intermolecular structure of water(215). This view is strengthened by the observation for D_2O $\theta = 11°$, which is thought due to stronger hydrogen bonds in this liquid.

Since the formation of micelles involves the transfer of monomers from aqueous region to nonpolar environment[217] and the observed micelle formation (Chapter IV) was accompanied by a volume change at C_o, the partial molal volume properties of non-ionic surfactants were also investigated by the same approach. The partial molal volumes of non-ionic surfactants below the C_o, and above the C_o were calculated at 25°C as described in Chapter IV (Figs. VII.10, VII.11). As can be seen in Table VII.I.2, the $\overline{V}_1$ is higher than the $\overline{V}_o$ in all non-ionic surfactants studied. (620.05 ml/mole and 624 ml/mole for $C_{16}E_{10}$ below the C_o and above the C_o respectively). However the $\overline{V}_1$ increases as the EO chain length increases (964.5 ml/mole and 2316.6 ml/mole for $C_{16}E_{18}$ and $C_{16}E_{60}$ respectively).

The observed $\overline{\Delta V_1}$ during the micelle formation (i.e. the volume change due to transfer of monomers to nonpolar environment) shows a decrement as the EO chain length increases (Table VII.I.2 3.95 ml/mole and 2.0 ml/mole for $C_{16}E_{10}$ and $C_{16}E_{30}$ respectively). Corkill et al.[217] have also observed similar behaviour for n-alkylsulphinyl alkanols at 25°C. $\Delta\overline{V}_1$ decreases also as the hydrophilic group increases (3.2 ml/mole and 2.7 ml/mole for n-alkylsulphinyl alkanols ($C_6SO(CH_2)_nOH$) containing two and four $-CH_2-$ group in hydrophilic group).

The increment in $\overline{V}_1$ is 29 ml/mole ($\overline{V1D^o}$) per ethylene oxide chain length ($-CH_2-CH_2-O-$). It is apparent that at C_o each addition to the EO chain length gives an increase in $\overline{V}_1$ as the environment of the monomers is changed. However Corkill et al.[217] showed that the increment in partial molal volume above the C_o is higher than below the C_o (17.3 ml/mole and 15.8 ml/mole respectively for $C_2SO(CH_2)_2OH$.

It is apparent that as the hydrophilic group increases while the hydrophobic surface area is constant, the volume change is positive

(1.5 ml/mole). On the other hand, in this work the observation indicates that the change in $\overline{V}_0$ per (-CH_2-CH_2-O-) group is lower than the change in $\overline{V}_1$ (Table VII.I.2, 28.7 ml/mole). The increment in partial molal volume per (-CH_2-CH_2-O-) is shown in Fig.VII.12. The difference between $\overline{V}1D°$ and $\overline{V}1C°$ is 0.3 ml/mole. This increment can be interpreted by the affinity of ethylene oxide chain length for water molecules, which causes the hydration. The number of water molecules bound per monomer of micelles, and the number of water molecules in core of micelles might be the reason for the increase in partial molal volume during micellization(267).

However the observed volume change at C_0 (0.3 ml/mole) is less compared with the value (1.5 ml/mole) given by Corkill et al.(217) This can be interpreted taking into account the particle shape of the micelles, and monomers since polyoxyethylene monohexadecyl ethers have a long hydrophobic group. It has been observed that the prolate type micelle is less hydrated than the spheroid micelle. Although the alkyl chain length appears more expanded in the core of the micelle than in the normal liquid form(217), the less increment in partial molal volume change can be attributed to the hydrophilic groups, which are closely packed near the hydrocarbon region (micellar core) squeezing water molecules out from the outer shell of the micelles(176).

Corkill et al.(217) have also shown that the methylene groups near to the hydrophilic centre show a contraction in the micellar state, as opposed to the expansion of the alkyl chain during the change of environment.

This is due to retention of the aqueous environment of methylene groups, which are in the proximity with the hydrophilic group on micellization. The increment in $\overline{V}_1$ during micellization as function of the alkyl chain length has been also discussed in terms of the retention of hydrocarbon-water contact by the methylene groups near to the hydrophilic centre in the micellar state.

A nuclear magnetic resonance study in several surface-active agents(268), and the measurements of the thermodynamic parameters of micellization have indicated a similar pattern. These facts confirm that the hydration of hydrophilic group, and the methylene groups near to the hydrophilic centre plays a unique role in the increment in $\overline{V}_1$ during the micellization.

VII.Ic - Light scattering from Polyoxyethylene Monohexadecyl ethers in aqueous solution and containing organic additives.

VII.Ic1- Light scattering from polymer single solvent systems.

A polymer solution at infinite dilution is considered to contain (n) solute molecules in a unit volume dV, and when it is illuminated by an unpolarized beam, each particle behaves as a dipole with a moment $p = \alpha' E$, under the influence of the electric field E of the incident beam. The intensity of scattered light at an angle of observation $\Phi = 90°$ by the (n) independent particles can be given by an equation(269)

$$R_{90} = \frac{8\pi^4 n}{\lambda_0^4} (a')^2 \qquad \text{VII-1}$$

For the dilute polymer solutions a' can be evaluated from the dielectric constant or the refractive index $\overline{n}$ $(D = \overline{n}^2)$

$$a' = \frac{\overline{n}^2 - \overline{n}_0^2}{4\pi n} \qquad \text{VII-2}$$

If the medium is infinitely dilute, $\overline{n}$ is a linear function of the solute concentration

$$\overline{n} - \overline{n}_0 = c \frac{d\overline{n}}{dc} \qquad \text{VII-3}$$

where $\frac{d\overline{n}}{dc}$ is the refractive index increment of the solution as a function of the polymer concentration. The number of particles per unit volume can be defined taking into account the molecular weight, and Avagadro number by $c = nM/N_0$ then the relation between a', and the optical properties of the system can be derived by combining equation (VII-2) and (VII-3),

$$a' = \frac{\bar{n}_0 M}{2\pi N_0} \frac{d\bar{n}}{dc} \qquad \text{VII-4}$$

and substituting equation (VII-4) into equation (VII-1) the Rayleigh ratio becomes

$$R_{90} = \frac{2\pi^2 \bar{n}_0^2}{\lambda_0^4 N_0} \left(\frac{d\bar{n}}{dc} \right)^2 cM \qquad \text{VII-5}$$

At an angle of observation Φ, when the Rayleigh ratio R_Φ for unpolarized light is corrected for light depolarization, then equation (VII-5) becomes

$$R_\Phi = K \left(\frac{d\bar{n}}{dc} \right)^2 cM \ (1+\mathrm{Cos}^2\Phi) \qquad \text{VII-6}$$

where

$$K = \frac{2\pi^2 \bar{n}_0^2}{\lambda_0^4 N_0}$$

However at a given angle Φ, the Rayleigh ratio for unpolarized light can be written taking into account the particle function

$$\frac{R_\Phi}{1+\mathrm{Cos}^2\Phi} - K \left(\frac{d\bar{n}}{dc} \right)^2 \left[\frac{1}{1/M p\Phi + 2BC} \right] \qquad \text{VII-7}$$

The equations described above are applicable to the dilute aqueous polymer solutions composed of a polymer dissolved in only one solvent. It is quite evident that when a third component is added to the system it brings local modifications of the refractive index, which affects the scattering by particles. In this case, when the turbidity or (scattering) is extrapolated to zero concentration of polymer, the results show deviation due to the second solvent or precipitant, which cannot be explained by the change in the refractive index increment of solution alone. Ewart et al.(257) have studied the light scattering of polymer systems containing additives. According to their observations of the polystyrene in benzene-methanol system, the value of Hc/τ extrapolated to zero concentration of polymer differs considerably from $(Hc/\tau)_{c=0}$ determined in pure benzene, and varied with the concentration of methanol.

Ewart et al.$^{(257)}$ have defined light scattering in terms of turbidity in the polymer systems containing various concentrations of organic additive by

$$\tau = \frac{8\pi^3}{3\lambda_o^4 N_o} \left(\frac{\epsilon - \epsilon_1}{c} \right)^2 M \qquad \text{VII-8}$$

ϵ and ϵ_1 are the dielectric constant of solution, and the dielectric constant of the medium surrounding the spheres. In the case of a mixed polymer solution $\epsilon_1$is no longer equal to the dielectric constant ϵ of the mixed solvent outside the polymer, due to the selective adsorption of the good solvent on the polymer, causes a modification of the binary solvent composition in the vicinity of the particle.

When the solvent composition is defined by the volume fraction ϕ of a good solvent, then the turbidity can be expressed by the relation

$$\left(\frac{\tau}{c} \right)_{c=0} = \frac{32\pi^3 \bar{n}^2}{3\lambda_o^4 N_o} M \left(\frac{d\bar{n}}{dc} + \alpha_a \frac{d\bar{n}}{d\phi} \right)^2 \qquad \text{VII-9}$$

where $d\bar{n}/d\phi$ represents the variation of the refractive index of the solution with the composition of the solvent. The parameter (α_a) represents the variation of composition of the binary solvent surrounding the particle

$$\alpha_a = - \frac{d\phi}{dc} \qquad \text{VII-10}$$

In other words, α_a is directly related to the preferential adsorption phenomena, which characterizes the variation of solvent composition $\frac{d\phi}{dc}$ in the vicinity of the polymer.

VII .Ic2 - Micellar properties of polyoxyethylene monohexadecyl ethers from Light Scattering Data

VII .Ic.2A Aqueous solution of Polyoxyethylene Surfactants

The scattering intensities of non-ionic surfactants in aqueous solution, and containing various concentration of aromatic alcohols, urea and urethane was observed by using the Photo Gonio Diffusometer(253), Model 4200 as described in Chapter VI. The observed scattering intensity is almost constant at low concentration, and does not change significantly as the concentration increases (Fig.VII.13). But at a critical concentration (5.2×10^{-5}mol.dm^{-3} and 3.4×10^{-5} mol.dm^{-3} for $C_{16}E_{10}$ and $C_{16}E_{18}$ respectively. Table VII.I.3), the slope of $S\phi_{90}$ - concentration curve markedly changed. The observation also confirms the results obtained from the hydrodynamic measurements that the C_0 decreases as the EO chain length increases (Fig.VII.8). The molecular weight of the micelles was calculated using the Debye relation (equation VI-31), and employing procedure as described in Chapter VI (Fig.VII.14). The degree of association of monomers decreases as the hydrophilic group increases. As can be seen in Table VII.I.6, the micellar molecular weight decreases as the hydrophilic chain increases in length.

The decrease in micellar size is due to the decreased affinity of the monomer for water (4.26×10^5 and 2.22×10^5 for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively). The micellar dimensions were calculated as described in this chapter. The observation indicates that the axial ratio of the prolate type of micelle increases as the dimensions of the micelle increases (3.7 and 7 for the axial ratio of A_a/A_b for $C_{16}E_{10}$ and $C_{16}E_{30}$ respectively Table VII.I.6), since the major axis A_a increases as the EO chain length increases. The particle scattering function PΦ was calculated using the Debye relation given by the equation(263)

$$\frac{Hc}{\tau} = \frac{1}{MP\Phi} + 2BC \qquad \text{VII-11}$$

when the dimensions of the scattering particles are big enough to compare with the wave length of the light in the medium (λ). The particle scattering function plays an important role for the scattering intensity of the particles. If the particle is larger than about λ/20, corresponding roughly to 200-270 Å, the light scattered from different points of the particle reaches the observer with different phases, consequently the scattering intensity is diminished due to interference. In view of this fact the calculated particle scattering function of the micelles ($P^{-1}\Phi$) is 1.456 and 0.337 for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively Table VII.I.6. The scattering function decreases sharply as the EO chain length increases, but the decrement in $P^{-1}\Phi$ after 30 EO chain length is not considerable (Fig.VII.22), which is due to the decrease in MW and minor axis (A_b) of the prolate micelle.

VII.I.c2B- Solution containing Aromatic alcohols.

When an aromatic alcohol is added to aqueous surfactant solution, the scattering intensity increases (0.3056×10^{-5} cm^{-1} for 1×10^{-4} mol.dm^{-3} $C_{16}E_{18}$ containing 0.01M phenol Table VIII.I.4.) As can be seen in Fig.VII.15 the scattering intensity increases gradually as the concentration increases. At a certain concentration the slope of the curve considerably increases.

On the addition of 0.01 phenol, the increase in C_0 is not significant compared with the aqueous surfactant solution (3.45×10^{-5} mol.dm^{-3} and 3.4×10^{-5} mol.dm^{-3} for $C_{16}E_{18}$ containing 0.01M phenol and in aqueous solution respectively.) However the addition of 0.02M phenol increased C_0 (3.6×10^{-5} mol.dm^{-3}). The further increase in concentration of second solvent shifts the C_0 to a lower value, as observed in cationic systems.

On the other hand the effect of phenol on C_0 was observed using surface tension measurement. The observation also indicates that C_0 increases up to 0.03M, then it decreases with increasing concentration (4.2×10^{-5} mol.dm^{-3}; 4.4×10^{-5} mol.dm^{-3} and 4.5×10^{-5} mol.dm^{-3} for $C_{16}E_{18}$ containing 0.01M, 0.02M and 0.03M phenol respectively Table VII.I.4, Fig.VII.17.)

As discussed in a previous section the addition of a third component alters the refractive index of the solvent which affects the scattering phenomena. The distribution of molecules in any unit volume element will vary with the time because of thermal motion of the molecules, and consequently each particular region will differ from its neighbours.

Thus the local density of the solvent around the molecule is constantly changing due to the possible selective adsorption of a third component such as phenol or benzyl alcohol on polyoxyethylene mono ether molecules. In such a state the refractive index of the solvent around the molecule is different from the refractive index of the bulk solution due to the density and concentration fluctuations in the solvent near to particles.

Ewart et al.(257) have showed that in the polystrene-benzene 80% - methanol 20% ststem, the solvent 1 (benzene) is preferentially adsorbed on polystrene ($\alpha_a = 0.405$) as the second virial coefficient and limiting viscosity number decreases. Tuzar-Kratochvil and Cowie-Bywater(270) have observed similar behavior of component 1 (solvent) for the adsorption on the polymer.

However Read(271) has used polystyrene-benzene (1) - cyclohexane (2) in order to investigate the preferential adsorption in the system. He has concluded that benzene is adsorbed on polystyrene rather than cyclohexane.

In view of these facts, it is reasonable to assume that the possible adsorption of aromatic alcohol on the non-ionic surfactant used is a major factor for an increase in $S\phi_{90}$ and turbidity of solution.

However when 0.01M benzyl alcohol is added to the aqueous solution of $C_{16}E_{18}$, the turbidity increases (5.1546×10^{-5} cm^{-1} for 1×10^{-4} mol.dm^{-3} of $C_{16}E_{18}$ Table VII.I.4.B, Fig.VII.15). The increment in turbidity also has a contribution from the density and concentration fluctuations in the refractive index of the solvent surrounding the particle.

It is apparent that the optical efficiency of aromatic alcohols give contributions which raise the Rayleigh ratio consequently turbidity.

The change in fluctuations in density and concentration is directed by the static dielectric constant of the aromatic alcohols. The decrement of static dielectric constant of the solution increases with increasing $-CH_2-$ group in substituted alcohol chain length.

The optical efficiency of fluctuations of the alcohols as second solvent on micelles contribute to an increase in Rayleigh ratio. Similar behaviour is observed when benzyl alcohol or phenylethanol is added to the system. But the effect of phenylethanol on C_0 differs appreciably from that of the lower alcohols. The addition of 0.01M phenylethanol has increased C_0 considerably (3.58×10^{-5} mol.dm^{-3}) compared with the observed values for lower alcohols. (Table VII.14D, Fig.VII.15A).

This behaviour can be attributed to the structure promoting effect of the alcohol due to an increase in the nonpolar nature of the alcohol molecule. On the addition of aromatic alcohol to the system hydrophobic interactions occur between the OH groups of alcohol and water molecules, interactions also occur between the hydrcarbon group and benzene ring through π electron clouds, and polyoxyethylene group and water molecules. These play an important role in micelle formation.

The hydrophobic interactions between these groups increase the complex type association of polyoxyethylene surfactants with aromatic alcohols in the system as discussed in Chapter V in the case of cationic surfactants. The alcohols behave as structure makers at low concentration. This effect is quite clearly observed through the increase in C_0 as the hydrophobic character is increased. The increase in C_0 at low concentration of added alcohol can be discussed in the light of structure promoting behaviour of alcohols and their complex type association through hydrophobic interactions with non-ionic surfactants.

However the solubility of aromatic alcohols also plays an important role in the increase of C_0. But, when the concentration of additive is increased, the observed behaviour is changed to the opposite direction. The decrement in C_0 probably arises from the increase in structure breaking effect of the alcohol molecules, and the decrement in solubility of alcohols in bulk solution and in the interior of the micelles. Due to these effects C_0 is shifted to the lower value with decreasing free energy of micellization as observed on addition of propanol and butanol to the cationic system (Chapter II).

The light scattering observation indicates that the micellar molecular weight increases as the concentration of additive increases (4.88×10^5 and 6.45×10^5 for $C_{16}E_{18}$ containing 0.01M and 0.02M phenol respectively. Table VII.I.7. Fig.VII.19). In the case of phenol the increase in MW is nonlinear while the increase is linear on the addition of benzyl alcohol and phenylethanol.

The observed dissymmetry is higher (1.05 and 1.06 for $C_{16}E_{18}$ containing 0.01M and 0.02M phenol respectively) compared with the standard (1.01). The dissymmetry of the micelles increases as the $-CH_2-$ group increases (1.07 and 1.08 for $C_{16}E_{18}$ containing 0.01 benzyl alcohol and phenylethanol respectively, Tables VII.I.4.B, VII.I.4.D). The observation indicates that the size of micelle is changed with addition of alcohol. In order to observe the size and shape of the mixed micelle, the oblate shape was taken into account as well as the prolate type micelle as an alternative model shape.

Disregarding the helical nature of the polyoxyethylene chain, the carbon-carbon bonds (1.5 Å) with the bond angles of 110° and carbon bonds (1.5 Å) were used to calculate the extended length of monomeric unit which is 3.5 Å, , then the extended length of $C_{16}E_{18}$ was determined taking into account the length of the hydrophobic and hydrophilic groups of surfactant (approximately 90°A),

The observation of the dimensions of oblate type micelles was carried out in view of Harkins's[(168)] approach, in order to estimate the semi-axis revolution and equatorial radius (A_a). Since the diameter of the rod type micelle is twice the length of monomer molecule and it can be approximated to the oblate shape, the monomer extended length (90 Å) was used as the length of semi-axis (A_b) revolution for computing (A_a).

Considering this approach one can calculate the equatorial radius taking into account the density of the micelle. The obtained value is 52 Å for semi-axis (A_a). As a result of this fact, the following argument can be put forward to examine the possibility of an oblate shape for the mixed micelles. It was observed that in aqueous solution the micelle of $C_{16}E_{18}$ is prolate type. The observed dimensions are 153 Å and 30.5 Å for (A_a) and (A_b) respectively.

When the aromatic alcohol is added to the system micellar size changes. If the micellar shape changes from prolate type to oblate shape with addition of alcohol, the molecular dimensions of the micelles must expand in two dimensions. It is assumed that it occurs in this system. Although the extended length of the monomer was used, the semi-axis (A_b) is 90°A while A_a is 52 Å. As far as the dimensions of the micelle are concerned, the observed lengths do not fit well into the oblate shape if the structure of the interior of the micelle is considered.

If the length of semi-axis (90°A) is compared with the semi-axis (A_b = 30.5) of $C_{16}E_{18}$ in aqueous solution it is considerably high, on the other hand the equatorial radius (A_a = 52 Å) is lower compared with the radius $C_{16}E_{18}$ (153 Å). However it is unlikely that the addition of any aromatic alcohol studied to the system will cause such a change in the dimensions of micelles (i.e. as in the case of added 0.01M phenol).

As observed with aqueous non-ionic surfactants, the semi-axis A_b does not change significantly as the molecular weight of micelle increases. The difference between the semi-axes of $C_{16}E_{10}$ and $C_{16}E_{30}$ is 10 Å which is due to the increase in the degree of coiling of hydrophilic group. The degree of coiling increases as the EO increases. In view of Peterlin's(291) theory the calculated effective length of $C_{16}E_{18}$ is 74 Å. If the effective length is compared with the extended length one can calculate that the degree of coiling in solution is 1.176.

It is quite evident that the expansion of micellar size is more favourable along the long axis (equatorial) rather than in both lengths.

However if the effective length of $C_{16}E_{18}$ is considered, then the semi-axis of equatorial diameter can be calculated in the same way as discussed above. The obtained (A_a) is 56 Å. Considering both extended and effective length of the monomer molecule, the calculated lengths of the oblate shape show that the hydrocarbon groups and benzene rings are located near the centre of the micelle causing a two dimensional change in shape from prolate to oblate.

If the axial ratio of the micelle is considered, (1.73 and 1.36 for the considered extended and effective lengths respectively) one can say that the shape of micelle is close to the spherical shape. If the shape of micelle is assumed to be oblate, the volume of micelle will be equal to that assumed for the other shape (prolate). If this is the case the monomer will be closely packed in the interior of micelle, which is not favourable if the interior of micelle is considered.

If one considers all the hydrocarbon chains and benzene rings are attracted towards the micellar centre effecting a two dimensional change in shape, with an increase in spherical volume, this can be in error due to the fact that the hydrocarbon chains cannot approach each other more closely than about 5 Å(158). On the other hand, the free volume of monomer will oppose the close packing in the interior of the micelle.

However in this work this type of change is found unrealistic in view of the geometry of the particles, the free volume of the hydrocarbon groups and the limitation on the closest distance between hydrocarbon groups. On the other hand to bring the hydrocarbon groups near the centre changing the dimensions will require extra energy.

In view of the above discussions, the prolate shape was considered as a possible shape of micelle. The density of hexadecane at 25°C was used to calculate the length (A_a) of micelle on the assumption that the semi-axis of revolution does not change (as discussed in this section for non-ionic surfactants in aqueous solution).

The calculated (A_a) of prolate micelles of $C_{16}E_{18}$ containing additives increases with increasing MW (260 Å and 1108 Å for $C_{16}E_{18}$ containing 0.01M and 0.08M phenol respectively. Table VII.I.7). Due to increase in micellar size the particle scattering function of micelles was taken into account to observe its effect on scattering intensity of particles on micellar state.

As can be seen in Table VII.I.7 and Fig.VII.22 $P^{-1}\Phi$ does not change significantly up to 0.05M phenol (0.623 and 1.074 for $C_{16}E_{18}$ containing 0.01M and 0.05M phenol respectively) as the concentration increases, then it gradually increases.

However in the case of benzyl alcohol and phenylethanol after 0.04M and 0.03M respectively the increase in $P^{-1}\Phi$ is greater in magnitude compared with $C_{16}E_{18}$ containing phenol. Since large dissymmetries were not observed and the concentration of monomer is low in the systems studied, it was assumed that depolarizations of the solutions and Cabannes factor were negligible.

VII.Ic3 - Non-ionic surfactant solution containing urea and urethane.

The addition of urea and urethane to the aqueous solution of non-ionic surfactant increase C_o (6.8×10^{-5} mol.dm^{-3} and 6.25×10^{-5} mol.dm^{-3} respectively. Table VII.I.5, Fig.VII.18). It is quite evident that on the addition of urea or urethane the structural order of water molecules is changed. The effect of urea on water structure was discussed taking into account the structure maker or structure breaker approaches which were postulated by different investigators.

As can be seen in Table VII.I.5 the Rayleigh ratio and turbidity increase when 1M urea and 0.7M urethane is added to the system ($\tau = 6.8008 \times 10^{-5}$ cm^{-1} and $\tau = 6.262 \times 10^{-5}$ cm^{-1} for 1×10^{-4} mol.dm^{-3} $C_{16}E_{18}$ containing 1M urea and 0.7M urethane respectively).

The increase in turbidity is due to possible adsorption of additive on the surfactant molecule and the change in density and concentration fluctuations in the refractive index of the solvent near to the surfactant molecule. On the other hand the interaction of non-ionic surfactant with urea or urethane through hydrophobic interactions also plays a unique role in the increase in scattering intensity and consequently in turbidity.

In this work, it is believed that urea and urethane participate in mixed cluster formation with water molecules to accommodate the surfactant molecule more efficiently than the water clusters around the non-polar and polar groups.

It is apparent that the participation of both additives in cluster formation arises from their ability to increase the structure of water molecules through hydrophobic interactions. On the addition of urea and urethane, the light scattering observation indicates that the MW increased (2.5×10^6 and 3.33×10^6 respectively, Table VII.I.7, Fig.VII.20).

Although the added concentration of urethane is less than urea, the increase in MW is higher compared with the $C_{16}E_{18}$ containing 1M urea. This is due to the chemical structure of urethane which has an extra oxygen atom instead of nitrogen atom. It is known that the hydrophilic group readily associates with water molecules in terms of hydrophobic interactions which might be the reason for the higher MW.

On the other hand, the observed dissymetry is higher in both cases (1.05) than unity (1.01). The micellar dimensions were calculated as described in this section. The obtained lengths of micelles are 1332 Å and 1774 Å for 1M urea and 0.7M urethane respectively. Since the length of micelles is higher than $\lambda/20$, the particle scattering function is higher compared with $C_{16}E_{18}$ containing aromatic alcohols (12.77 and 6.723 for urea and urethane respectively).

Due to this fact the scattering intensity is affected considerably because of the increase in size of the micelles.

VII.Id - Critical Micelle concentrations of polyoxyethylene Monohexadecyl Ethers in aqueous solution.

VII.Id1- Purification of surfactants.

The commercial impure non-ionic surfactant (100g) was mixed in a separating funnel with 100 ml 5N aqueous solution of sodiumchloride(272). This mixture was then equilibrated with an equal volume of ethylacetate (BDH A.R)(134). The mixture was shaken for 15 minutes to separate the free polyethylene glycol from the non-ionic surfactant molecules. After the separation of layers the organic layer which contains the non-ionic surfactant, and the aqueous layer containing polyoxyethylene glycol were collected. This procedure was repeated several times, then the organic solution was reextracted several times by 100 ml 5N sodium chloride to remove the remaining free polyethylene glycol. Following this process the organic solution which contains non-ionic surfactant was evaporated on a water bath and dried under vacuum.

The obtained surfactant was dissolved in acetone, filtered to remove remaining sodium chloride, evaporated and dried under vacuum. The purity of the non-ionic surfactants was checked using surface tension measurements (Du Nouy tensiometer, as described in Chapter II) and the above procedure was repeated until a fine intersection was obtained on the surface tension concentration curve.

VII.Id2 - The characterization of Non-ionic Surfactants by NMR spectrometer.

The non-ionic surfactants were characterised using a A-60A NMR spectrometer(273). The instrument was set according to the instrument manual. The non-ionic surfactant was characterized in terms of the hydrophilic group assuming that the hydrophobic group was known and did not vary. The specifications of the instrument used were the operating frequency (60 MHz), the magnetic field strength (14.092 G), the average R-F field at sample (0.005 to 0.5 mG), the sample tube size (4.28 mm ID), the resolution (0.3Hz).

The sensitivity of the instrument was sufficient to detect a

0.007 molar concentration of hydrogen nuclei occurring in a single line of less than 0.6 Hz natural line width. The integral reproducibility was 1% electronic accuracy in integrating circuit. Spectral reproducibility after 24 hours warming up was, in an environment with temperature variation $\leq \pm 1°C$ (1 Hz/hr), the average deviation for five successive 250-sec scans (0.4 Hz) in the temperature change $\leq \pm 3°$ (2 Hz/hr) and corresponding average deviation for successive 250-sec scans (0.6 Hz). Resolution 0.3 Hz was less than 0.6 Hz in 16 hours run. The calibrated instrument was used according to the instrument manual.

The spectra of a 10% CCl_4 solution of non-ionics surfactants were recorded at 25°C using (TMS) as internal reference at a sweep width 500 cps using 250 sec-sweep time at spectrum amp.(10), integral amp.(80), filter band width (14) and R-F field (0.03).

The manufacturer's$^{(274)}$ code A_{10},A_{18},A_{30} and A_{60} show the approximate value of ethylene oxide unit. Carbon tetrachloride was chosen as a solvent because it contains no interfering protons, and the selected internal reference gives a single sharp line of a relatively high value of the magnetic field due to its hydrogen atoms being equivalent. The obtained spectrum was interpreted in the following manner: the theoretical formula;

$$\underset{a}{CH_3} - \underset{b}{(CH_2)_{14}} - CH_2 - O - \underset{d}{(C_2H_4)_n} - \underset{c}{OH} \qquad \text{VII.i-1}$$

Since each step in the integral corresponds to the number of protons giving a signal in the spectrum, in order to determine the number of protons which correspond to the various functional groups in the NMR spectrum, the functional groups in the molecule were denoted by the letters (a,b,c,d). The absence of signals other than those identified as due to internal reference, or alkyl polyoxyethylene surfactant is also the indication of the relative purity of the compound (purified non-ionic surfactant spectrum).

The number of protons present in the polyoxyethylene group of non-ionics (impure and purified) was calculated using the ratios of the integrals of the $(-CH_2-CH_2-O-)_n$ peak to the integral of the hydrophobic group (known) of the molecule. As can be seen in Table VII.I.8, the calculated total of protons of the $(-CH_2-CH_2-O-)$ group is 125 and 294 for $A_{10}$and,A_{60} respectively. However the calculated number of moles of $(-CH_2-CH_2-O-)$ group from NMR spectrum for non-ionic surfactants are shown in Table VII.I.8.

VII.Id3 - Volumetric method.

In order to check the ethylene oxide content of the surfactant molecule, which was determined by NMR measurement, a titration procedure was employed(275) in the following manner;

A. 1.00g surfactant was weighed into a 100 ml beaker, then 25 ml of DMF (BDH), and 5 ml benzene (BDH A.R) were added to the flask. The sample was dissolved by swirling, and the temperature (25°C) was kept constant using an ice bath. Double distilled water was added from a 50 ml burette in about 2 ml increments, and the flask was swirled after each addition. Since the temperature rises due to the heat of solution hydration, the flask was kept in the ice bath after each addition of water to maintain the solution at 25°C.

When the solution on the addition of water becomes turbid before swirling, the quantity of titrating water was reduced to 0.5 ml. At a certain concentration the end point of titration was reached, and the volume of water was recorded. If the ethylene oxide chain length of the surfactant has the number of $(-CH_2-CH_2-O-)$ unit which was calculated from NMR spectrum, then a linear relationship must be observed between the volume of titrant, and number of ethylene oxide group. It is reasonable to consider that A_{10} and A_{18} can be easily purified with the liquid distribution method employed since the excess of $(-CH_2-CH_2-O)$ group impurity is 2.3 mole, and 4.3 mole for A_{10} and A_{18}. When the corresponding titrants of the surfactants are plotted versus ethylene oxide groups, as can be seen in Fig.VII.9 a straight line plot is obtained. If A_{60} has 60 ethylene oxide group, then the titrant volume must be on the volume of titrant-EO group plot. As is seen in Fig.VII.9 there is a linear relationship between the volume of titrant and corresponding EO chain length. This procedure confirms also that the non-ionic surfactants contain the exact number of moles of ($-CH_2-CH_2-O$) group, which was determined by NMR spectrometer.

VII.Id4 - Cloud Point Relation in aqueous surfactant solution.

When the temperature of a non-ionic solution is increased to a certain temperature, it becomes turbid in a narrow temperature range. This temperature is called the cloud point.Hydration is rather sensitive to temperature, and when the temperature is increased at a certain temperature dehydration occurs, as a result of this the polyoxyethylene surfactant becomes less soluble at increased temperatures.

The mechanism of clouding phenomenon is not yet clear. It has been discussed(158) that the micellar weight of a non-ionic surfactant becomes larger with increasing temperature,then at a certain temperature the micelles grow so large that the solution becomes turbid. This temperature might be called the cloud point. When the micelles become larger, phase separation occurs as the result of the formation of giant aggregates which finally separate from the water phase. The cloud points of the non-ionic suefactants was determined as follows.

A 1.00g surfactant was dissolved in 100 ml of water, and cooled in an ice bath until the solution was clear, then the temperature was raised slowly until the solution became turbid. As can be seen in Table VII.I.1.B the cloud point of the surfactant increases with increasing ethylene oxide chain length (50°C and 79,60°C for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively). It has been discussed(158) that the non-ionic surfactant having a longer hydrophilic group indicates a higher cloud point, and capacity to hydrate. However the obtained cloud points indicate that the observed low value is due to the less hydration of the surfactant molecule, which causes a decrement in solubility. The g.water/g.surfactant quantity decreases ith (Table VII.I.6) increasing EO group. As a result of this fact, the dehydration is reached at low temperature, which is due to the less amount of hydrated water molecules bound to the surfactant molecule.

VII.Id5 - The critical micelle concentration of non-ionic surfactants in aqueous solution.

The micelle formation in aqueous solution for non-ionic surfactants resembles that of the ionic surfactants. The C_o in general is lower than for ionic surfactant. It has been discussed that the C_o increases as the hydrophilic group increases when the concentration data are expressed in units of weight per volume. However, Carless et al.(276) and Schick et al.(172) have found that the C_o decreases with increasing chain length when the concentration is increased on a molal basis. On the other hand Elworthy-Macfarlane(264,277) and Corkill et al.(278) have discussed the increment in C_o with increasing ethylene oxide chain length.

In this work, the C_o of non-ionic surfactants in aqueous solution was measured, using viscosity, surface tension and light scattering methods. The observations indicate that the C_o decreases as the ethylene oxide chain length increases (5.6×10^{-5} mol.dm^{-3}, 6.0×10^{-5} mol.dm^{-3} and 5.2×10^{-5} mol.dm^{-3} for $C_{16}E_{10}$ corresponding the viscosity, surface tension and light scattering measurements respectively. Tables VII.I.1 and VII.I.3). As is seen in Fig.VII-4 the surface tension of non-ionic surfactant (i.e. $C_{16}E_{10}$) decreases gradually as the concentration decreases. After reaching certain concentration, it increases with increasing concentration. The observed minimum on the surface tension - concentration curve is due to the impurities. After the purification of surfactants as is seen in Fig.VII.5, the minimum on the surface tension-curve does not occur.

On the other hand the C_o of non-ionic surfactant ($C_{16}E_{10}$) was observed in terms of the aqueous solution, which was prepared on weight-volume basis. As seen in Fig.VII.7, the C_o of $C_{16}E_{10}$ is which is equivalent to 5.85×10^{-5} mol.dm^{-3} .The adsorption of surfactant on to glassware was also examined. It was observed that the adsorption only occurs in small quantities (Fig.VII.6), which does not affect the C_0 value. Corkill et al.(279) have discussed that homogenous non-ionics in the solution are not stable. The minimum on the surface tension-concentration curve, and the gradual decrementin the surface tension above the C_0 as the concentration increases have been discussed by Elworthy et al.(280) in terms of impurity of the non-ionics in aqueous solution. The observation of C_0 of the surfactants, and the question of decrement in C_0 as the hydrophilic group increases, can be expanded to obtain a reasonable explanation about the phenomenon.

Staudinger(281) has postulated two types of structure for polyoxyethylene chains which are zigzag and meander configurations. He has concluded that at a low degree of polymerization, the chain exhibits a zigzag structure, and the chain contraction increases with increasing ethylene oxide chain length. The oxygen atoms of the main polyoxyethylene groups attract each other, the magnitude of this attraction increases considerably beyond a degree of polymerization of 9, consequently it causes chain contraction.

Rösch(282) has given an alternate explanation. According to his view the contraction is due to electrostatic attraction. Marchal-Benoit(283) have shown that the individual dipole moments (dipole moment of dimethylether of oxyethylene unit) diminish with increasing length of the polymeric chain. Rösch's(282) explanation of the contraction of polyoxyethylene is supported by the fact that it is based on intramolecular, coaxial electrostatic attraction. Ionic surfactants also exhibit zigzag chain configurations. The only difference between the paraffin chain and oxyethylene groups is the presence of a hetero atom. This hetero atom, ether oxygen causes dipole attractions towards the neighbouring methylene groups, and consequently exerts electrostatic forces to the polyoxyethylene chain.

When the oxyethylene chain length is increased, the large electrical moment in the coaxial direction contracts the chain length (ethylene oxide) and transforms it to the meander configuration. The meander configuration is less extended than the zigzag configuration. It has been shown(284) by X-Ray investigation that the zigzag configuration is transformed to the meander configuration at a degree of polymerization of 20 to 40. In bulk state, with surface active derivatives of polyoxyethylene, the change in modification is obtained at a degree of EO unit of 15 to 20.

The width of polyoxyethylene chain in the meander configuration is 4.5 Å, while it is 2.5 Å in the zigzag configuration. The related cross-sectional area is 28 $Å^2$ for the meander chain, and 19 $Å^2$ for the zigzag chain(284).

The helical configuration of the polyoxyethylene polymers has also been put forward to analyse the orientation of the hydrophilic group. Miyazawa et al.(285) have measured the polarized infrared spectra of crystalline films of polyoxyethylene glycol in the region 3500-400 cm^{-1}. The structural configuration of polyethylene glycol has been discussed in terms of the equations for the helical parameters. The model which has been introduced has seven repeating units, and two helical turns per fibre period of 19.25 Å. On the other hand, the internal rotation angles for the helical model have been calculated to be 60° for c-c bond and 191.5° for the c-o bond.

Tadokoro et al.(286) have studied the molecular structure of polyoxyethylene oxide $(-CH_2-CH_2-O-)_n$ by X-Ray diffraction and infrared adsorption spectroscopic methods. They have concluded that the polyoxyethylene molecule has a helical structure in the crystalline state, which contains seven chemical units and two turns in the fibre period of 19.3 Å. The calculated trans, trans and gauche conformations are related to the corresponding internal rotation angles of the molecule, which are 64.58 and 188.5° for $(O-CH_2-CH_2-O)$ and $(-CH_2-CH_2-O-CH_2-)$ respectively.

Yoshihara et al.(287) have also examined the molecular structure of polyoxyethylene at various temperature using infrared spectroscopic method. They have shown that the results they obtained are in good agreement with the results given in literature for the helical structure of polyoxethylene oxide.

VII.Id6 - Configurations of the polyoxyethylated molecules in solution.

Due to Brownian motion particles, or polymer segments, are driven forward by collisions with the moving molecules in the medium(288). Because of this fact, fluctuations in tension take place within the polymer molecule. This behaviour causes cooperative motion of segments in the molecule, and consequently the polymer chain is pulled in, and out of a number of configurations. Debye-Bueche(289) have calculated root- mean-square end to end distances, taking into account Einstein's theory. A permeable sphere of radius Rs has been considered as a polymer molecule, which occupies average space. They have further assumed that this sphere contains a uniformly distributed system of resisting points. The permeability of the sphere has been accounted for by a hydrodynamic factor $\phi(\sigma)$. The dimensions of the polymer molecule has been given by the relation,

$$(\overline{R}s^2)^{\frac{1}{2}} = (36/10)^{\frac{1}{2}} \left[300M[\eta]\Big/4\pi \, No \;\; \phi(\sigma)\right]^{3/2} \qquad \text{VII-12}$$

Kirkwood-Riseman(290) have examined the random-coil model. This theory allows the hydrodynamic interaction of the molecular segments in terms of inhibited flow through the chain. The polymer dimension has been defined by an equation

$$[\eta] = (6\pi^3)^{\frac{1}{2}} \, No \; be^3 \; Z^{\frac{1}{2}} \; x \; Fo(X)/3600M_o$$
$$\left(\overline{Rs^2}\right)^{\frac{1}{2}} = be \; Z^{\frac{1}{2}} \qquad \text{VII-13}$$

Peterlin(291) has introduced a model of a polymer molecule with the random distributed chain elements. Due to the molecular elements, it has been considered that the solvent flow through the molecule is hindered.

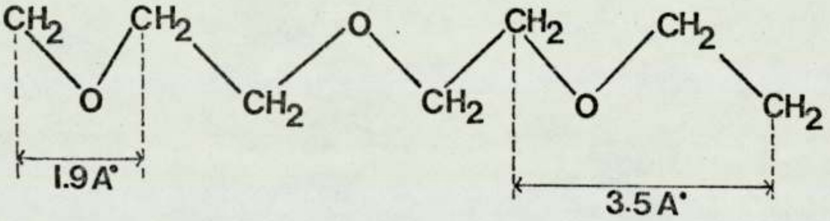
The transition from a free draining coil to an impermeable coil has been discussed by means of the intrinsic viscosity.

The dimension of the polymer has been given by

$$(\bar{R}s^2)^{\frac{1}{2}} = 1.52 \times 10^{-8} \, (\cot\alpha)^{\frac{1}{3}} \, M^{\frac{1}{2}} . \qquad \text{VII-14}$$

VII.Id7 - The proposed configurations of Polyoxyethylene surfactants in aqueous solution.

As has been discussed in this section, the polyoxyethylene non-ionic surfactant of a lower degree of polymerization exists in zigzag configuration. If the length of ethylene oxide group is considered to be in this configuration, then one can calculate (approximately) that the zigzag chain length of EO unit of $C_{16}E_{10}$ is 35 Å. The configuration can be illustrated as follows[284]

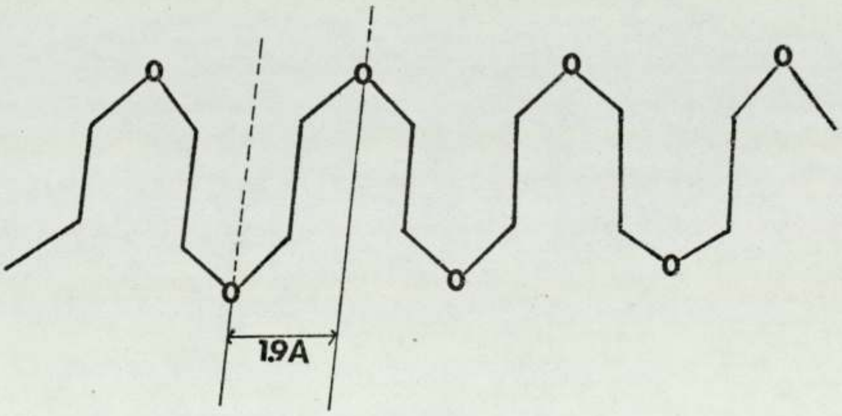


VII.i.2

The hydration of polyoxyethylated surfactants shows that the extent of hydration decreases as the hydrophilic chain is increased. On the other hand the cloud points of the non-ionics are lower. This is also an indication of the hydration and solubility of the surfactant molecules. With the observed non-ionics, the water of hydration does not require the higher temperature for it to be released, in other words, the temperature shows that the hydrated number of water molecules are less. However one can say, considering the above view that the lower non-ionic surfactant should have a higher cloud point, since it has a higher quantity of hydrated water molecules. The lower cloud point of $C_{16}E_{10}$ (50 °C) comparing $C_{16}E_{60}$ (79.60 °C) is due to the difference in the configurational orientations in aqueous solution.

When the degree of polymerization is increased, due to the increase in length, the large electrical moment in coaxial direction causes contraction of the hydrophilic chain length and transforms it to the meander configuration(284). It is believed that the meander configuration of oxyethylene groups exist in higher oxyethylated non-ionics in aqueous solution. If the length of the unit oxyethylene group is of the order of 1.9 Å, then the length of the hydrophilic group is approximately 118 Å. Taking into account the zigzag configuration of the hydrophobic group (22 Å), one can calculate the length of the $C_{16}E_{60}$ which is 140 Å.

The extended length of a monomeric unit is obtained in terms of the length of the oxyethylene unit (3.5 Å) which is 232 Å. When the polyoxyethylene length is increased at constant hydrocarbon area it exerts inter penetration, and greater density in packing of oxyethylene group occurs due to the random coiling, which is entropically favourable. If the hydration of oxyethylene groups, increases with the increasing of hydrophilic chain length, then the polyoxyethylene chain must be in extended configuration. However, the observed results of hydration of non-ionics are contrary to the above considerations. The meander configuration of higher polyoxyethylene surfactants can be illustrated(284) as follows



VII.i.3

If it is assumed that the surfactant molecules in aqueous solution exist in a combination of zigzag (hydrophobic group) and meander configuration, then the difference between the extended length, and configurational length can be used as a parameter to interpret the molecular dimensions of the surfactants. This approach can be extended, taking into account Peterlin's theory(291). Peterlin has examined the polymer molecule in solution, and has concluded that the molecules resemble a loosely coiled chain. On the other hand, due to the chain elements near the centre have greater density, it has been considered that the flow of solvent through coil is impeded towards the centre rather than periphery. Because of this fact the solvent is partly immobilized in the centre part of the coil configuration. This situation, according to his view, is reflected in the dependence of the intrinsic viscosity. When the flow is totally hampered, he has shown that the intrinsic viscosity, and sedimentation coefficient increase in proportion to the square root of the moleculear weight M, or the degree of polymerization considering the mean distance of the two chain elements. The effective length shows the same square root dependency upon the number of links involved. The relation between intrinsic viscosity and statistical coil effective length has been defined by an equation

$$[\eta] = \frac{\pi}{4} \frac{a_o A_o^2}{M_o} \frac{N}{1 + 1.2(6/\pi)^{\frac{1}{2}} (a_o/A_o) N^{\frac{1}{2}}} \qquad \text{VII-15}$$

In this approach It is considered that the effective length, and the resistance of the molecule do not depend on the way in which the flexibility of the molecule is taken into account. In order to know how many statistically independent fundamental units are joined to form segments, the valency angles and the rotational hindrance can be used in terms of the parameter $\xi = \frac{Z}{N}$.

He has introduced(291) an equation, by means of the slope of the plot $M/[\eta]$ against $M^{\frac{1}{2}}$, the uncertain factor 1.2 and Avagadro number by

$$\mathrm{Re} = \left(3^{1/6}\ \ 2^{5/6}/\pi^{\frac{1}{2}}\right)\left(1.2\ \mathrm{Cot}\alpha/\mathrm{No}\right)^{\frac{1}{3}}\ M^{\frac{1}{2}} \qquad \text{VII-16}$$

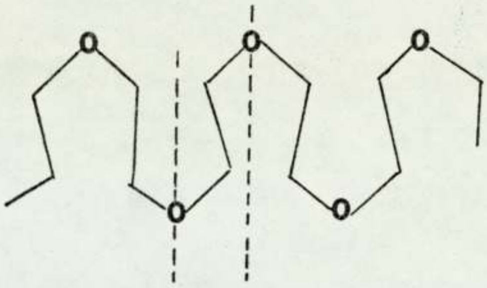
$$\mathrm{Re} = 1.52 \times 10^{-8}\ (\mathrm{Cot}\alpha)^{\frac{1}{3}}\ M^{\frac{1}{2}}$$

Although the factor (1.2) found for higher linear polymer is uncertain, in the light of the above discussion, one can calculate the effective length of the linear polymer in terms of the slope α, and molecular weight of the polymer. As can be seen in Fig.VII.21 there is a linear relationship between $M/[\eta]$ and $M^{\frac{1}{2}}$. The slope of the line has been substituted into equation (VII-16) to obtain the effective length of the molecule. The derived approximate effective length of $C_{16}E_{60}$ is 120 Å. It is 20 Å less than the straight meander length of $C_{16}E_{60}$ (140 Å).

If the extended length (232 Å) of molecule is compared with the straight meander length and effective length, there is considerable decrement in the length of the molecule in the aqueous solution. If the configuration of polyoxyethylene in aqueous solution is assumed in the meander type of configuration and straight (this assumption is contrary with the observed hydration quantity) then the degree of coiling can be calculated which is (1.16). The degree of coiling of MW of 5×10^4 is equal to 20 in water at 35°C (Flory-Fox theory)$^{(292)}$. If the degree of coiling is considered to be proportional with the $M^{\frac{1}{2}}$ then the degree of coiling is obtained to be (1.15), which is very close to the observed value.

Due to the coiling of polyoxyethylene group the surface area of the hydrophilic group will be decreased because of the reducing surface area, then because of being in meander configuration nearly half of the oxygen atoms of oxyethylene group will be inside the coiled configuration. When the degree of polymerization is high (i.e. $C_{16}E_{60}$), the dipole contraction increases, which is equal to 4.2×10^{-4} dyne for $C_{16}E_{60}$.

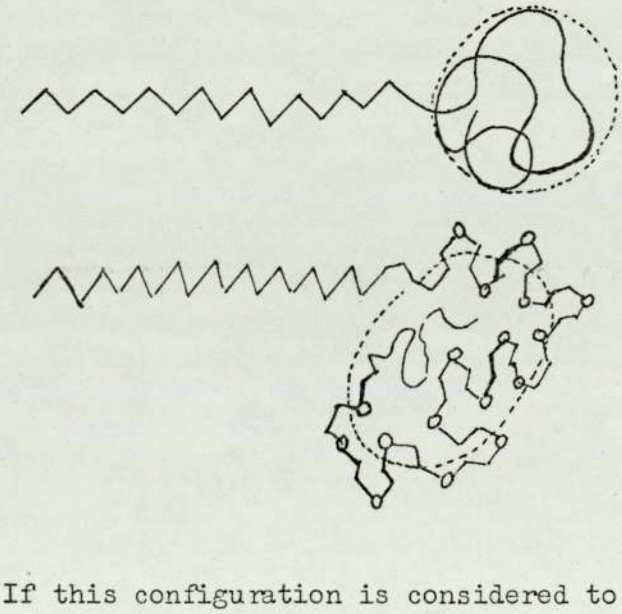
Consequently the length between (-O-CH_2-CH_2-O) group as illustrated



VII.i.4

will be reduced. In view of this treatment it is reasonable to postulate that the contact area of the hydrophilic group with water molecules will be reduced. The existence of some quantity of water in the interior of the configuration will stabilize the coiled meander configuration through hydrophobic interaction with oxygen atom.

Whatever the geometry of the configuration of the head group of surfactant is, the minimum one third or half oxygen atoms of the hydrophilic group will be the inside of the coiled head group. The geometry of the possible configurations can be illustrated such as,



VII.i.5

If this configuration is considered to have constant density, the solvent to penetrate only partially and to be spherical, then the radius of the head group theoretically can be calculated. It is reasonable to consider that the hydrophobic group in zigzag configuration is not much affected due to contraction, because of not having hetero atoms like oxygen, then the diameter of the head group can be obtained, taking into account the effective length (120), the radius of the sphere is 49 Å. The volume occupied by the head group is 493000 $Å^3$, the volume which the meander unit can accommodate is 8216 $Å^3$. Due to this fact the whole molecule of non-ionic surfactant increases its hydrophobicity. The increase in hydrophobic surface area decreases C_o, the extended length of C_{16} is approximately equal to 25 Å which is one fourth of the diameter of the configuration of the spherical head group. It is apparent that the hydrophobic group has increased the surface area four times bigger than the hydrocarbon chain length. Because of the increment in hydrophobicity, C_o shifts to a lower value, and the solubility of the surfactant tends to reverse direction (decrement in solubility)(172,292)

In the case of $C_{16}E_{30}$,$C_{16}E_{18}$ and $C_{16}E_{10}$ the zigzag configuration of oxyethylated hydrophobic group is considered. The obtained effective length is 91 Å; 74 Å, and 60 Å and the degree of coiling is 1.39 and 1.14 for $C_{16}E_{30}$,$C_{16}E_{18}$ and $C_{16}E_{10}$ respectively Table VII.I.6.

In the case of $C_{16}E_{10}$ the effective length is equal to the zigzag length of the molecule. This observation indicates that $C_{16}E_{10}$ does not coil in aqueous solution which is reasonable, since the hydration of oxyethylene group is high. The decrement in C_o for lower polyoxyethylated surfactants can be discussed in the same way as performed in this section.

VII.Ie - Conclusions.

The micellar properties of non-ionic surfactants in aqueous solution and containing additives, were examined in terms of viscosity, surface tension and light scattering techniques, taking into account the adsorption of molecules on glassware. The observations show that the C_o decreases with increasing ethylene oxide chain length, and the observed adsorption does not affect the C_o. The C_o of the non-ionic surfactant ($C_{16}E_{10}$) was also examined on a weight volume basis. The obtained value of C_0 confirmed also the results observed by the mol.g. volume basis.

The decrement in C_0 was discussed in terms of the coiling of the polyoxyethylene group decreasing its hydrophilic surface area. The examination of this phenomenon was carried out on the basis of zigzag, and meander configuration of polyoxyethylene chains in aqueous solution, employing Peterlin's theory. In view of Peterlin's approach the calculated effective lengths are less than straight configurational lengths of the hydrophilic groups. The degree of coiling, and the dipole contraction force decreases with decreasing degree of polymerization.

This observation indicates that the hydrophilic group is coiled, considerably reducing its contact area with water molecules. Due to this fact the hydrophobicity of the molecule is increased because of the considerable number of ether oxygen atoms remaining inside the configuration of the head group. When the hydrophilic character of the molecule is reduced because of the existence of the coiled configuration, the hydrophobic surface area is increased, which decreases the affinity of the molecule for the water molecules, then the solubility of non-ionic decreases, consequently the C_0 shifts to a lower value as the hydrophobicity increases.

The observed quantity of hydration is decreased as the hydrophilic group increases, which is contrary to the concept of the hydration of the polyoxyethylene surfactant given in literature. The amount of water molecules hydrated per g. surfactant decreases with increasing ethylene oxide chain length. The intrinsic viscosity of micelles increases with increasing hydrophilic chain length. Although the relative viscosity of the aqueous solution of non-ionic surfactant is high, the increment in intrinsic viscosity is not significant compared with cetyltrimethyl ammonium bromide. The major contribution for the increment in intrinsic viscosity arises from particle shape and size of the micelles. The other factors involved are hydration, and hydrophobic interactions between nonpolar, polar and water molecules. In view of hydration and light scattering data it was concluded that the micelles were of prolate type.

The cloud points of the non-ionic surfactants increase with increasing ethylene oxide chain length. However the observed cloud points are not high compared with the values given in literature. These results confirm also that the amount of hydrated water molecules by non-ionic surfactants are not significant. The micellar molecular weight decreases as the hydrophilic chain length increases, with decreasing semi-axis of revolution of the micelles.

The partial molal volumes of the non-ionic surfactants increase below the C_0, and above the C_0 as the hydrophilic group increases. It is quite evident that the formation of micelles is accompanied by volume change during the micellization. The increment in partial molal volume of the monomer is the indication of the volume change, when the monomer is transferred from aqueous environment to a nonpolar region. The increment in partial molal volume of the micelles decreases with increasing ethylene oxide chain length.

The micellar properties of non-ionic surfactants have also been observed by adding organic additives to the system. The effect of aromatic alcohols, urea and urethane was examined by means of light scattering technique. The scattering intensity of mixed solutions is high compared with that of aqueous surfactant solution. The increment in turbidity was discussed taking into account the change in density and concentration fluctuations in the refractive index of the solution near to the solute particle, and selective adsorption of the additive on polymer molecule. It is also believed that the effect of alcohols on the optical efficiency of the micelles plays a unique role for the increment in turbidity. The effect of alcohols on C_0 was interpreted in terms of hydrophobic interactions between possible orientations, the degree of solubility of alcohols, and the structure breaker and maker character of the alcohol molecules. The C_0 increases when 0.01M alcohol is added to the system. As the concentration of alcohol increases, the behaviour of alcohol on C_0 tends to reverse direction as was observed for the cationic systems. The micellar molecular weight increases with increasing concentration of alcohol, and $-CH_2-$ group of alcohol chain length, and the observed shape of micelle is prolate type.

The addition of urea and urethane has considerably changed the micellar properties of non-ionic surfactants. The C_0 increased in both cases. But the increment in C_0 is higher on the addition of 1M urea to the system compared with the urethane. The increment in scattered intensity and turbidity was also discussed. The effect of concentration and density fluctuations on the solvent molecules near the solute, and the preferential adsorption of the organic solute on the surfactant molecule. The increment in turbidity is higher when the 0.7M urethane is added to the system. This is due to more polar character of the urethane than the urea.

It is believed that in both cases, the additives take an active part in the mixed cluster formation in terms of the hydrophobic interactions with water molecules. It is further assumed that these additives are structure promoters since the mixed clusters are larger than water clusters, which readily accommodate the large hydrophobic group inside the cavity.

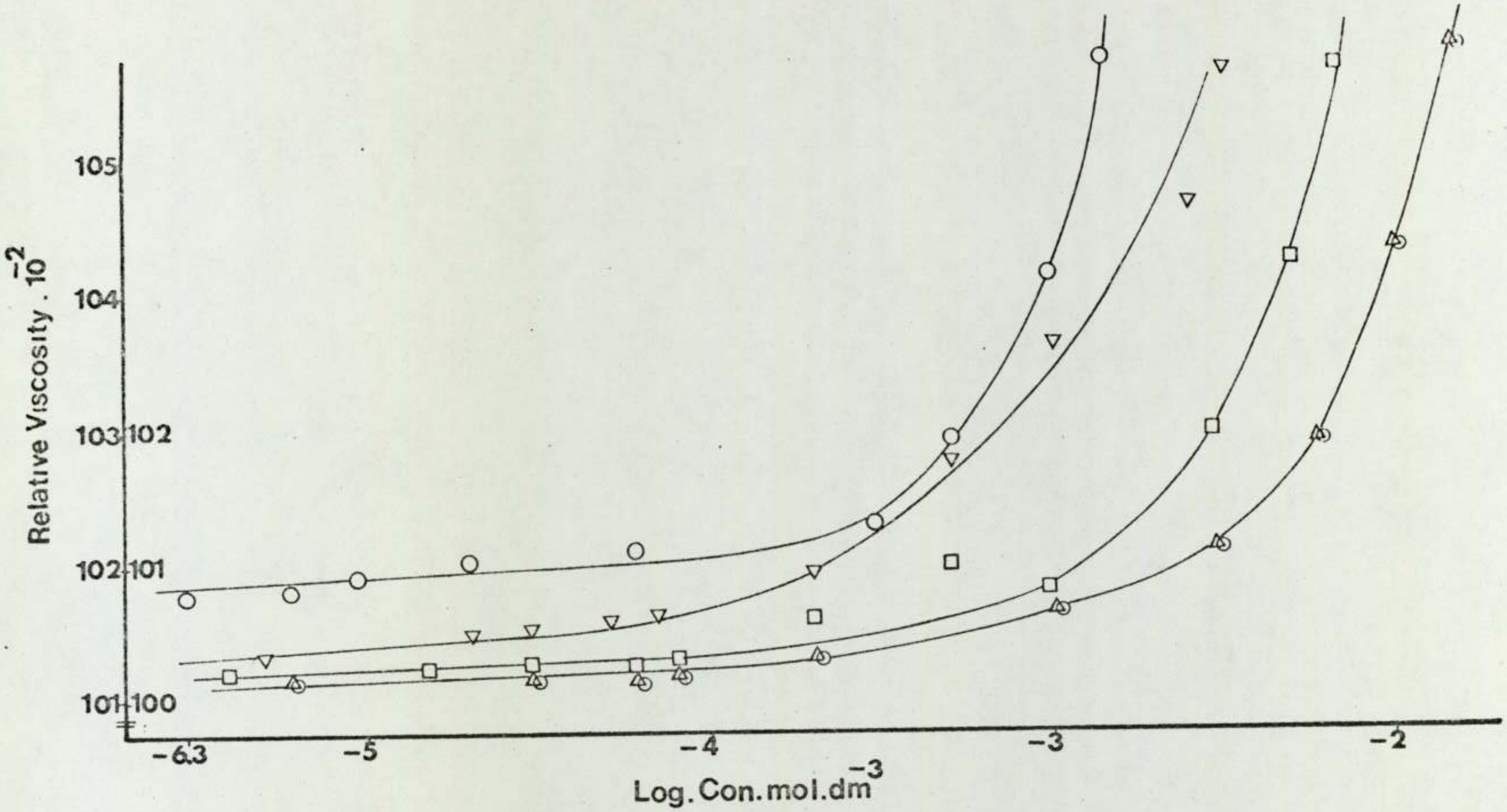


Fig. VII.1 Plots of relative viscosities of the polyoxyethylene mono hexadecyl ethers in water at 25° C; △○ EO_{10} , □ EO_{18} , △ EO_{30} , and ○ EO_{60}

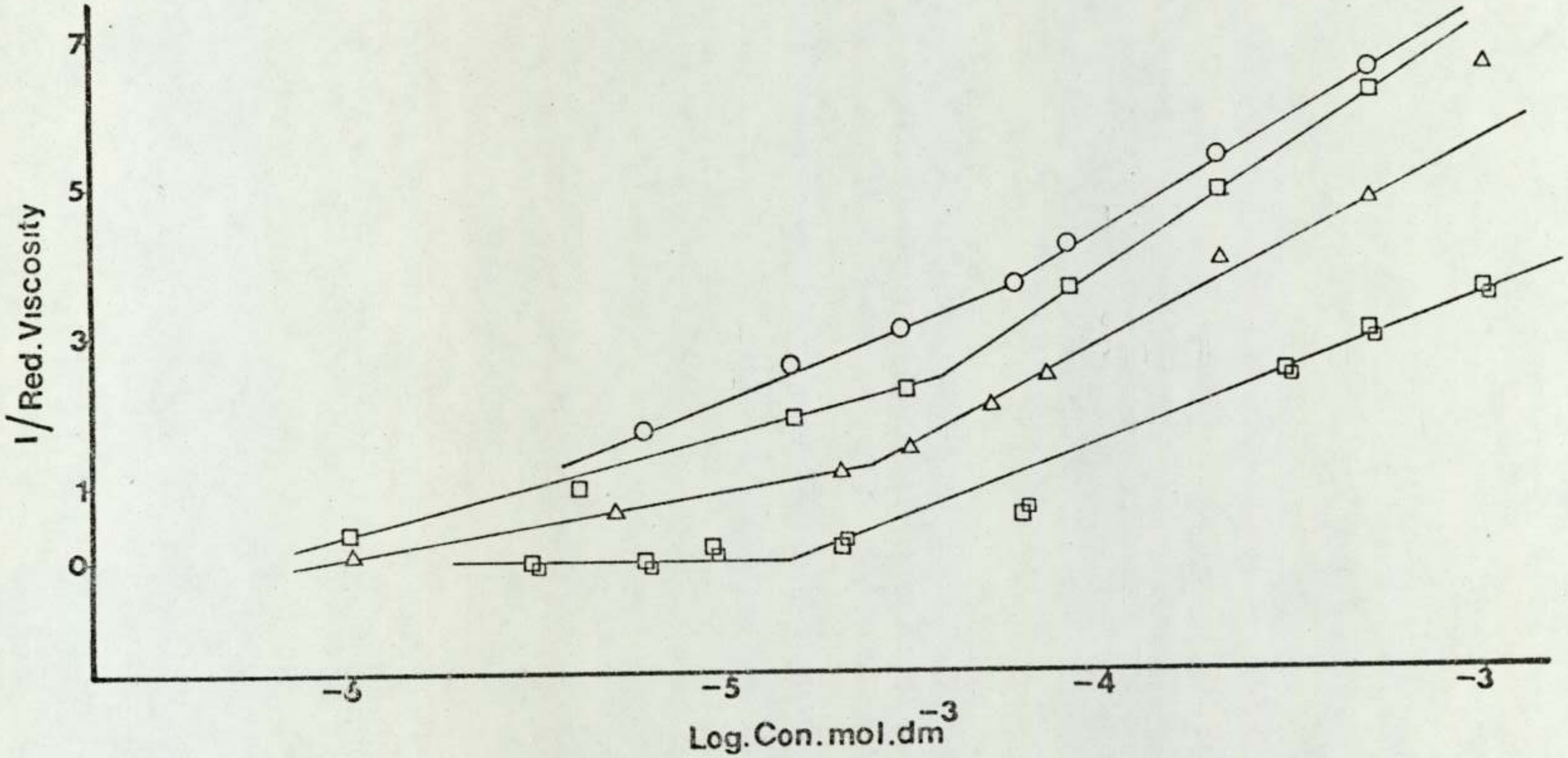


Fig.VII.2 Reciprocal reduced viscosities as a function log. concentration of the polyoxyethylene mono hexadecyl ethers at 25° C; ○ EO_{10}, □ EO_{18}, △ EO_{30}, and ⊞ EO_{60}

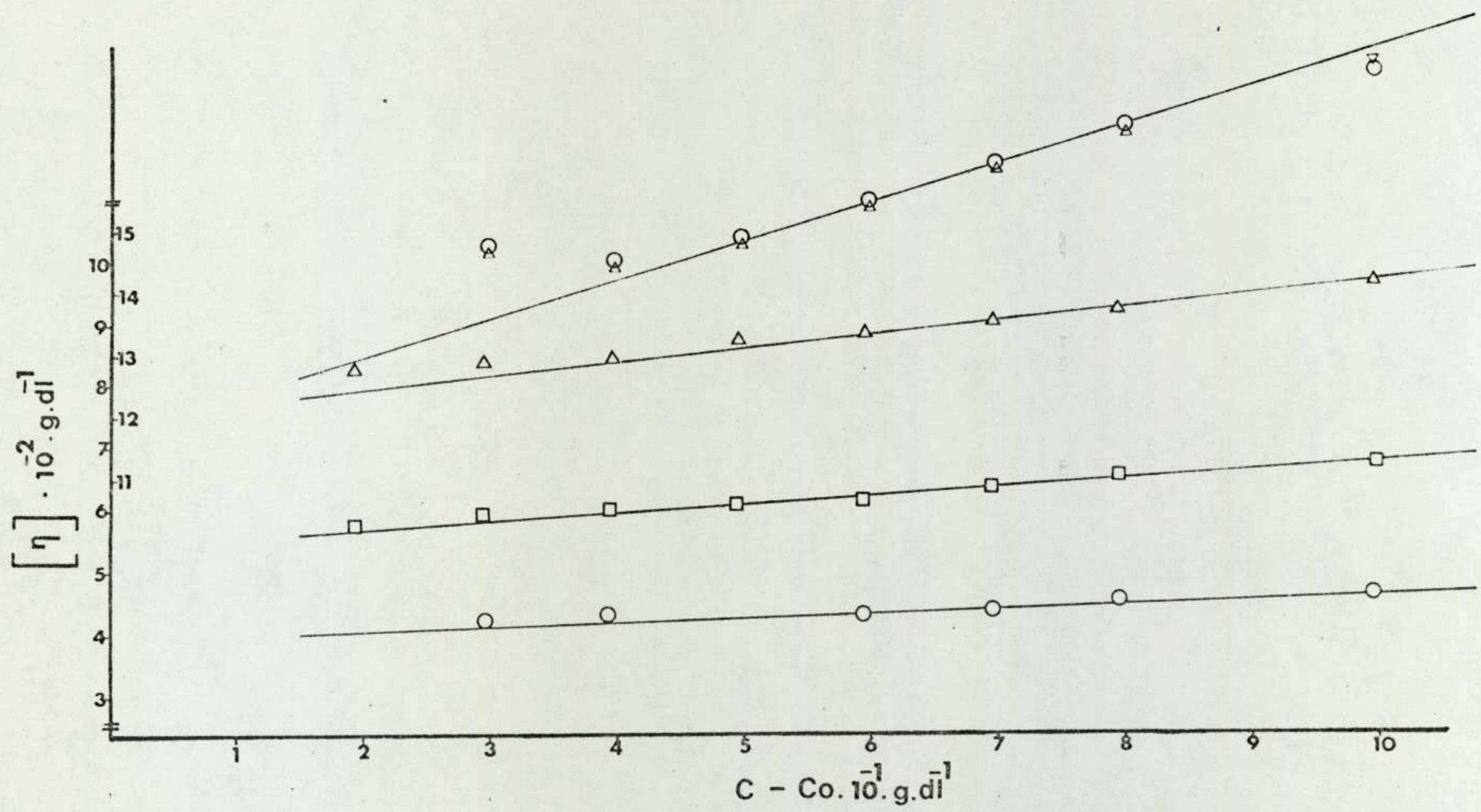


Fig. VII.3 The intrinsic viscosity of micelles versus concentration for the polyoxyethylene mono hexadecyl ethers in water at 25° C; ⊗ EO_{60}, △ EO_{30}, □ EO_{18}, and ○ EO_{10}

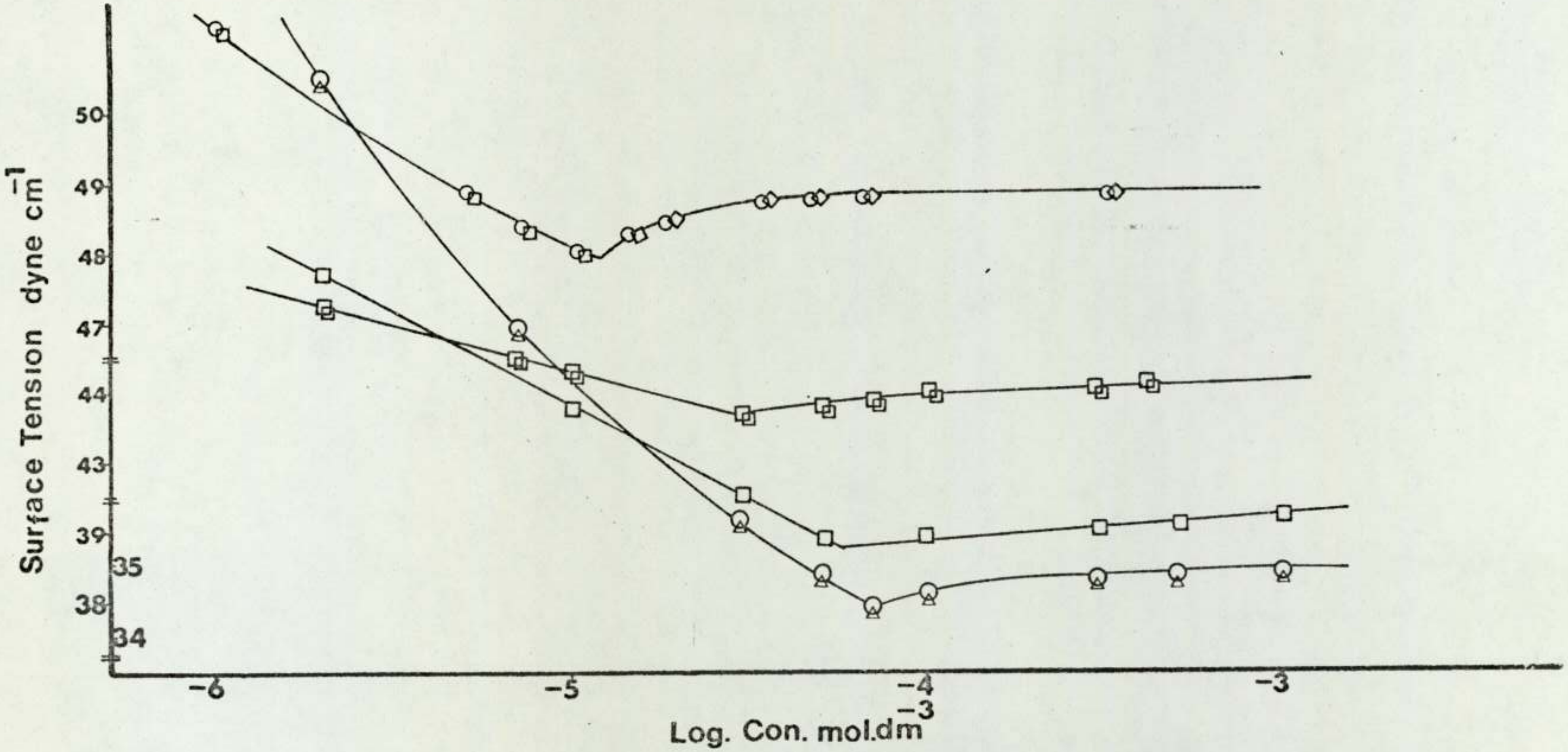


Fig. VII.4 Plots of surface tension versus log. concentration for the impure polyoxyethylene mono hexadecyl ethers in water at 25° C; ⊗ EO_{60}, ⊞ EO_{30}, □ EO_{18}, and ⊗ EO_{10}

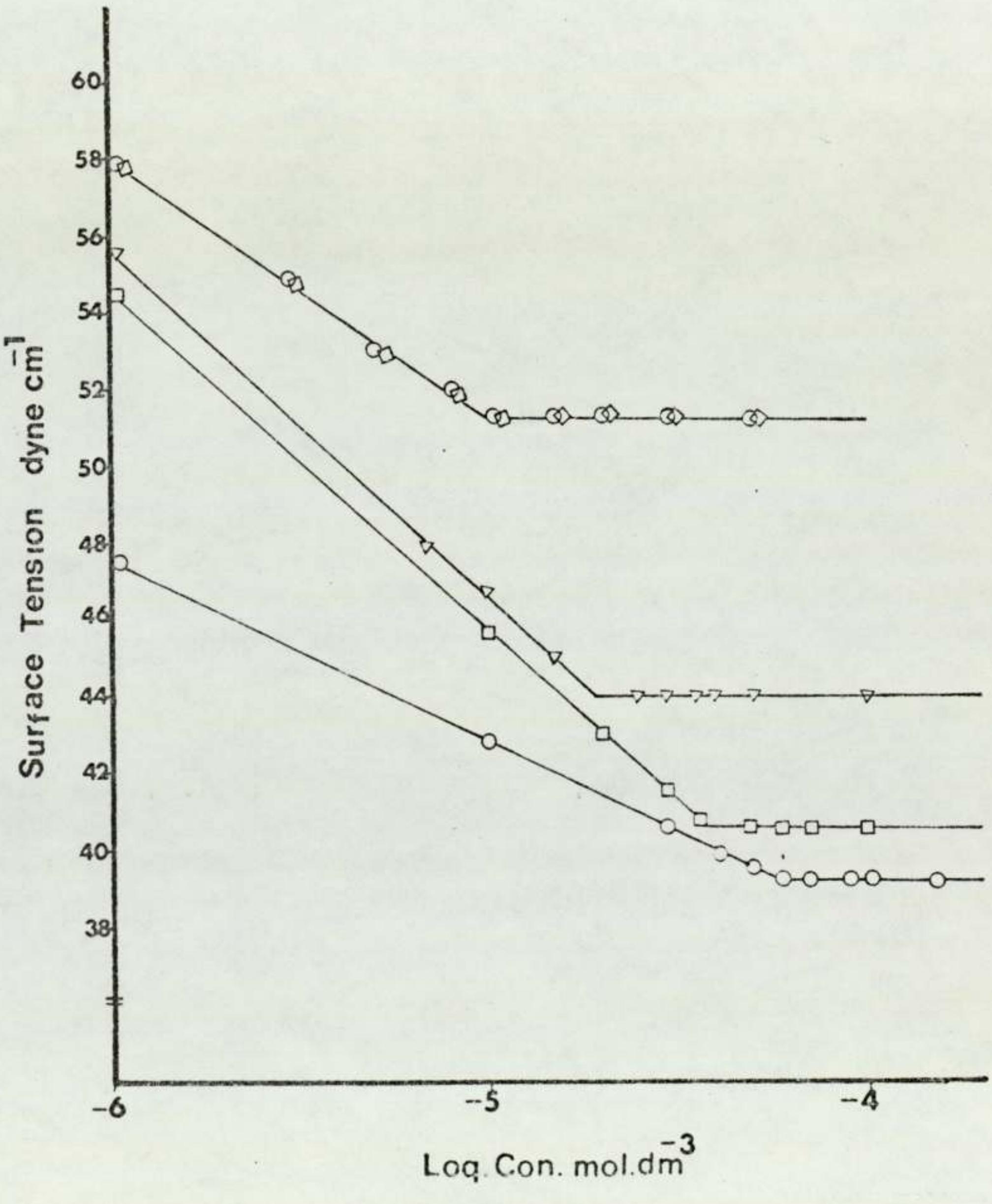


Fig.VII.5 Plots of surface tension versus log. concentration for the purified polyoxyethylene mono hexadecyl ethers in water at 25° C; ⊗◇ EO_{60}, △ EO_{30}, □ EO_{18}, and ○ EO_{10}

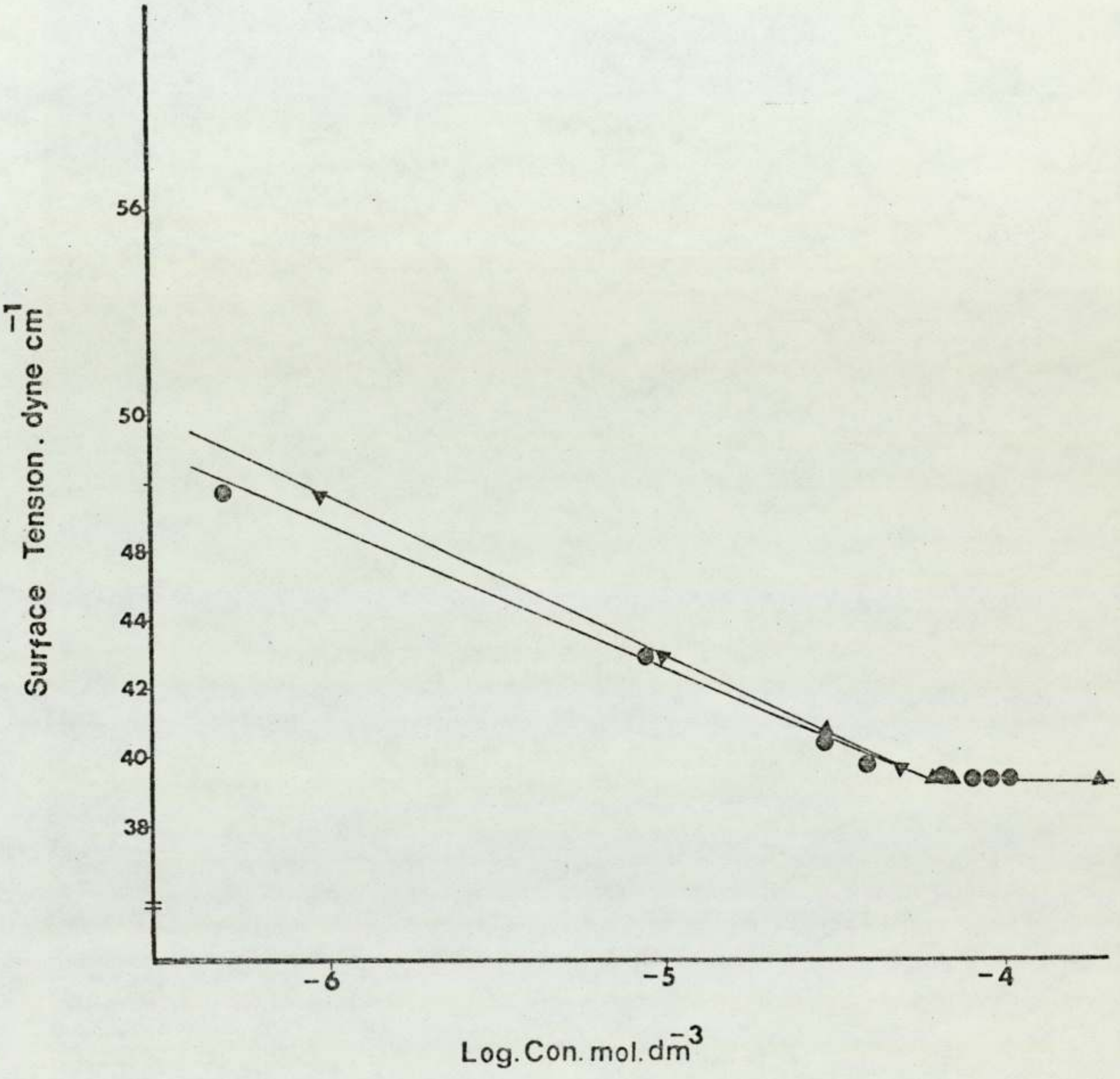


Fig.VII.6 Plots of surface tension versus corrected and incorrect concentration for the absorption of polyoxyethylene mono hexadecyl ether (A 10) on glassWear in water at 25° C; ● Incorrect con. ▲ corrected

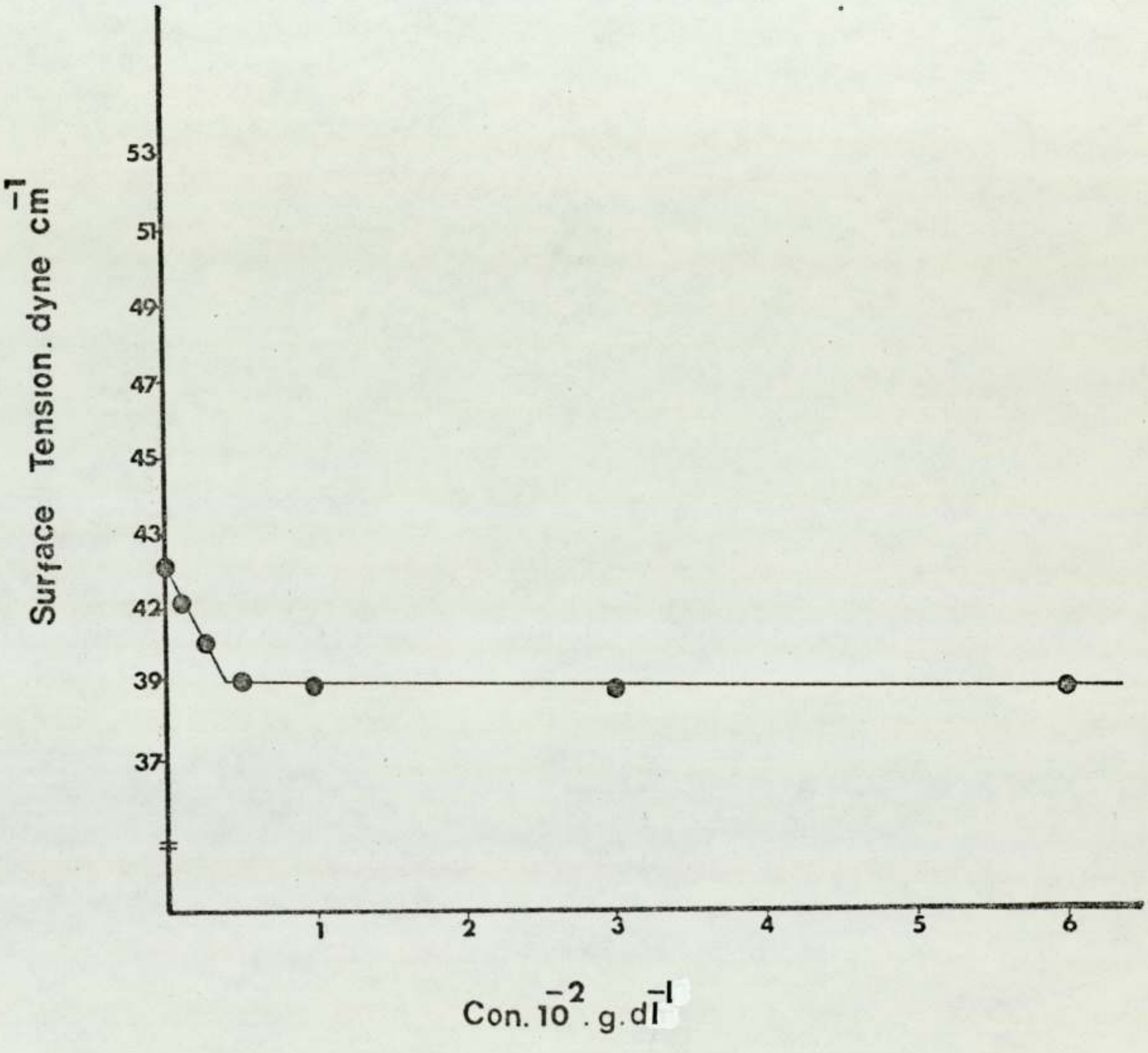


Fig.VII.7 Surface tension versus concentration weight/ Volume curve for the polyoxyethylene mono hexadecyl ether (A_{10}) in water at 25° C;

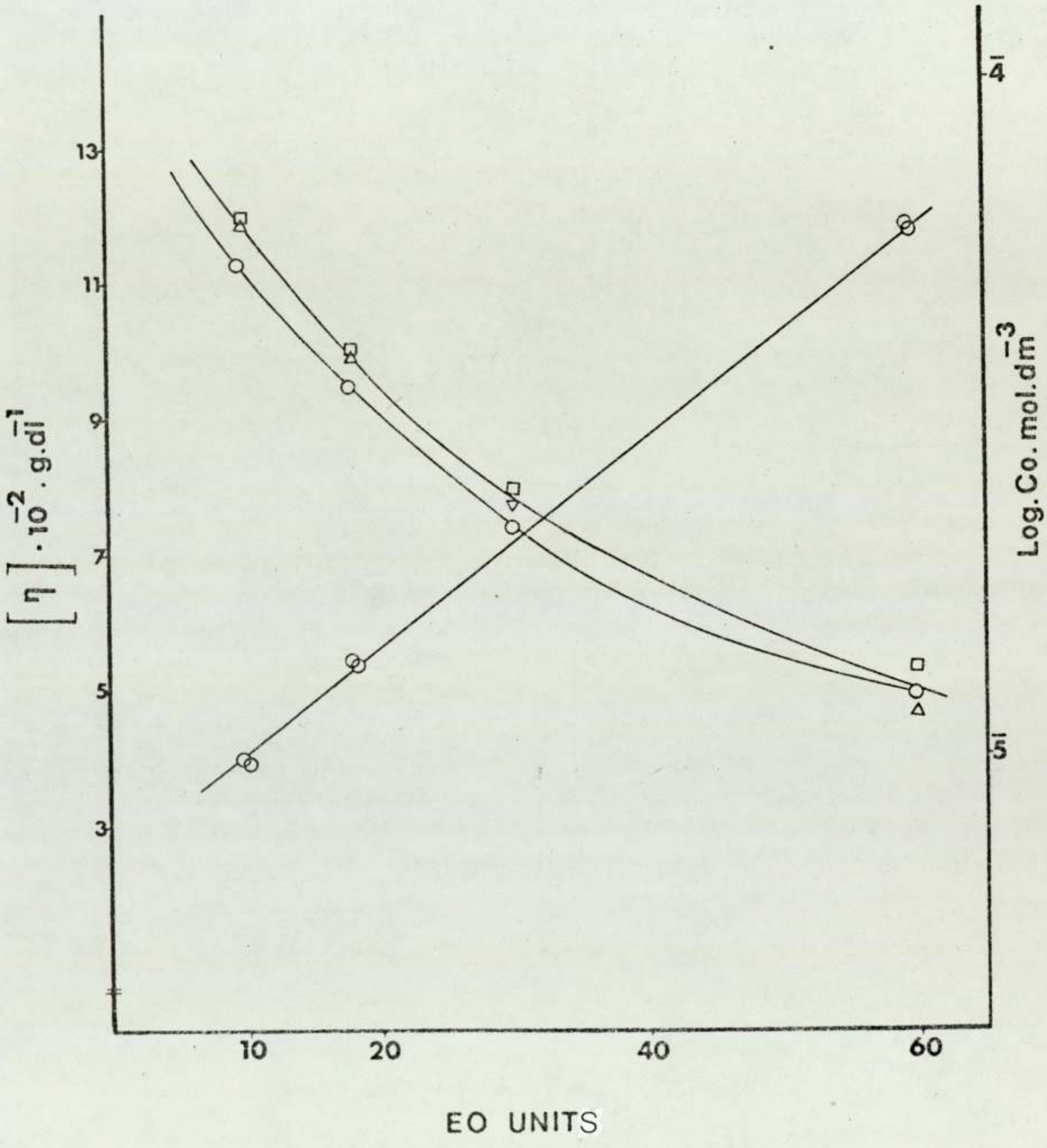


Fig.VII.8 Dependence of Co and intrinsic viscosity of the micelles of polyoxyethylene mono hexadecyl ethers on the ethylene oxide chain length in water at 25° C; □ Viscosity, ○ Surface Tension , △ Light Scattering (C_o) ; ⚭ $[\eta]$

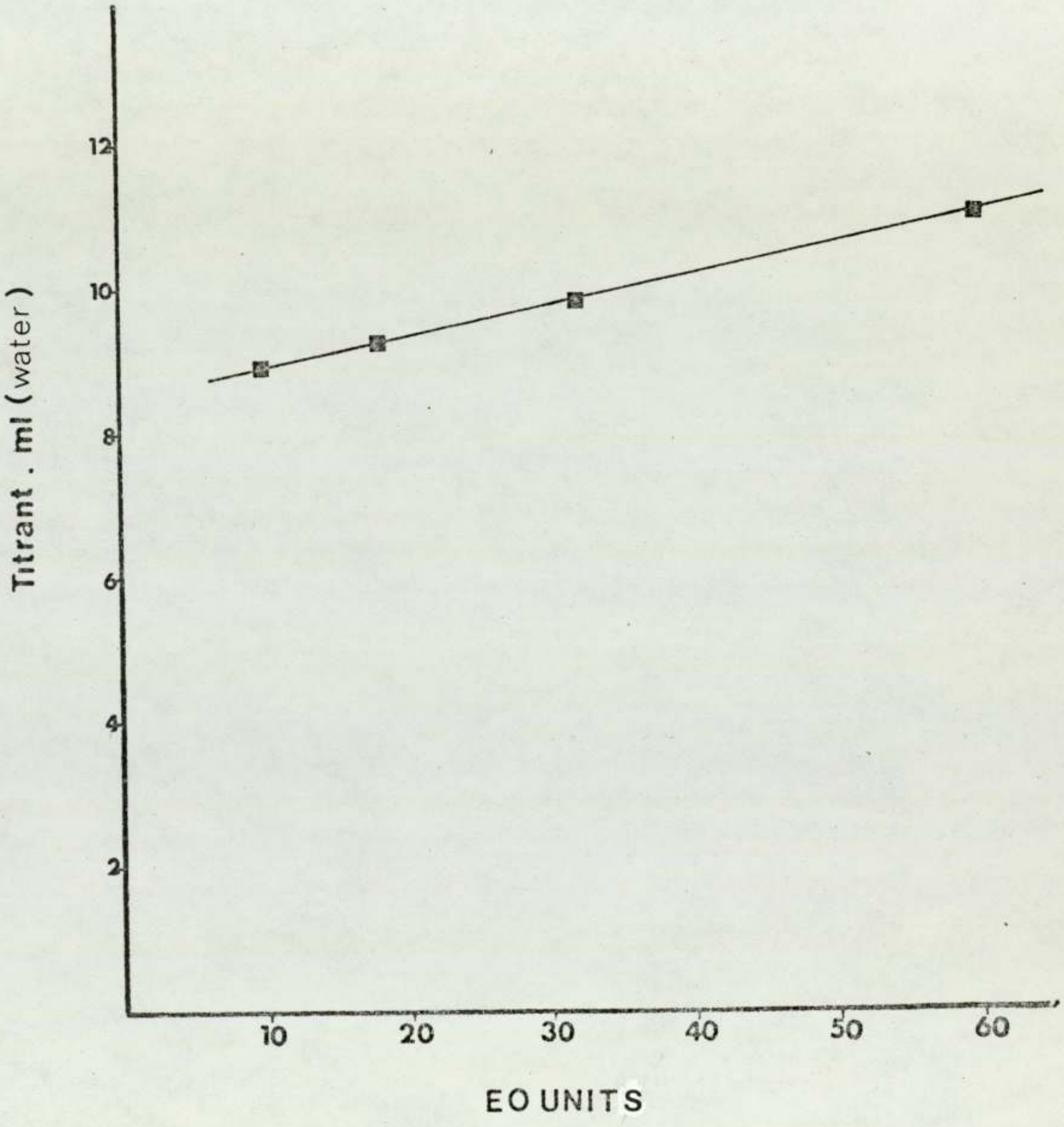


Fig.VII.9 Titrant versus ethylene oxide units curve for the polyoxyethylene mono hexadecyl ethers in 25 ml DMF and 5 ml Benzene at 25° C;

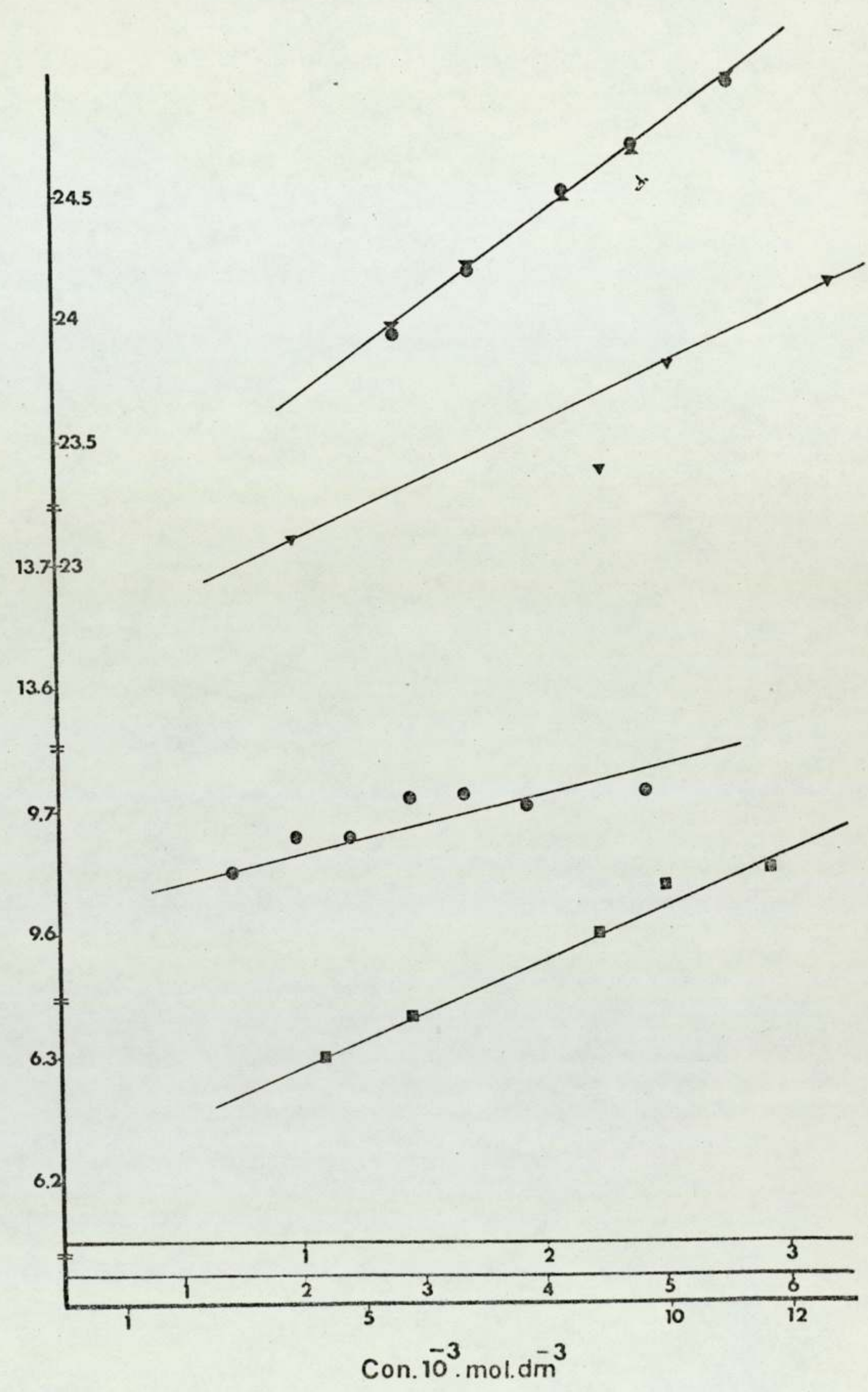


Fig.VII.10 Volumetric properties of the polyoxyethylene mono hexadecyl ethers below the Co at 25° C; ■ EO_{10}, ● EO_{18}, ▼ EO_{30}, and ⧗ EO_{60}

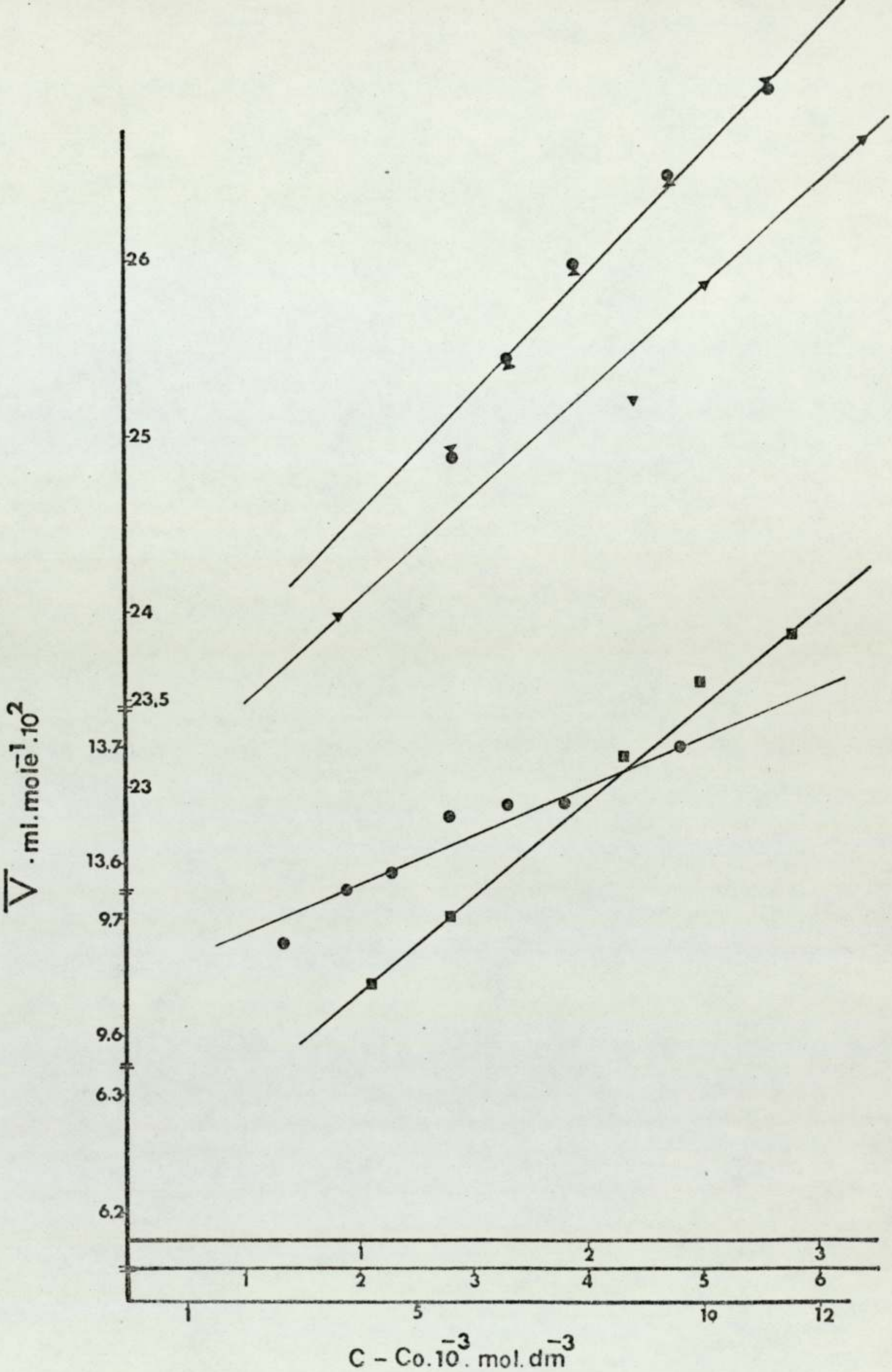


Fig.VII.11 Volumetric properties of the polyoxyethylene mono hexadecyl ethers above the Co at 25° C; ■ EO_{10}, ● EO_{18}, ▼ EO_{30}, and ⧗ EO_{60}

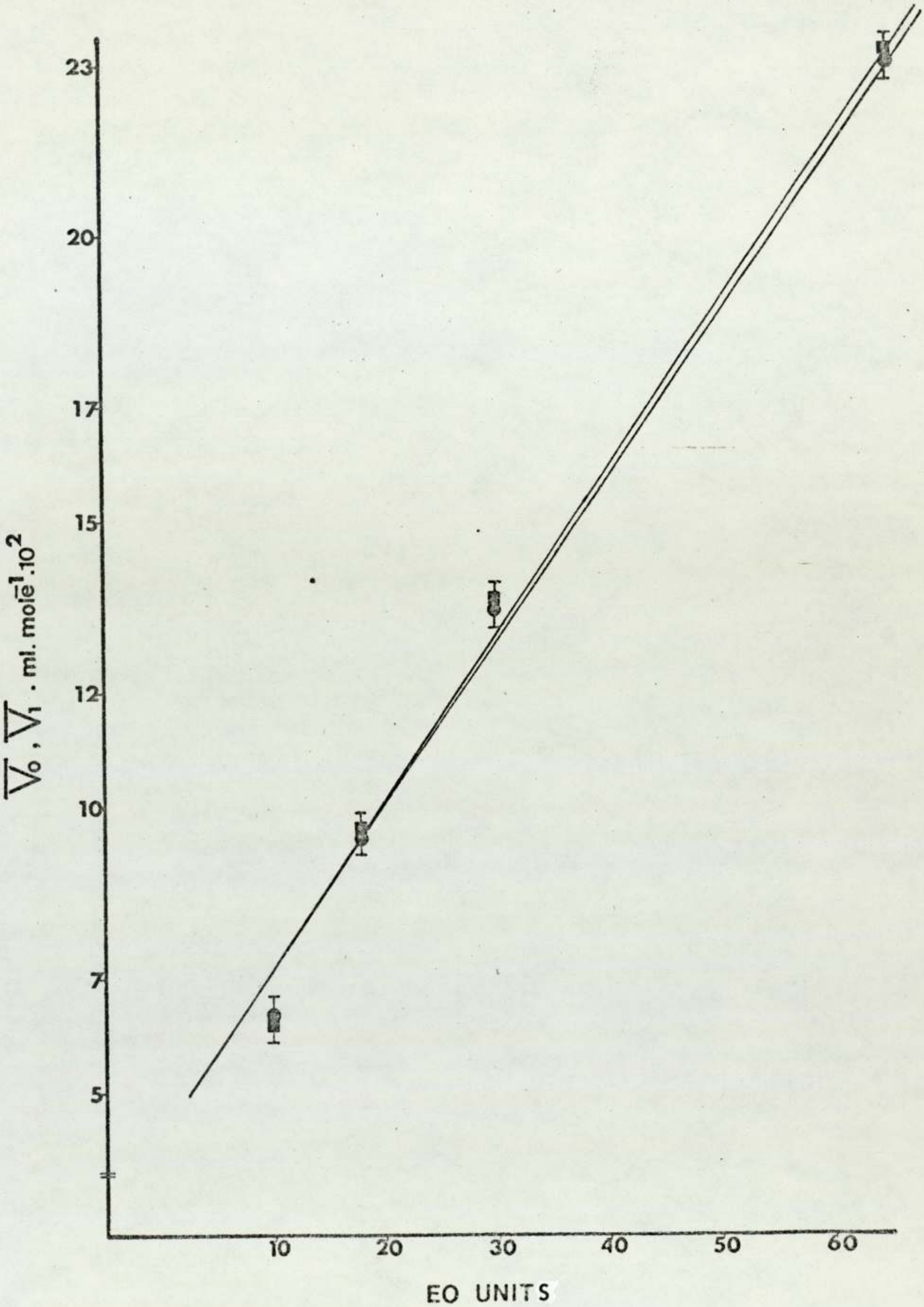


Fig.VII.12 Partial molal volumes of the polyoxyethylene mono hexadecyl ethers below the Co and above the Co as a function of the ethylene oxide chain length at 25° C; ■ above the C_o, ● below the C_o

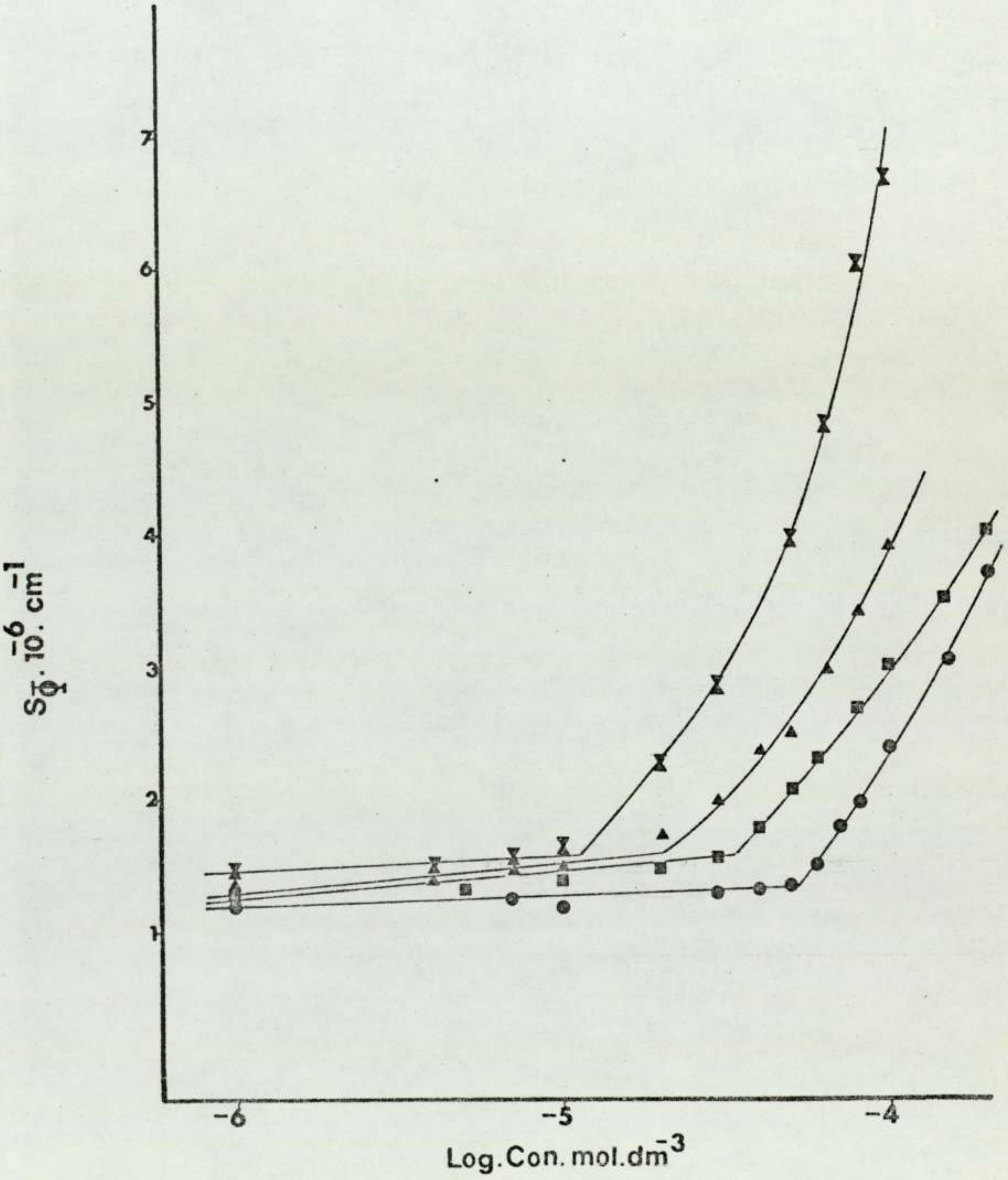


Fig.VII.13 Light scattering at 90° by polyoxyethylene mono hexadecyl ethers in water at 25° C; ● EO_{10} , ■ EO_{18} , ▲ EO_{30} , and ⧗ EO_{60}

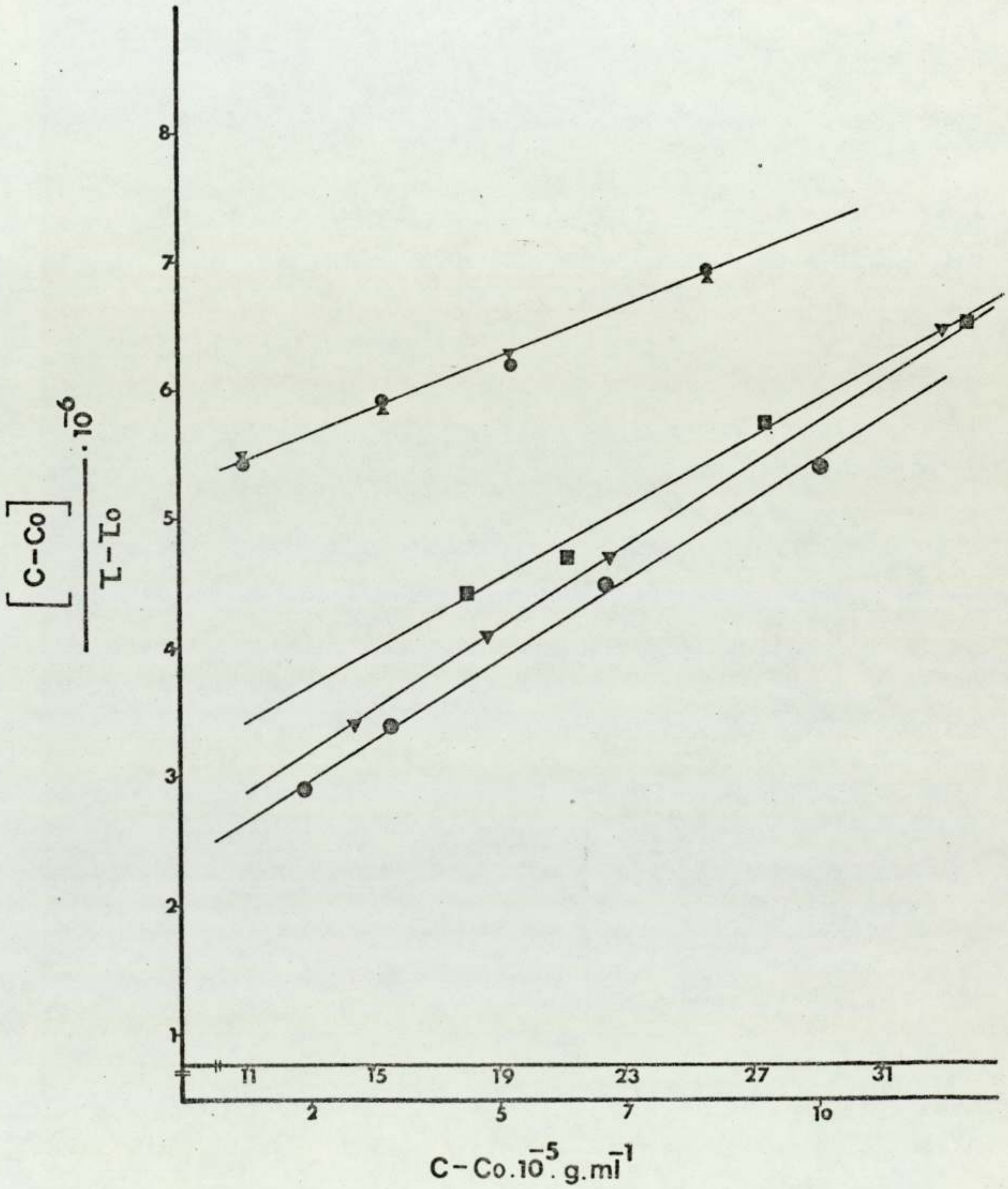


Fig.VII.14 Plot of H (C-Co)/T-To versus C-Co for the polyoxyethylene mono hexadecyl ether in water at 25° C; ● EO_{10} , ▲ EO_{18} , ■ . EO_{30} , and EO_{60}

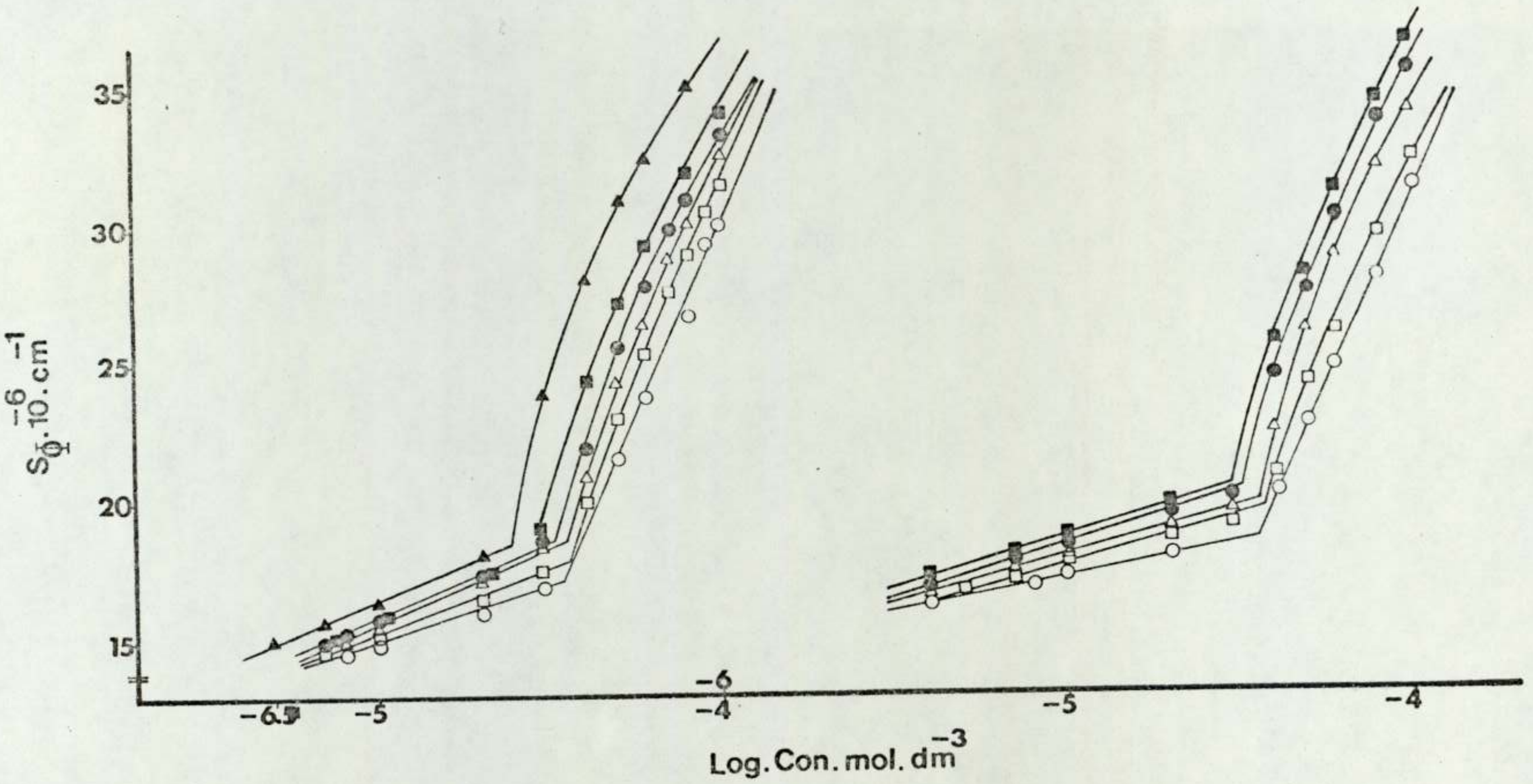


Fig. VII.15 Light scattering at 90° by polyoxyethylene mono hexadecyl ether (A_{18}) containing various concentration of the phenol and benzylalcohol in water at 25 °C; Phenol: ○0.01m, □ 0.02m, △ 0.03m, ● 0.04m, ■0.05m, and ▲0.08m, Benzylalcohol: ○0.01m, □0.02m, △0.03m, ● 0.04m, and ■ 0.05m

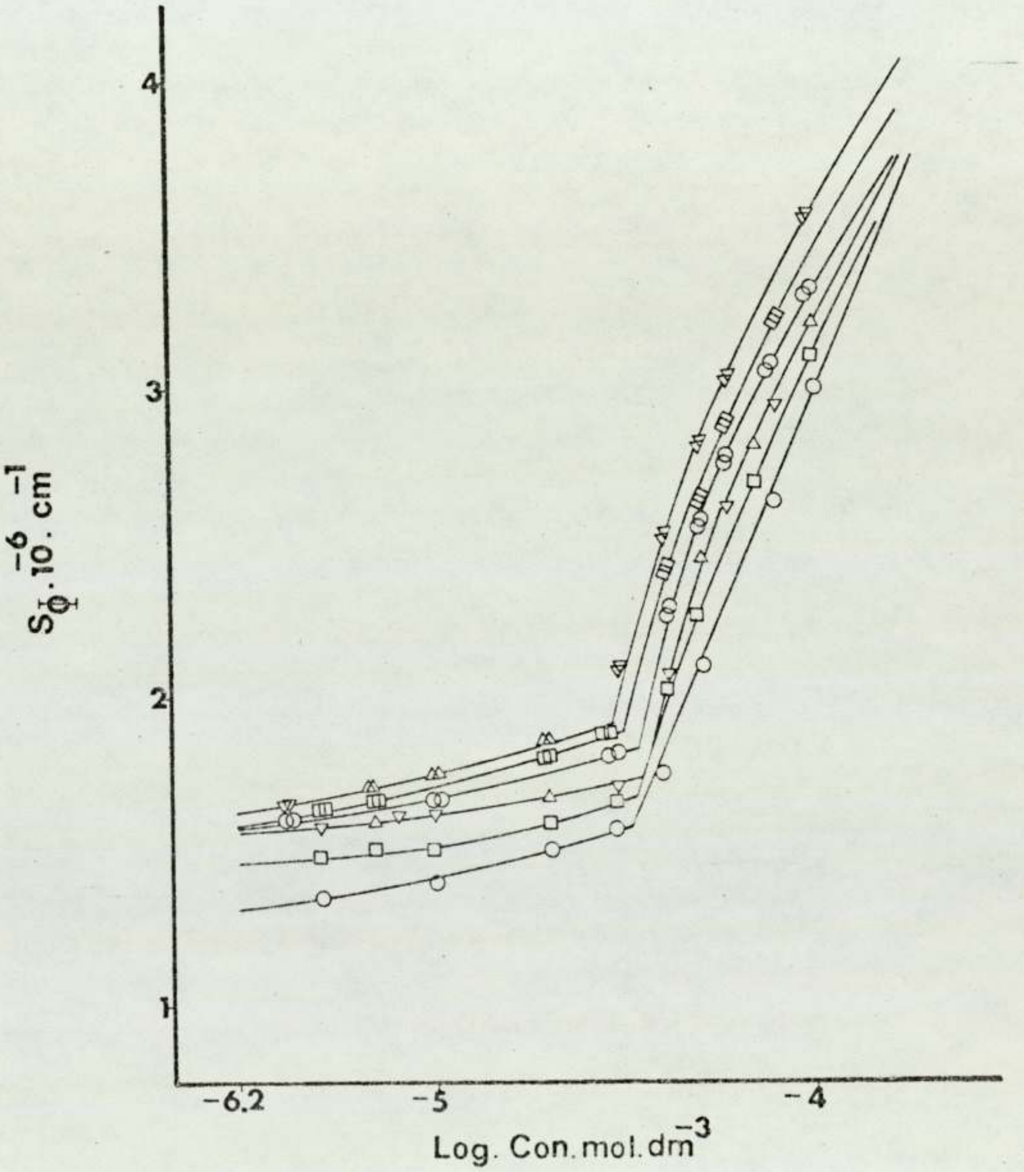


Fig.VII.15.A Light scattering at 90° by polyoxyethylene mono hexadecyl ether (A_{18}) containing various concentration of the phenylethanol in Water at 25° C; ○ in Water, Phenylethanol: □ 0.01m, △ 0.02m, ⦾ 0.03m, ▥ 0.04m, ⟁ 0.05m

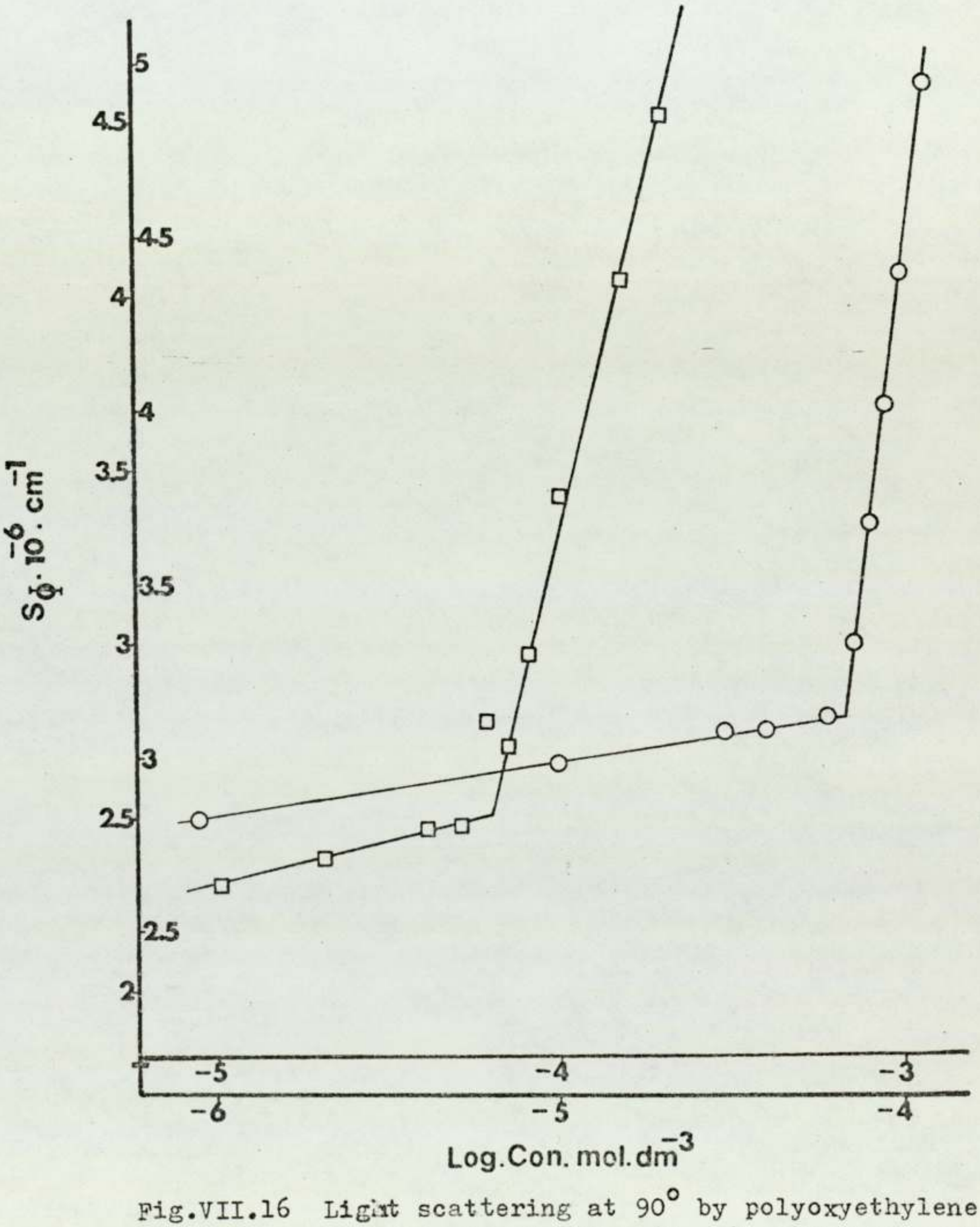


Fig.VII.16 Light scattering at 90° by polyoxyethylene mono hexadecyl ether (A_{18}) containing urea and urethane in water at 25° C; ○ 1M Urea, □ 0.7M Urethane

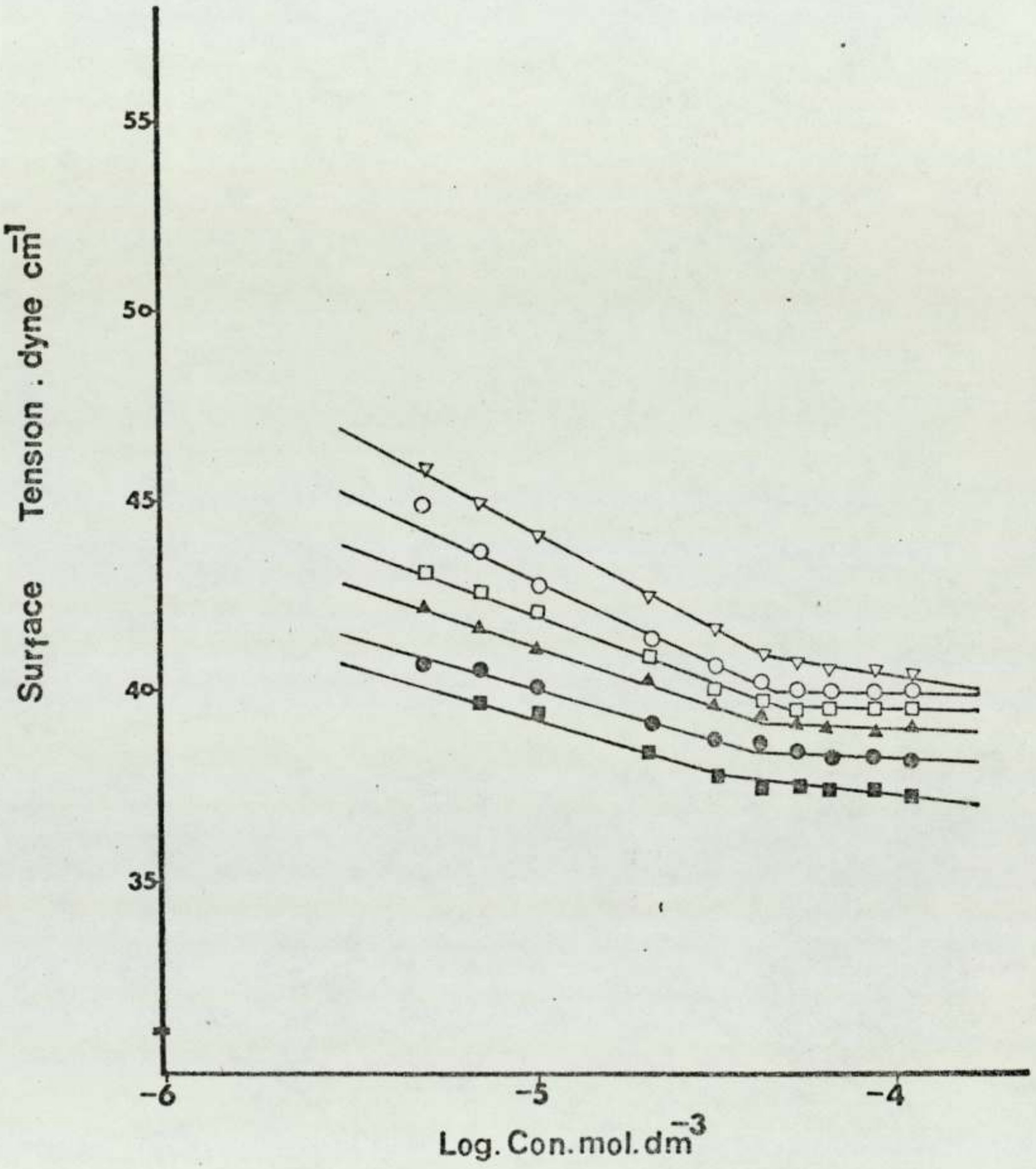


Fig.VII.17 Surface tension versus log. concentration for the polyoxyethylene mono hexadecyl ether (A_{18}) containing various concentration of phen in water at 25° C; ■ 0.01m, ● 0.02m, ▲ 0.03m, □ 0.04, ○ 0.05m, and ▽ 0.08m

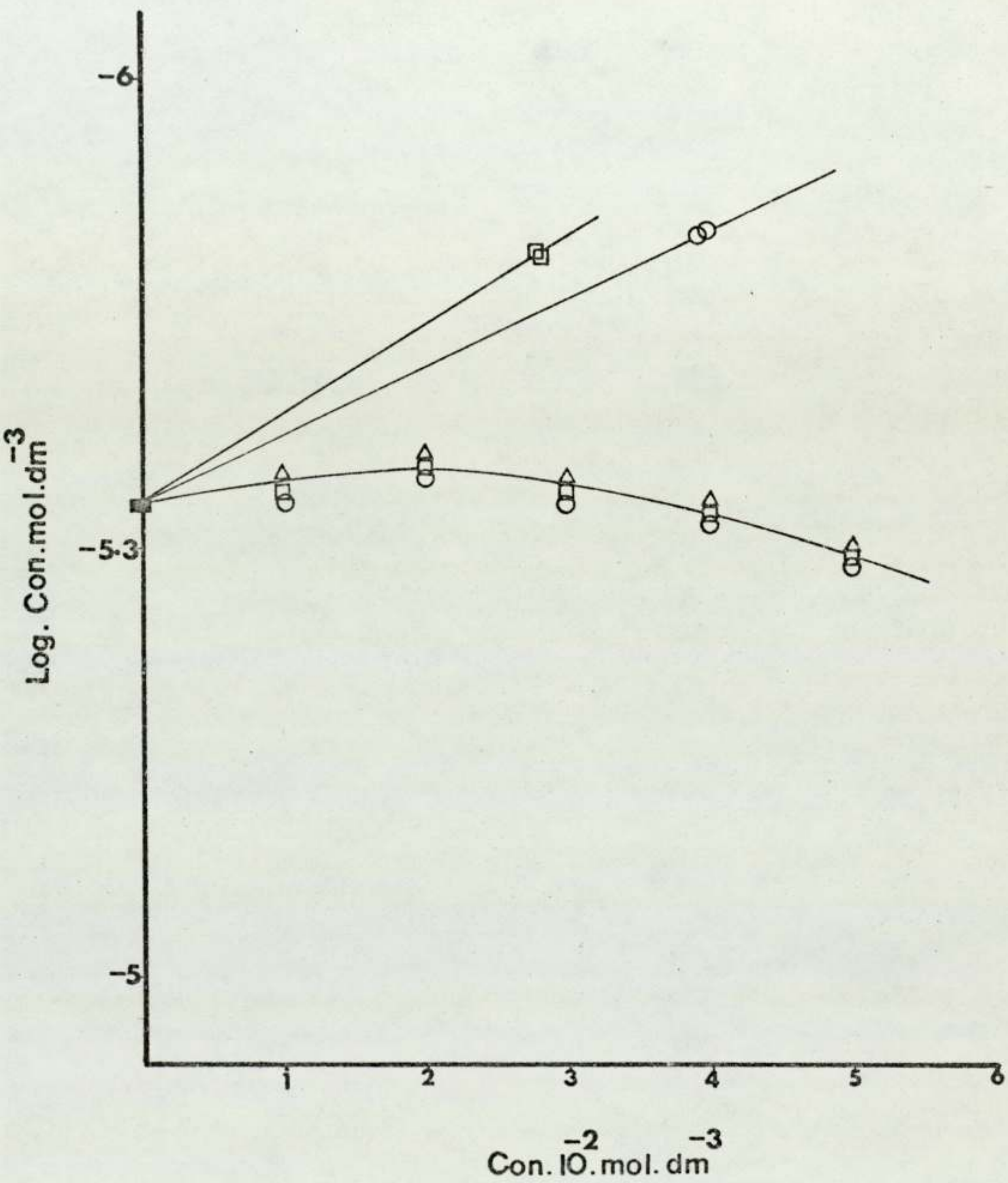


Fig. VII.18 The effect of the aromatic alcohols, urea and urethane on the Co of the polyoxyethylene mono hexadecyl ether (A $_{18}$) at 25° C; ⊞ Urethane, ↀ Urea, ○ Phenol, □ Benzylalcohol, and △ Phenylethanol

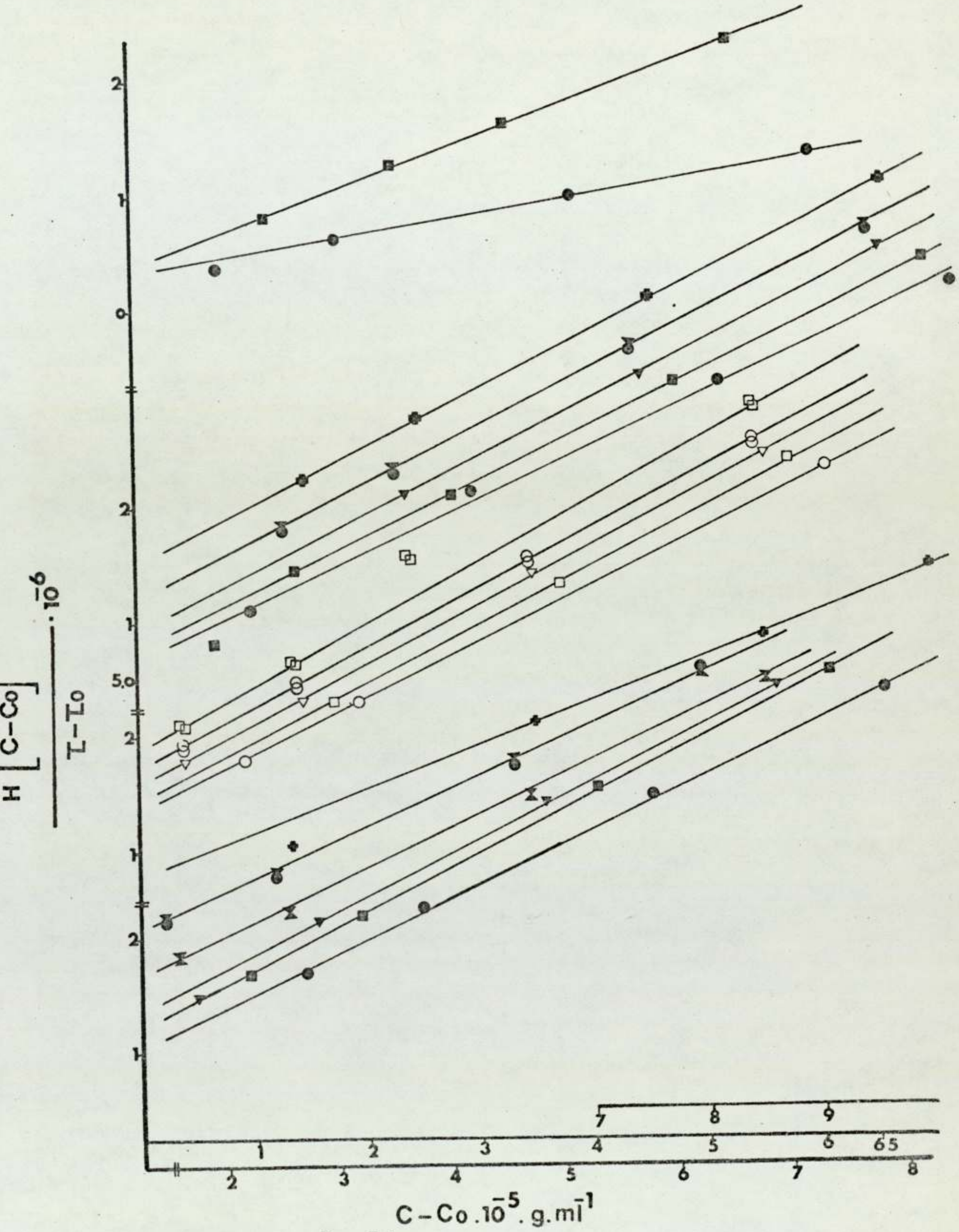


Fig.VII.19 $H[C-C_0]/T-T_0$ versus C-Co for the polyoxyethylene mono hexadecyl ether (A_{18}) containing various concentration of the aromatic alcohols, urea and urethane in water at 25° C;

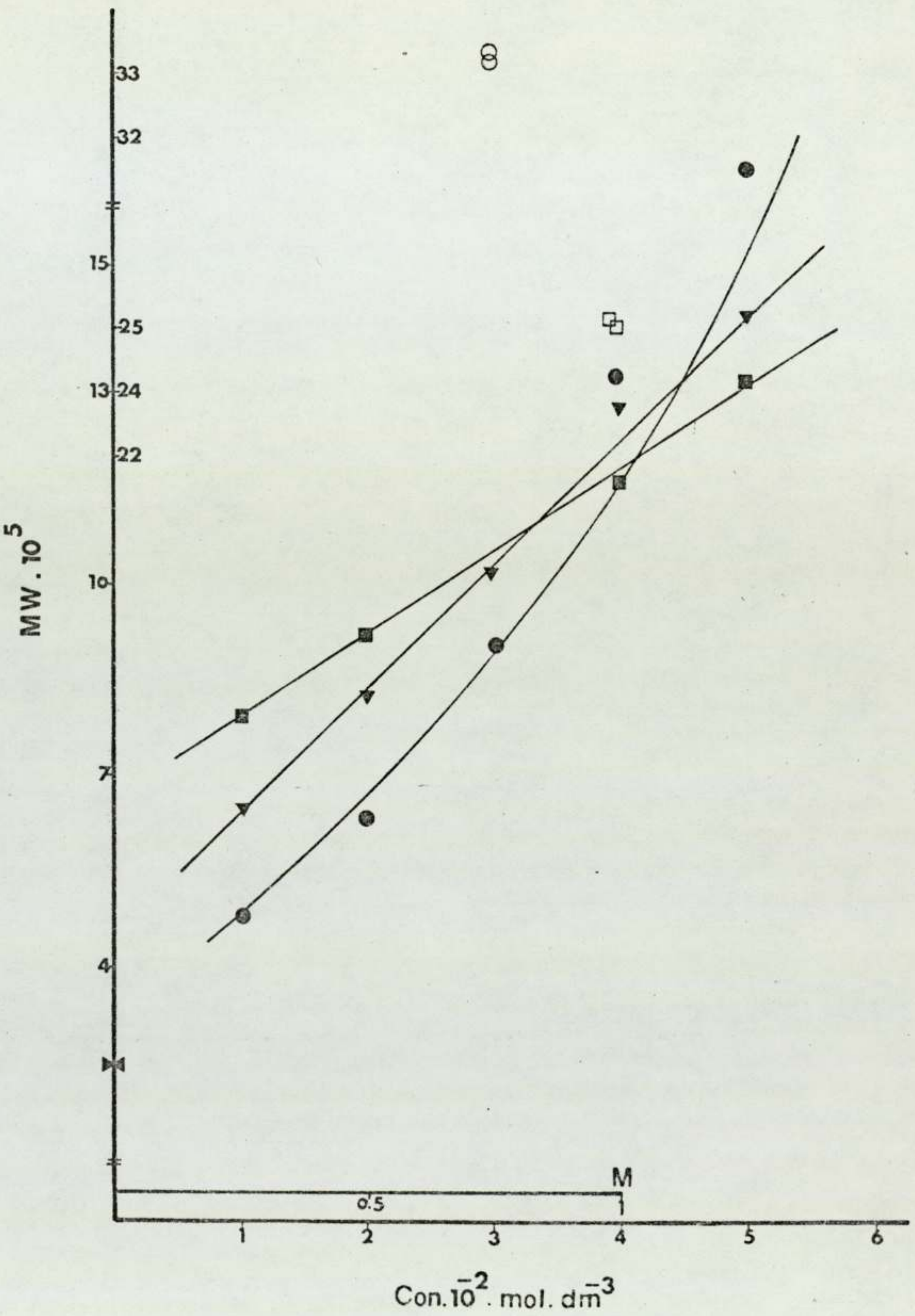


Fig.VII.20 The aromatic alcohols, urea and urethane concentration dependence of micellar molecular weight of the polyoxyethylene mono hexadecyl ether (A $_{18}$) in water at 25° C; ● Phenol, ■ Benzylalcohol, ▼ Benzylethanol, ⊗ Urea, and ⊖ Urethane

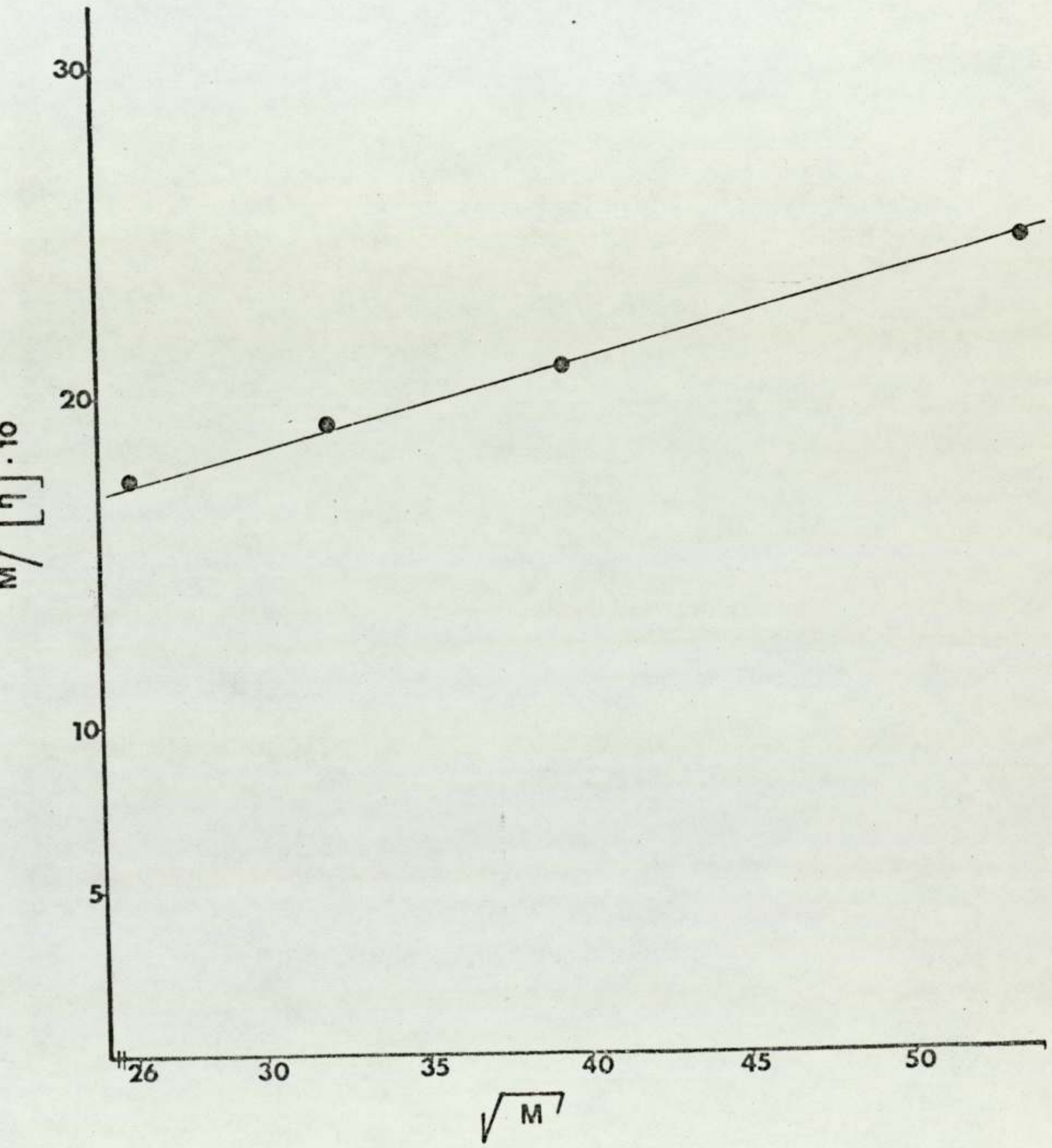


Fig.VII.21 $M/[\eta]$ versus $M^{1/2}$ for the polyoxyethylene mono hexadecyl ethers in water at 25° C;

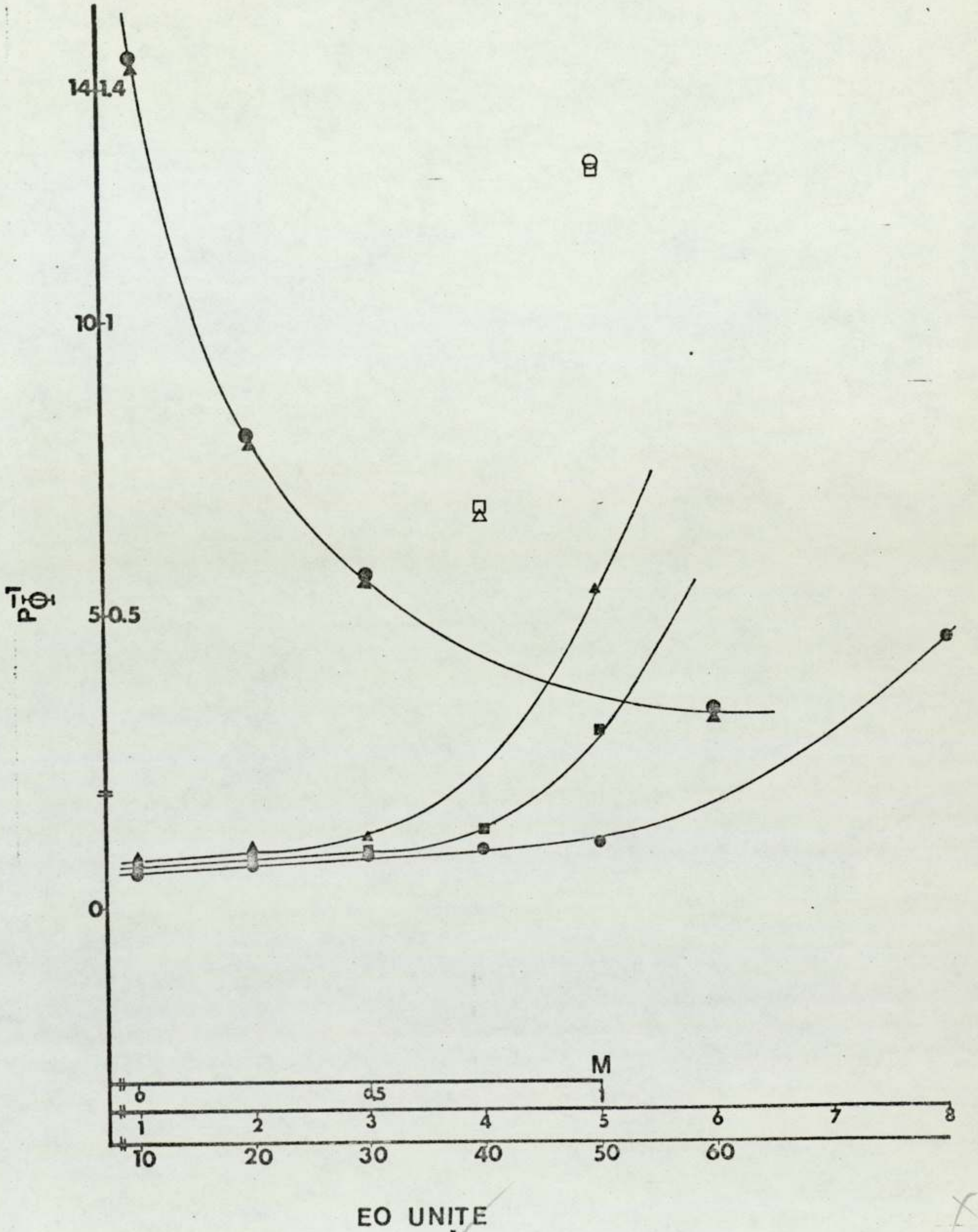


Fig.VII.22 Dependence of $P\Phi^{-1}$ of the polyoxyethylene mono hexadecyl ether (A_{18}) on the concentration of the aromatic alcohols, urea and urethane at 25° C; ● EO_n, ⊟ Urea, ⊠ Urethane, ● Phenol, ■ Benzylalcohol, and ▲ Benzylethanol

VISCOSITY AND SURFACE TENSION DATA FOR THE AQUEOUS SOLUTIONS OF
POLYOXYETHYLENE MONOHEXADEDECYL ETHERS AT 25° C

TABLE VII.I.1

Viscocity							Surface Tension		Correc. Surface Ten.	
C $mol.dm^{-3}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$\frac{1}{\eta_{sp}}$ / C	C_o $mol.dm^{-3}$	C $mol.dm^{-3}$	γ $dyne.cm^{-1}$	γ $dyne.cm^{-1}$	C_o $mol.dm^{-3}$
$C_{16}EO_{10}$										
1×10^{-3}	0.99721	0.9002	1.0059	0.0059	11.46	5.6×10^{-5}	2×10^{-4}	39.21		6.0×10^{-5}
5×10^{-4}	0.99720	0.8996	1.0053	0.0053	6.44		1×10^{-4}	39.23	39.24	
2×10^{-4}	0.99718	0.8972	1.0025	0.0025	5.44		9×10^{-5}	39.31	39.25	
8×10^{-5}	0.99717	0.8961	1.0013	0.0013	4.20		8×10^{-5}	39.24	39.32	
6×10^{-5}	0.99715	0.8958	1.0011	0.0013	3.70		7×10^{-5}	39.22	39.21	
3×10^{-5}	0.99714	0.8955	1.0006	0.0006	3.03		6×10^{-5}	39.25	39.23	
1.5×10^{-5}	0.99713	0.8953	1.0004	0.0004	2.40		5×10^{-5}	39.62	39.60	
4×10^{-6}	0.99712	0.8952	1.0003	0.0003	1.70		4×10^{-5}	39.95	39.85	
							3×10^{-5}	40.65	40.55	
							1×10^{-5}	42.83	42.91	
							1×10^{-6}	47.60	47.72	
$C_{16}EO_{18}$										
5×10^{-4}	0.99723	0.9024	1.0083	0.0083	6.17	3.89×10^{-5}	4×10^{-4}	40.62		3.85×10^{-5}
2×10^{-4}	0.99722	0.8987	1.0043	0.0043	4.86		1×10^{-4}	40.63		
8×10^{-5}	0.99721	0.8968	1.0022	0.0022	3.76		8×10^{-5}	40.61		
5×10^{-5}	0.99721	0.8964	1.0017	0.0017	3.08		7×10^{-5}	40.62		
3×10^{-5}	0.99721	0.8962	1.0014	0.0014	2.15		6×10^{-5}	40.64		
1.5×10^{-5}	0.99721	0.8956	1.0008	0.0008	1.91		5×10^{-5}	40.62		
4×10^{-6}	0.99720	0.8953	1.0004	0.0004	0.89		4×10^{-5}	40.61		
1×10^{-6}	0.99720	0.8951	1.0003	0.0003	0.36		3×10^{-5}	41.62		

TABLE VII.I.1.A

-	-	-	-	-	-	-	2×10^{-5} 1×10^{-5} 1×10^{-6}	43.15 43.72 54.56	-
$C_{16}EO_{30}$									
1×10^{-3} 5×10^{-4} 2×10^{-4} 7×10^{-5} 5×10^{-5} 3×10^{-5} 2×10^{-5} 5×10^{-6} 1×10^{-6}	0.99732 0.99728 0.99727 0.99725 0.99724 0.99723 0.99722 0.99721 0.99721	0.9172 0.9095 0.9018 0.8991 0.8984 0.8978 0.8973 0.8961 0.8956	1.0249 1.0163 1.0077 1.0046 1.0039 1.0033 1.0026 1.0013 1.0009	0.0249 0.0163 0.0077 0.0046 0.0039 0.0033 0.0026 0.0013 0.0009	6.39 4.78 4.04 2.36 1.98 1.43 1.19 0.58 0.18	2.4×10^{-5}	3×10^{-4} 1×10^{-4} 5×10^{-5} 4×10^{-5} 3×10^{-5} 2×10^{-5} 1.5×10^{-5} 1×10^{-5} 8×10^{-6} 1×10^{-6}	44.00 44.10 44.13 44.14 44.15 44.12 45.00 46.72 48.00 55.65	2.20×10^{-5}
$C_{16}EO_{60}$									
1×10^{-3} 5×10^{-4} 3×10^{-4} 6×10^{-5} 2×10^{-5} 9×10^{-6} 6×10^{-6} 3×10^{-6}	0.99750 0.99746 0.99743 0.99739 0.99735 0.99730 0.99727 0.99724	0.9412 0.9217 0.9152 0.9139 0.9133 0.9126 0.9114 0.9110	1.0517 1.0299 1.0226 1.0212 1.0205 1.0197 1.0184 1.0180	0.0517 0.0299 0.0226 0.0212 0.0205 0.0197 0.0184 0.0180	3.64 3.14 2.49 0.53 0.18 0.085 0.062 0.031	1.4×10^{-5}	5×10^{-5} 4×10^{-5} 3×10^{-5} 2×10^{-5} 1.5×10^{-5} 1×10^{-5} 8×10^{-6} 5×10^{-6} 3×10^{-6} 1×10^{-6}	51.25 51.23 51.20 51.24 51.25 51.40 51.90 53.05 54.82 58.00	1.15×10^{-5}

TABLE VII.I.1.B

C $g.dl^{-1}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$\frac{\eta_r - 1}{C - C_o}$ $g.dl^{-1}$	$[\eta]$ $g.dl^{-1}$	Cp C°	H_k
EO_{10}								
1.0	0.99765	0.9366	1.0466	0.0466	0.0467	3.9x10^{-2}	50	5.84
0.8	0.99756	0.9283	1.0373	0.0373	0.0468			
0.7	0.99751	0.9225	1.0308	0.0308	0.0445			
0.6	0.99749	0.9182	1.0262	0.0262	0.0439			
0.4	0.99741	0.9106	1.0175	0.0175	0.0441			
0.3	0.99738	0.9065	1.0130	0.0130	0.0439			
0.2	0.99734	0.9037	1.0099	0.0099	0.0495			
EO_{18}								
1.0	0.99772	0.9556	1.0678	0.0678	0.0681	5.4x10^{-2}	68.80	4.98
0.8	0.99761	0.9424	1.0531	0.0531	0.0666			
0.7	0.99753	0.9349	1.0447	0.0447	0.0643			
0.6	0.99749	0.9282	1.0371	0.0371	0.0623			
0.5	0.99743	0.9225	1.0309	0.0309	0.0623			
0.4	0.99737	0.9164	1.0239	0.0239	0.0606			
0.3	0.99732	0.9110	1.0180	0.0180	0.0609			
0.2	0.99727	0.9052	1.0115	0.0115	0.0587			
EO_{30}								
1.0	0.99821	0.9812	1.0964	0.0964	0.0967	7.5x10^{-2}	72	3.95
0.8	0.99802	0.9617	1.0746	0.0746	0.0937			
0.7	0.99795	0.9519	1.0637	0.0637	0.0915			
0.6	0.99789	0.9426	1.0533	0.0533	0.0895			
0.5	0.99763	0.9344	1.0442	0.0442	0.0889			
0.4	0.99753	0.9251	1.0337	0.0337	0.0852			
0.3	0.99747	0.9174	1.0252	0.0252	0.0849			
0.2	0.99741	0.9096	1.0165	0.0165	0.0838			
EO_{60}								
1.0	0.99841	1.0522	1.1757	0.1757	0.1765	11.7x10^{-2}	79.60	4.63
0.8	0.99820	1.0140	1.1331	0.1331	0.1672			
0.7	0.99810	0.9957	1.1127	0.1127	0.1619			
0.6	0.99802	0.9775	1.0923	0.0923	0.1549			
0.5	0.99790	0.9605	1.0733	0.0733	0.1478			
0.4	0.99781	0.9456	1.0567	0.0567	0.1433			
0.3	0.9977	0.9314	1.0408	0.0408	0.1379			

PARTIAL MOLAL VOLUMES OF THE POLYOXYETHYLENE MONOHEXADECYL ETHERS IN WATER AT 25° C

TABLE VII.I.2

C $mol.dm^{-3}$	$\emptyset$ $ml.mole^{-1}$	$\overline{V}$ $ml.mole^{-1}$	$\overline{V}_o$ $ml.mole^{-1}$	$\overline{V}_1$ $ml.mole^{-1}$	$\Delta\overline{V}_1$ $ml.mole^{-1}$	$\overline{V}^o_{1C}$ $ml.mole^{-1}$	$\overline{V}^o_{1D}$ $ml.mole^{-1}$	S_{pv} $ml.g^{-1}$
EO10								
0.0146	646.72	677.68	620.05	624.0	3.95	28.70	29.0	0.91361
0.0117	645.14	669.95						
0.0102	644.29	665.93						
0.0088	640.16	658.83						
0.0058	633.48	645.78						
0.0044	629.98	639.31						
EO18								
0.0097	973.13	984.62	961.50	964.5	3.0			0.91188
0.0077	970.91	980.03						
0.0067	973.05	980.98						
0.0058	972.19	979.06						
0.0048	968.56	973.68						
0.0039	968.04	972.66						
0.0029	964.89	968.32						
EO30								
0.0064	1392.57	1422.22	1363	1365	2.0			0.87276
0.0051	1385.82	1409.45						
0.0045	1377.41	1398.26						
0.0038	1358.36	1375.96						
0.0025	1395.00	1406.58						
0.0019	1372.24	1381.00						
EO60								
0.0035	2514.66	2777.86	2300	2316.6	16.6			0.80270
0.0028	2496.54	2707.10						
0.0024	2472.97	2653.45						
0.0021	2451.62	2609.54						
0.0017	2419.20	2547.04						
0.0014	2382.77	2487.28						

LIGHT SCATTERING BY POLYOXYETHYLENE MONO HEXADECYL ETHERS IN WATER AT 25° C

TABLE VII.I.3

C $mol.dm^{-3}$	$S_Ø$ $.10^{-5}.cm^{-1}$	τ $.10^{-5}.cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}.cm^{2}.g^{-2}$	C_o $mol.dm^{-3}$
EO_{10}						
2×10^{-4}	0.3699	6.1945	1.05	0.145	2.31	5.2×10^{-5}
1.5×10^{-4}	0.3150	5.2752				
1×10^{-4}	0.2450	4.1030				
8×10^{-5}	0.1976	3.3091				
6×10^{-5}	0.1520	2.5455				
5×10^{-5}	0.1352	2.2641				
4×10^{-5}	0.1364	2.2842				
3×10^{-5}	0.1313	2.1988				
1×10^{-5}	0.1199	2.0079				
7×10^{-6}	0.1379	2.3093				
1×10^{-6}	0.1272	2.1301				
EO_{18}						
2×10^{-4}	0.3995	6.6903	1.06	0.144	2.25	3.4×10^{-5}
1.5×10^{-4}	0.3499	5.859				
1×10^{-4}	0.3035	5.0826				
8×10^{-5}	0.2680	4.4881				
5×10^{-5}	0.2120	3.5502				
4×10^{-5}	0.1757	2.9423				
3×10^{-5}	0.1598	2.6761				
2×10^{-5}	0.1516	2.5387				
1×10^{-5}	0.1384	2.3177				
5×10^{-6}	0.1263	2.1151				
1×10^{-6}	0.1298	2.1737				

TABLE VII.I.3.A

C mol.dm^{-3}	S_{ϕ} .10^{-5}cm^{-1}	τ .10^{-5}cm^{-1}	D_R	ΔI ml.g^{-1}	H .10^{-6}cm^{2}.g^{-2}	C_0 mol.dm^{-3}
EO_{30}						
1×10^{-4}	0.3848	6.4441	1.05	0.148	2.38	2.1×10^{-5}
8×10^{-5}	0.3392	5.6804				
6.5×10^{-5}	0.2966	4.9671				
5×10^{-5}	0.2492	4.1732				
4×10^{-5}	0.2469	4.1347				
3×10^{-5}	0.2141	3.5855				
2×10^{-5}	0.1845	3.0898				
1×10^{-5}	0.1483	2.4835				
7×10^{-6}	0.1544	2.5856				
4×10^{-6}	0.1423	2.3831				
1×10^{-6}	0.1313	2.1988				
EO_{60}						
1×10^{-4}	0.6791	11.3730	1.05	0.149	2.45	1.15×10^{-5}
8×10^{-5}	0.6133	10.2710				
6.5×10^{-5}	0.4767	7.9831				
5×10^{-5}	0.3990	6.6819				
3×10^{-5}	0.2806	4.6991				
2×10^{-5}	0.2363	3.9572				
1×10^{-5}	0.1825	3.0563				
7×10^{-6}	0.1456	2.4383				
4×10^{-6}	0.1373	2.2993				
1×10^{-6}	0.1466	2.4560				

LIGHT SCATTERING AND SURFACE TENSION DATA FOR THE POLYOXYETHYLENE MONO HEXADECYL ETHER ($C_{16}E_{18}$) IN WATER CONTAINING AROMATIC ALCOHOLS AT 25° C

TABLE VII.I.4

Light Scattering							Surface Tension		
C mol.dm^{-3}	$S_{\emptyset}$ .10^{-5}cm^{-1}	τ .10^{-5}cm^{-1}	D_R	ΔI ml.g^{-1}	H .10^{-6}cm^{2}g^{-2}	C_0 mol.dm^{-3}	C mol.dm^{-3}	γ dyne.cm^{-1}	C_0 mol.dm^{-3}
EO$_{18}$ 0.01 M Phenol									
$2x10^{-4}$	0.360	6.0288	1.05	0.1435	2.25	$3.45x10^{-5}$	$1x10^{-4}$	40.2	$4.2x10^{-5}$
$1x10^{-4}$	0.3056	5.1177					$8x10^{-5}$	40.64	
$9x10^{-5}$	0.2999	5.0223					$6x10^{-5}$	40.53	
$8x10^{-5}$	0.2750	4.6053					$5x10^{-5}$	40.98	
$7x10^{-5}$	0.2546	4.2637					$4x10^{-5}$	41.04	
$6x10^{-5}$	0.2399	4.0175					$3x10^{-5}$	41.82	
$5x10^{-5}$	0.2142	3.5871					$2x10^{-5}$	42.86	
$4x10^{-5}$	0.2013	3.3711					$1x10^{-5}$	44.09	
$3x10^{-5}$	0.1799	3.0127					$7x10^{-6}$	44.98	
$2x10^{-5}$	0.1601	2.6811							
$1x10^{-5}$	0.1510	2.5287							
$8x10^{-6}$	0.1482	2.4818							
0.02 M									
$1x10^{-4}$	0.3142	5.2618	1.06	0.1418	2.20	$3.6\ x10^{-5}$	$1x10^{-4}$	39.85	$4.4x10^{-5}$
$9x10^{-5}$	0.3022	5.0608					$8x10^{-5}$	40.09	
$8x10^{-5}$	0.2932	4.9101					$6x10^{-5}$	39.85	
$7x10^{-5}$	0.2781	4.6572					$5x10^{-5}$	39.55	
$6x10^{-5}$	0.2292	4.2285					$4x10^{-5}$	40.25	
$5x10^{-5}$	0.2292	3.8383					$3x10^{-5}$	40.70	
$4x10^{-5}$	0.2032	3.4029					$2x10^{-5}$	41.21	
$3x10^{-5}$	0.1753	2.9356					$1x10^{-5}$	42.74	
$2x10^{-5}$	0.1662	2.7833					$7x10^{-6}$	43.8	
$1x10^{-5}$	0.1499	2.5103					$5x10^{-6}$	44.99	
$7x10^{-6}$	0.1473	2.4667							
0.03 M									
$1x10^{-4}$	0.3223	5.3974	1.05	0.1417	2.2	$3.4\ x10^{-5}$	$1x10^{-4}$	39.62	$4.5x10^{-5}$
$8x10^{-5}$	0.3014	5.0474					$8x10^{-5}$	39.68	
$7x10^{-5}$	0.2901	4.8582					$6x10^{-5}$	39.64	
$6x10^{-5}$	0.2651	4.4395					$5x10^{-5}$	39.68	
$5x10^{-5}$	0.2444	4.0928					$4x10^{-5}$	39.79	
$4x10^{-5}$	0.2062	3.4532					$3x10^{-5}$	40.19	
$3x10^{-5}$	0.1799	3.0127					$2x10^{-5}$	40.87	
$2x10^{-5}$	0.1722	2.8837					$1x10^{-5}$	42.18	
$1x10^{-5}$	0.1523	2.5505					$7x10^{-6}$	42.58	
$7x10^{-6}$	0.1491	2.4969					$5x10^{-6}$	43.08	

TABLE VII.I.4.A

Light Scattering							Surface Tension		
C mol.dm^{-3}	$S_{\emptyset}$ 10^{-5}.cm^{-1}	τ .10^{-5}.cm^{-1}	D_R	ΔI ml.g^{-1}	H .10^{-6} cm^{2}.g^{-2}	C_0 mol.dm^{-3}	C mol.dm^{-3}	γ dyne.cm^{-1}	C_0 mol.dm^{-3}
0.04M									
$1x10^{-4}$	0.3303	5.5314	1.06	0.1417	2.19	$3.3x10^{-5}$	$1x10^{-4}$	39.05	$4.0x10^{-5}$
$8x10^{-5}$	0.3096	5.1847					$8x10^{-5}$	38.79	
$7x10^{-5}$	0.3021	5.0592					$6x10^{-5}$	39.09	
$6x10^{-5}$	0.2777	4.6505					$5x10^{-5}$	39.23	
$5x10^{-5}$	0.2563	4.2922					$4x10^{-5}$	39.55	
$4x10^{-5}$	0.2196	3.6775					$3x10^{-5}$	39.68	
$3x10^{-5}$	0.1846	3.0914					$2x10^{-5}$	40.35	
$2x10^{-5}$	0.1713	2.8687					$1x10^{-5}$	41.24	
$1x10^{-5}$	0.1542	2.5823					$7x10^{-6}$	41.77	
$7x10^{-6}$	0.1503	2.5170					$5x10^{-6}$	42.28	
0.05M									
$1x10^{-4}$	0.3401	5.6955	1.06	0.142	2.2	$2.9x10^{-5}$	$1x10^{-4}$	38.28	$3.7x10^{-5}$
$8x10^{-5}$	0.3186	5.3354					$8x10^{-5}$	38.48	
$6x10^{-5}$	0.2953	4.9452					$6x10^{-5}$	38.28	
$5x10^{-5}$	0.2721	4.5567					$5x10^{-5}$	38.48	
$4x10^{-5}$	0.2453	4.1079					$4x10^{-5}$	38.77	
$3x10^{-5}$	0.1902	3.1852					$3x10^{-5}$	38.80	
$2x10^{-5}$	0.1752	2.9340					$2x10^{-5}$	39.22	
$1x10^{-5}$	0.1632	2.7330					$1x10^{-5}$	40.12	
$7x10^{-6}$	0.1521	2.5471					$7x10^{-6}$	40.5	
$5x10^{-6}$	0.1435	2.4031							
0.08M									
$1x10^{-4}$	0.3663	6.1344	1.06	0.142	2.2	$2.4x10^{-5}$	$1x10^{-4}$	37.31	$3.1x10^{-5}$
$8x10^{-5}$	0.3486	5.8378					$8x10^{-5}$	37.55	
$6x10^{-5}$	0.3235	5.4175					$6x10^{-5}$	37.47	
$5x10^{-5}$	0.3102	5.1948					$5x10^{-5}$	37.72	
$4x10^{-5}$	0.2804	4.6957					$4x10^{-5}$	37.55	
$3x10^{-5}$	0.2461	4.1213					$3x10^{-5}$	37.98	
$2x10^{-5}$	0.1812	3.0345					$2x10^{-5}$	38.50	
$1x10^{-5}$	0.1635	2.7381					$1x10^{-5}$	39.50	
$7x10^{-6}$	0.1583	2.6509					$7x10^{-6}$	39.85	
$5x10^{-6}$	0.1502	2.5153					$5x10^{-6}$	40.70	

TABLE VII.I.4.B

C $mol.dm^{-3}$	$S_Ø$ $.10^{-5}\ cm^{-1}$	τ $.10^{-5}\ cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}\ cm^{2}.g^{-2}$	C_0 $mol.dm^{-3}$
			0.01 M Benzyl alcohol			
$1x10^{-4}$	0.3078	5.1546	1.07	0.1475	2.38	$3.45x10^{-5}$
$7x10^{-5}$	0.2706	4.5316				
$6x10^{-5}$	0.2513	4.2084				
$5x10^{-5}$	0.2287	3.8299				
$4x10^{-5}$	0.2043	3.4213				
$3x10^{-5}$	0.1651	2.7648				
$2x10^{-5}$	0.1610	2.6962				
$1x10^{-5}$	0.1499	2.5103				
$7x10^{-5}$	0.1551	2.5974				
$5x10^{-5}$	0.1499	2.5103				
			0.02 M			
$1x10^{-4}$	0.3210	5.3756	1.07	0.1470	2.35	$3.65x10^{-5}$
$8x10^{-5}$	0.2922	4.8933				
$7x10^{-5}$	0.2855	4.7811				
$6x10^{-5}$	0.2579	4.3193				
$5x10^{-5}$	0.2461	4.1213				
$4x10^{-5}$	0.2039	3.4146				
$2x10^{-5}$	0.1691	2.8318				
$1x10^{-5}$	0.1620	2.7129				
$7x10^{-6}$	0.1600	2.6794				
$5x10^{-6}$	0.1592	2.6661				
			0.03M			
$1x10^{-4}$	0.327	5.4762	1.07	0.1475	2.39	$3.4x10^{-5}$
$8x10^{-5}$	0.304	5.0909				
$6x10^{-5}$	0.2771	4.6405				
$5x10^{-5}$	0.2540	4.2535				
$4x10^{-5}$	0.2342	3.9221				
$3x10^{-5}$	0.1830	3.0646				
$1x10^{-5}$	0.1670	2.7966				
$8x10^{-6}$	0.1624	2.7196				
$4x10^{-6}$	0.1660	2.7799				

TABLE VII.I.4.C

C mol.dm^{-3}	$S_ø$ .10^{-5} cm^{-1}	τ .10^{-5} cm^{-1}	D_R	ΔI ml.g^{-1}	H .10^{-6} cm^{2}.g^{-2}	C_0 mol.dm^{-3}
0.04M						
1x10^{-4}	0.3389	5.6754	1.07	0.1467	2.35	3.18x10^{-5}
8x10^{-5}	0.3202	5.3622				
6x10^{-5}	0.2888	4.8364				
5x10^{-5}	0.260	4.3541				
4x10^{-5}	0.2410	4.0359				
2x10^{-5}	0.1820	3.0478				
1x10^{-5}	0.1720	2.8804				
7x10^{-6}	0.1692	2.8335				
5x10^{-6}	0.1601	2.6811				
0.05M						
1x10^{-4}	0.3564	5.9685	1.07	0.1465	2.35	2.9 x10^{-5}
6x10^{-5}	0.2999	5.0223				
5x10^{-5}	0.2765	4.6304				
4x10^{-5}	0.2498	4.1833				
3x10^{-5}	0.2108	3.5348				
2x10^{-5}	0.1891	3.1667				
1x10^{-5}	0.1752	2.9340				
8x10^{-6}	0.171	2.8636				
4x10^{-6}	0.164	2.7464				

TABLE VII.I.4.D

C mol. dm^{-3}	S$_ø$ .10^{-5}.cm^{-1}	τ .10^{-5}.cm^{-1}	D$_R$	ΔI ml.g^{-1}	H .10^{-6}.cm^{2}.g^{-2}	C$_0$ mol.dm^{-3}
0.01 M Ph.ethanol						
$1x10^{-4}$	0.3107	5.2032	1.08	0.1485	2.41	$3.58x10^{-5}$
$8x10^{-5}$	0.2786	4.6656				
$6x10^{-5}$	0.2454	4.1096				
$5x10^{-5}$	0.2253	3.7730				
$4x10^{-5}$	0.2013	3.3711				
$3x10^{-5}$	0.1892	3.1684				
$2x10^{-5}$	0.1792	3.0010				
$1x10^{-5}$	0.1717	2.8754				
$8x10^{-6}$	0.1659	2.7783				
$4x10^{-6}$	0.1624	2.7196				
0.02 M						
$1x10^{-4}$	0.3242	5.4292	1.08	0.1487	2.42	$3.75x10^{-5}$
$8x10^{-5}$	0.2966	4.9671				
$6x10^{-5}$	0.2570	4.3038				
$5x10^{-5}$	0.2427	4.0644				
$4x10^{-5}$	0.2081	3.4849				
$3x10^{-5}$	0.1923	3.2204				
$2x10^{-5}$	0.1821	3.0495				
$1x10^{-5}$	0.1752	2.9340				
$7x10^{-6}$	0.1681	2.8151				
$5x10^{-6}$	0.1642	2.749				
0.03 M						
$1x10^{-4}$	0.3381	5.6620	1.08	0.1487	2.42	$3.6\ x10^{-5}$
$8x10^{-5}$	0.3193	5.3472				
$6x10^{-5}$	0.2856	4.7828				
$5x10^{-5}$	0.2570	4.3038				
$4x10^{-5}$	0.2204	3.6909				
$3x10^{-5}$	0.1942	3.2522				
$2x10^{-5}$	0.1914	3.2053				
$1x10^{-5}$	0.1754	2.9373				
$8x10^{-6}$	0.1740	2.9139				
$4x10^{-6}$	0.1633	2.7347				

TABLE VII.I.4.E

C $mol.dm^{-3}$	$S_ø$ $.10^{-5}.cm^{-1}$	τ $.10^{-5}.cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}.cm^{2}.g^{-2}$	C_0 $mol.dm^{-3}$
			0.04M			
1×10^{-4}	0.3528	5.9082	1.08	0.1481	2.4	3.3×10^{-5}
8×10^{-5}	0.3348	5.6067				
6×10^{-5}	0.2999	5.0223				
5×10^{-5}	0.2710	4.5383				
4×10^{-5}	0.2413	4.0409				
3×10^{-5}	0.2031	3.4012				
2×10^{-5}	0.1963	3.2873				
1×10^{-5}	0.1833	3.0696				
7×10^{-6}	0.1789	2.9959				
5×10^{-6}	0.1769	2.9624				
			0.05M			
1×10^{-4}	0.3812	6.3838	1.08	0.1481	2.4	3×10^{-5}
8×10^{-5}	0.3422	5.7307				
6×10^{-5}	0.3067	5.1362				
5×10^{-5}	0.2832	4.7426				
4×10^{-5}	0.2529	4.2352				
3×10^{-5}	0.2024	3.3895				
2×10^{-5}	0.1974	3.3057				
1×10^{-5}	0.1862	3.1182				
8×10^{-6}	0.1821	3.0495				
4×10^{-6}	0.1712	2.8670				

LIGHT SCATTERING BY POLYOXYETHLYLENE MONO HEXADECYL ETHER ($C_{16}E_{18}$)

IN WATER CONTAINING UREA AND URETHANE AT 25° C

TABLE VII.I.5

C $mol.dm^{-3}$	$S_ø$ $.10^{-5}.cm^{-1}$	τ $.10^{-5}.cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}.cm^{2}.g^{-2}$	C_0 $mol.dm^{-3}$
0.7 M Urethane						
2×10^{-4}	0.4837	8.1004	1.05	0.1045	1.19	6.25×10^{-5}
1.5×10^{-4}	0.4360	7.3020				
1×10^{-4}	0.3739	6.2620				
9×10^{-5}	0.3349	5.610				
8×10^{-5}	0.3292	5.5130				
7×10^{-5}	0.3033	5.0790				
5×10^{-5}	0.2804	4.6960				
4×10^{-5}	0.2809	4.7041				
2×10^{-5}	0.2691	4.5065				
1×10^{-5}	0.2641	4.4227				
1M Urea						
1.2×10^{-4}	0.460	7.7035	1.05	0.151	2.48	6.8×10^{-5}
1×10^{-4}	0.4061	6.8008				
9×10^{-5}	0.3680	6.1627				
8×10^{-5}	0.3350	5.6101				
7×10^{-5}	0.310	5.1915				
6×10^{-5}	0.280	4.6891				
4×10^{-5}	0.276	4.6221				
3×10^{-5}	0.2786	4.6656				
1×10^{-5}	0.2658	4.4512				
8×10^{-6}	0.2386	3.9957				

MICELLAR DIMENSIONS OF POLYOXYETHYLENE MONO HEXADECYL ETHERS IN WATER

FROM LIGHT SCATTERING AND VISCOSITY DATA

TABLE. VII.I.6

Light Scattering							Viscosity					
S.A.A	A	B g.ml	MW	E_L A°	N_A	P^{-1}ø	Vh $ml.10^{-18}$	$Wg.g.s^{-1}$	K	A_R	A_a A°	A_b A°
EO_{10}	2.35×10^{-6}	0.0313	4.26×10^{5}	60	624	1.456	0.642	0.648	4.3	3.7	130	35
EO_{18}	2.6×10^{-6}	0.032	3.85×10^{5}	74	372	0.798	0.594	1.231	5.8	5.0	153	30.50
EO_{30}	3.25×10^{-6}	0.023	3.08×10^{5}	91	197	0.557	0.444	2.133	8.6	7.0	175	25
EO_{60}	4.5×10^{-6}	0.002	2.22×10^{5}	120	77	0.337	0.295	3.886	14.57	10.4	198	19

MICELLAR DIMENSIONS OF THE POLYOXYETHYLENE MONO HEXADECYL ETHER

(C_{16} E_{18}) IN WATER CONTAINING AROMATIC ALCOHOLS

TABLE VII.I.7

C mol.dm^{-3}	A	B g.ml	MW	N_A	$P\text{ø}^{-1}$	L/2 A°
			Phenol			
0.01	2.05×10^{-6}	0.0437	4.88×10^{5}	471	0.623	260
0.02	1.55×10^{-6}	0.0450	6.45×10^{5}	623	0.748	344
0.03	1.1×10^{-6}	0.0463	9.10×10^{5}	879	0.916	485
0.04	0.75×10^{-6}	0.0487	1.333×10^{6}	1287	1.068	710
0.05	0.6×10^{-6}	0.0500	1.667×10^{6}	1610	1.074	888
0.08	0.48×10^{-6}	0.0465	2.08×10^{6}	2009	1.459	1108
			Benzylalcohol			
0.01	1.25×10^{-6}	0.0533	8×10^{5}	773	0.644	426
0.02	1.08×10^{-6}	0.0514	9.26×10^{5}	895	0.938	493
0.03	0.98×10^{-6}	0.0587	1.02×10^{6}	985	0.533	543
0.04	0.85×10^{-6}	0.050	1.17×10^{6}	1136	1.137	627
0.05	0.75×10^{-6}	0.0484	1.333×10^{6}	1287	1.302	710
			Ph.ethanol			
0.01	1.5×10^{-6}	0.0487	6.67×10^{5}	644	0.685	355
0.02	1.2×10^{-6}	0.0512	8.33×10^{5}	804	1.002	444
0.03	0.95×10^{-6}	0.0527	1.05×10^{6}	1014	1.098	559
0.04	0.78×10^{-6}	0.0480	1.28×10^{6}	1236	1.577	682
0.05	0.7×10^{-6}	0.0487	1.43×10^{6}	1381	1.541	762
			Urea			
1.0	0.4×10^{-6}	0.0313	2.5×10^{6}	2415	12.770	1332
			Urethane			
0.7	0.3×10^{-6}	0.0169	3.33×10^{6}	3216	6.723	1774

NMR DATA FOR THE POLYOXYETHYLENE MONOHEXADECYL

ETHERS IN CARBONTETRACHLORIDE AT 25 °C

TABLE VII.I.8

S.A.A	Protons	Chem. Shift of P.P.M (τ)	Proton per mol. cal. from Spect.	EO	$EO_{av.}$
IMPURE NON-IONICS					
A_{10}	C_2H_4	6.4 (2)	125	12.3	-
A_{18}	<	6.4 (8)	130	22.3	-
A_{30}	<	6.5	168	52	-
A_{60}	<	6.4 (9)	294	73	-
PURIFIED NON-IONICS					
Spect.s					
A_{10}	C_2H_4	6.5 6.4 (8)	97 100	9.65 8.6	9.6
A_{18}	<	6.4 (6) 6.5	107 116	18.1 17.5	17.8
A_{30}	<	6.4 (6) 6.4 (8)	174 170.5	30.6 30	30.3
A_{60}	<	6.5 6.4 (9)	150.5 133	60.8 60.1	60.45

CHAPTER VIII - Thermodynamics of Micellization

VIII.Ia - The theory of micelle formation

It is universally accepted that energy changes occur with micelle formation. However, details of the micellization process are not clearly known. The thermodynamics of micelle formation have been discussed from two stand points. Both approaches introduce familiar macroscopic treatments of micelles. The thermodynamic analysis of micellization is usually performed, in terms of a dynamic equilibrium between monomers and micelles.

In view of monomer - micellar equilibrium, the thermodynamic description of micellar solutions have been examined by means of mass action, and phase separation approaches as follows;

A_o Phase Separation Model

In this approach the micelles have been considered as constituting a distinct phase in a solution by Stainsby-Alexander(146), Matijevic-Pethica(294), and Hutchinson et al.(295,296). The phase change is assumed to occur at C_o.

The equilibrium between surfactant ions S_i^+, counter ions C_i^-, and micelles M can be written by the relation

$$NS_i^+ + NC_i^- \rightleftharpoons M \qquad \text{VIII.i.1}$$

treating the micelle, charged monomer, and equivalent number of counter ions bound to the micelle as a separate phase(297). The above expression takes the form for standard free energy of micellization (per mole of monomer)

$$\Delta G_{Mp} = - \frac{RT}{N} \ln \frac{F_M(M)}{F_{S_i}{}^N (S_i^+)^N (F_{C_i}{}^-)^N} \qquad \text{VIII-1}$$

The concentration of S_i^+ is equal to C_o when the micellar phase is present. The expression (VIII.i.1) can be rewritten by the following expression, taking into account the standard state of S_i^+ in micellar phase, Fm and (M) which are equal to unity

$$\Delta G_{Mp} = RT \ln f_{\pm}^{2} (C_o)(C_i) \qquad \text{VIII-2}$$

where $f_{\pm}$ is defined by $(F_{S_i}/F_{C_i})^{\frac{1}{2}}$. Since $f_{\pm}^{2}$ is close to unity in the absence of salt, the free energy of micellization can be given by the equation

$$\Delta G_{Mp} = 2RT \ln C_o \qquad \text{VIII-3}$$

when expression (VIII.i.1) is combined with the Gibbs-Helmholtz equation

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2} \qquad \text{VIII-4}$$

The standard enthalpy of micellization can be derived as follows,

$$\Delta H_{Mp} = -RT^2 \frac{d}{dt}\left[\ln f_{\pm}^{2} (C_o)(C_i^-)\right] \qquad \text{VIII-5}$$

then the standard entropy of micellization can be obtained from

$$\Delta S_{Mp} = (\Delta H_{Mp} - \Delta G_{Mp})/T \qquad \text{VIII-6}$$

Since the free energy of micellization is zero under equilibrium condition, the entropy change is given by

$$\Delta S_{Mp} = \Delta H_M/T \qquad \text{VIII-7}$$

The basic assumption of this approach is that the monomer activity remains constant above C_o. This model has been modfied for ionic systems by Shinoda-Hutchinson(296), treating the micelles as a charged phase.

However the phase change has been treated as the separation of the colloidal electrolyte itself, in a dispersed form from the dispersion medium by Hutchinson et al.(295) and Stainsby-Alexander (146). Matijevic-Pethica (294) have considered that the micelles do not simply consist of the monomer alone; the micelles include also the components such as H_3O^+, and OH^- from water phase, and water molecules themselves. Their argument also allows the fact that the micellar phase will include the electrical double layer, since it is electrically neutral.

B_o Mass Action Model

This modal has considered micellization as the reversible formation of a large aggregate. The law of mass action has been applied by Jones-Bury(298), Hartley(143), Murray-Hartley(299), Vold(300) and Phillips(301) to the micellization in terms of considering the micelle as the reaction product. The equilibrium between the micelles and monomer can be written by the expression(297)

$$NS_i^+ + (N-z)C_i^- \rightleftharpoons M^{+z} \qquad \text{VIII.i.2}$$

The standard states of the various ionic species have been considered in a way that the mole fractions are unity. The thermodynamic equilibrium can be defined by the relation

$$K_m = \frac{F(M^{+z})}{(S_i^+)^N \, (C_i^-)^{N-z}} \qquad \text{VIII.8}$$

where $F = Fm/F_{S_i}^{\,N} \; F_{C_i}^{\,N-z}$.

If the value of F in the above equation is reasonably constant, K_m can be rewritten as follows

$$K_m = \frac{M^{+z}}{(S_i^+)(C_i^-)^{N-z}} \qquad \text{VIII-9}$$

The standard free energy per mole of monomeric surfactant ions (micellization) can be defined, in combination with expression (VIII.i.2) as follows(297),

$$\Delta G_{Mb} = - \frac{RT}{N} \ln K_m = - \frac{RT}{N} \ln \frac{F(M^{+z})}{(S_i^+)\,(C_i^-)^{N-z}} \qquad \text{VIII-10}$$

when N is larger, there is no added salt, and the value of C_o is used, the equation (VIII-10) takes the form with the approximations of

(S_i^+) and (C_i^-) by C_o and neglecting $(^1/N)\ln F(M^{+z})$

$$\Delta G_{Mb} = (2-z/N)RT \ln C_o \qquad \text{VIII-11}$$

when the micelles have zero charge (e.g. z is zero) the equation reduces to

$$\Delta G_{Mb} = 2RT \ln C_o \qquad \text{VIII-12}$$

In this approach the total number of moles at the C_o is equal to the sum of moles of micelles, free counter ions, water and surfactant ions. If no counter ions are bound to the micelle the equation becomes

$$\Delta G_{Mb} = RT \ln C_o \qquad \text{VIII-13}$$

Vold(300) has considered a series of equilibria between monomer and all possible micellar species, in terms of a series of equilibrium constants. This approach has an advantage because of N is fixed for each micellear species. Due to this fact, it can be also applied to multicomponent micelles.

Besides the described approaches Aranow(302), Hoeve-Benson(130) and Poland-Scheraga(145,303) have treated micelle formation within the framework of statistical mechanics. The application of this method to the micellization is more difficult because of the ionic solvation, and counter ion binding.

VIII.Ib - Standard free energy, enthalpy and entropy effects in micellization

Different views have been given by several authors(143,144,146,304) for micelle formation. However, the magnitude of standard free enegy change for micelle formation, can be evaluated by taking into account the monomer contributions to the micellization.

The hydrocarbon chain contribution can be derived by its arbitrary partition into hydrocarbon and electrical parts(297). Since electrical work is involved in micelle formation (Fel), which is positive, one can calculate the contribution of the hydrocarbon part Fch, subtracting the value of Fel from ΔG_M.

If the obtained value of Fch is compared with the free energies of transfer of hydrocarbons from aqueous to another region, it can provide the hydrocarbon chains role in the micelle formation.

Overbeek-Stigter(305) have observed Fel for a spherical micelle, taking into account its electrical double layer. They have also included the assumption that the charge of micelle is smeared out over its surface.

Emerson-Holtzer(306) have calculated that the contribution of dodecyl group (Fch) to micellization is of the order of -14.5 RT. On the other hand, Wishnia(307) has examined the solubility of hydrocarbons in surfactant solution, in terms of hydrophobic interactions. According to his investigation the hydrocarbon contribution to the free energy of micelle formation is in the range of -12.0 RT to -18.2 RT.

Mukerjee(308) has observed that the free energy change per $-CH_2-$ group (-1.15 RT = -0.68 K cal/mole), when a hydrocarbon chain is transferred from aqueous surroundings to the micelle, is close to the free energy change of transfer to the hydrocarbon solution (-1.39 RT = -0.825 K cal/mole).

In view of this fact he has concluded that the free energy change per $-CH_2-$ group, on transfer from aqueous to the nonpolar region (micelle) is due to the interaction of the organic chains between themselves. According to his view, the tendency of hydrocarbon chains of the monomers to associate with each other, reducing the extent of contact with water molecules causes the formation of micelles.

The free energy change per $-CH_2-$ group (1.08 RT) for short chain alcohols, has been examined by Shinoda in terms of the solubility of alcohols(178). In view of these observations one can assume that a "rule of four" appears better, on complete transfer from aqueous solution to the hydrocarbon environment than the "rule of three",(308).

On the other hand, the transfer free energy to a hydrocarbon-water interface(309,310), is 1.37 RT (0.810-0.82 K cal/mole). The effect of the hydrophilic nature of the polar head group, on the free energy of transfer of $-CH_2-$ group from an aqueous solution to nonpolar environment, has been examined by Adderson-Taylor(311). The energy change involved on transfer of $-CH_2-$ group ranges from -1.06 RT to -1.53 RT.

Since the enthalpy and entropy are related to the free energy by the expression,

$$G = H - TS$$

The evaluation of changes in these quantities, which occur during the micelle formation, provide important information about the role of participants in the process. A small negative enthalpy effect has been observed by Stainsby-Alexander(146), on examining heat effects involved in aggregation. They have assumed that the main factor involved in the aggregation of hydrocarbon chains in aqueous solution is the change in the hydrocarbon-water interface.

In their opinion(146), the hydrocarbon chains of surfactant ions surrounded by water molecules are curled up. Because of this fact the internal motions of monomers are considerably restricted, while the hydrocarbon chains of monomers are more flexible, and extended position in the micelle. The changes in enthalpy effects and entropy have been attributed to the internal motions of the monomers in the micelle formation.

The heats of micelle formation of several paraffin chain salts have been investigated by Goddard et al.(129). According to their observation the structural effects exist in water surrounding ions during the micellization process. The obtained small enthalpy of micelle formation, has been interpreted by the iceberg concept introduced by Frank-Evans(4).

However the decrement in structural order of water molecules, contributes a small positive contribution to the entropy change involved in the micelle formation. When the temperature is increased micellization becomes enthalpic in nature, due to the negative enthalpy, which arises from the loss of translational energy of monomer, and when hydrocarbon chains condense.

The change in sign of ehthalpy between 20°-40° for ionic surfactant, have been attributed to the structural melting of icebergs around the nonpolar parts of surfactant ions(128,312). On the other hand, micelle formation has been investigated in terms of hydrophobic interactions(145,179,308). In this approach the aggregation of hydrocarbon chains due to hydrophobic interactions with ordered water molecules, cause an increase in entropy. The decrement in the structural order of water molecules is one of the possible explanations for an entropy increase.

Aranow-Witten(89) have discussed the entropy effect of hydrocarbons, on transferring from a state of internal torsional oscillation, to the state of hindered internal rotation, neglecting the changes in water structure.

VIII.Ic - Thermodynamics of micellization of alkylammonium bromides in water.

The thermodyanmic properties of micelle formation in aqueous solution of alkylbromides, has been examined using micro calorimetry at 25°C as described in this chapter. The standard free energy change involved during the micellization, has been observed in terms of the following relation

$$\Delta G_M = RT \ln C_o$$

Since the standard free energy of micellization depends on the concentration unit used, and on the choice of standard state, the hypothetical standard state of unit mole fraction referred to the infinitly dilute solution has been adopted. As can be seen in Fig.VIII.1

and Table VIII.I.1 ΔG_M of micellization decreases as the chain length increases. (-4.0 K cal/mole and -4.8 K cal/mole for C_{10} and C_{12} respectively).

The standard free energy change involved due to the transfer of the hydrocarbon molecule from one state to another, has been attributed to the entropy effect rather than the potential energy by Aranow-Witten(89). However the decrement in ΔG_M has been discussed by Corkill et al.(304), in terms of the elimination of interfacial interaction between the monomers and water molecules, or decrement in hydrocarbon water interface.

Poland-Sheraga(145,157) introduced the idea that the free energy of the micellar system has three contributions such as, a, the external free energy of micelle, b, the free energy due to the hydrophobic interactions between structural water and monomer, and c, the energy due to the decrease in hydrophobic association during the micellization (internal free energy).

In addition to these factors Emerson-Holtzer(179) and Poland-Sheraga(157) have also considered the contribution of electrostatic free energy, and a free energy arising from the solvation of the charged head group. Since the aggregation is an energy effect, which results from the elimination of hydrocarbon-water interface in micelle formation, it is reasonable to introduce the idea that the major factor of change in the standard free energy during the micellization, is due to the release of energy because of the decrement in structural order of water molecules around the monomers, and transferring of the monomer to the nonpolar environment, which is thermodynamically favourable for nonpolar solutes.

In this critical state micelles occur at a certain concentration changing the collective properties of surfactant ions in solution. The change in standard free energy per $-CH_2-$ group on transferring from aqueous solution to micellar region has been found -0.5 K cal/mole, which is lower compared with the values given in literature(313,314) (-0.8 - 0.9 K cal/mole). In this observation, as it can be seen ΔH_M decreases (-0.65 K cal/mole and -1.4 K cal/mole for C_{10} and C_{12} respectively. Fig.VIII.2, Table VIII.I.1 as the ΔG_M decreases). The effect of increase in total hydrocarbon content to the ΔH_M, has been discussed by Corkill et al.(304), in view of exothermic process rather than endothermic. The enthalpic contribution to micellization has been discussed by Adderson-Taylor(313) in terms of three factors which are,

a_1 - the aggregation of charged head groups,

b_1 - decrement in structural order of water molecules, and

c_1 - the transfer from polar environment to nonpolar region (micelle).

Besides these factors, the increase in kinetic energy of the monomer, the release of heat when the hydrocarbon chains condense in micelle, and the loss of translational energy of surfactant ions can be introduced as possible reasons for the negative(297,314) ΔH_M.

Poland-Scheraga(157) have concluded that the reaction such as,

free charged monomer → charged monomer in a micelle is accompanied by a large negative enthalpy change due to the change in water structure around the charged head groups, when the above reaction occurs. They have also taken into account the effect of charge on water structure. The observed enthalpic contribution (-0.34 K cal/mole per methylene group) to the free energy change of micellar system is close to the value given by Benjamine(315) for aliphatic alcohols (0.590 K cal/mole).

The change in entropy during the micellization, compared with the free energy change per monomer is not significant (3.35 K cal/mole and 3.4 K cal/mole for C_{10} and C_{12} respectively), and is lower compared with the value given by Barry et al.(314) for impure alkylammonium bromides.

(9.1 K cal/mole and 7.4 K cal/mole for C_{12} phase separation and mass action models respectively).

The abnormal solubility of small nonpolar solutes (rare gases), and small hydrocarbons in aqueous solution has suggested the idea that these solutes increase the structuring of water molecules. The formation of these structural regions, has been interpreted by the term "icebergs", which leads to a loss of entropy.(11), The transfer of nonpolar solute from an aqueous region to nonpolar environment, decreases the ordered structure of water molecules, and consequently a positive entropy change occurs. The other entropy effect is due to the increase in flexibility of hydrocarbon chains in nonpolar region(89).

However the temperature variation of the C_o, and direct calorimetric measurements have shown that(129;315,318) the entropy change plays a unique role in micelle formation. The positive entropy changes that accompany micelle formation, can be attributed to the greater freedom of rotation of hydrocarbons in micelle than in polar medium, and the hydrophobic interactions between monomers and water molecules make a positive contribution to the entropy(129,318) of micellization. On the other hand, the loss of hydration(319) of monomer when it is transferred from an aqueous region to the micellar state, is also responsible for the positive ΔS_M of micellization.

VIII.Id - Experimental Procedure.

The calorimeter vessel consisted of a Dewar flask cemented to a flange to which the head of the Dewar flask could be bolted. An O-ring was used to produce a water tight seal between the head and flange. The calorimeter was immersed in a water bath, the temperature of which was controlled by a regulator to ± 0.01°C. Cold water passing through a copper cooling coil controlled by a needle valve was used to provide a constant leak for the water bath, which was housed in an air thermostat controlled to ± 1°C. The off balance current from the bridge was amplified using a Pye D.C. amplifier (Cat.No.11370), and displayed on a Sunvic d.c. recorder.

Current from a 2V accumulator bank was fed via a 100 ohm resistance through a standard 1 ohm resistance. The voltage across the standard resistance in the calorimeter circuit was measured with a Pye potentiometer, and it was used to check the resistance of the heating coil, and to calculate the current passed through the heating coil in the circuit. The calorimeter was capable of detecting heat changes of ~ 0.01 cal.

The calorimeter was calibrated in terms of the heating coil in series with standard 1 ohm resistance by measuring the heat of sodium chloride solution at 25°C. In order to measure the heat of 1M NaCl solution, 150 ml double distilled water was placed in the Dewar vessel, than the more concentrated NaCl solution in the mixing device, which was sealed at the bottom with silver foil and attached to the breaking mechanism by means of a screwed brass collar. Following this procedure the stirring motor was put into operation. Due to the stirring effect, at the beginning the recorded curve was not linear. After temperature equilibrium was reached (linear relation on the curve), the solution of NaCl (concentrated) was mixed with 150 ml water so that the concentration of final solution of NaCl is 1M. When the solution was mixed with the solvent the slope of curve on the recorder increased, then forming a small plateau, kept constant. Following this process (thermal equilibrium) the current was turned on to the heating coil. The slope of curve increased until the current was switched off. The time was recorded, and the potential drop across a standard resistance and heating coil was measured by potentiometer. After that with 15 minutes thermal equilibrium intervals the same procedure was repeated increasing the time of flow of the current in the circuit.

The work of stirring which is negative, and can be written in terms of the first law of thermodyanmics as follows

$$\Delta H = Q - \omega_s \qquad \text{VIII-14}$$

where Q is equal to the electrical energy dissipated in the resistor (heating coil) due to the current I for time t (in sec.). In this work, the heat of stirring, and the dilution of solution are assumed negligible, then the equation becomes

$$\Delta H = Q \qquad \text{VIII-15}$$

On the other hand it was considered that the resistance of the heating coil was constant throughout all the different heating periods of the solution. If the resistance of heating coil is constant and it is in series with the standard resistance, then with the measurement of potential drop across the two resistances, one can write the electrical work by the relation

$$\Delta H = \frac{R_H}{R_S^2} \int E_p^2 \, dt \qquad \text{VIII-16}$$

when the resistance is in ohms, potential in volts and time in seconds. The work given by the equation is in joules. It is converted to caloric by dividing by 4.184 joule. Since the heat input was dissipated in the system, the corresponding heat per molecule can then be calculated. The calculated heats of the solution at different time intervals were plotted against the time in sec. The slope of the curve, which was linear is the increment in heat of the solution per second, due to the heat input. The obtained curve was extrapolated to zero. The intercept on the ordinate gives the heat of the solution of 1M NaCl at 25°C (0.90 K cal/mole), which is in a good agreement with the value given in literature (320).

The same procedure was applied for the measurement of heat of the micellization of cationic and non-ionic surfactant when 20 ml of concentrated cationic solution was mixed with 150 ml double distilled water after 15 minutes thermal equilibrium (at 25°C). The slope of the curve on the recorder decreased, which is an indication of exothermic heat involved in the solution. After a certain time, the current was turned on, then the slope of curve reached its original slope (before mixing) then it increased until the current was switched off.

In the case of non-ionic surfactants the behaviour was different. When the same quantity (in ml) was mixed, after a certain equilibrium time, the slope of the curve on the recorder increased (endothermic) then making a small plateau kept unchanged until the current was turned on, the same procedure was applied to calculate the heat of micellization of both surfactants in aqueous solution at 25°C using equation (VIII-16), and plotting heat of the solutions, which were obtained in terms of the dissipation of heat, produced by known current at different time intervals, against the time in seconds. (Table VIII.I.1, Fig. VIII.1).

VIII.Ie - Application of small system thermodynamics to micellization of non-ionic surfactants.

Hill(231) has introduced an important new area of thermodynamics employing small systems. This approach is significant for analysis of micellization. The small system thermodyanmics considers the degree of association of the monomers in micellar state, and subdivision potential in a way that can be easily applied to micellization (322).

The advantage of using small system thermodyanmics to micelle formation over alternative approaches (such as mass-action and phase-separation) is that the actual intrinsic thermodyanmic functions of micelles can be discussed. In view of this approach the aggregation number as an thermodynamic variable, and the variations in the thermodynamic functions of micelle formation can be examined in terms of the degree of association of monomers, and the concentration of micelles.

The thermodynamic functions of micelle formation can be discussed as follows in view of the small system thermodynamics introduced by Hill. Consider a non-ionic monomer as single component (a), and the solvent (water) as component (b) at equilibrium

$$\mu_a^{s} = \mu_a^{m} = \mu_a \qquad \text{VIII-17}$$

and this relation takes the form for transition between equilibrium states

$$d\mu_a^{s} = d\mu_a^{m} \qquad \text{VIII-18}$$

The chemical potential of component (a) can be defined taking into account the standard chemical potential of component a and its activity coefficient by the relation

$$\mu_a^{s} = \mu_a^{os} + kT \ln x_a^{s}\, Ce_a^{s} \qquad \text{VIII-19}$$

then it takes the form in terms of temperature variation

$$d(\mu_a^{s}/T) = d(\mu_a^{os}/T) + kd \ln x_a^{s}\, Ce_a^{s} \qquad \text{VIII-20}$$

The above equation can be rewritten taking into account the temperature variation of the enthalpy and volume per monomer of component (a) at standard state such as,

$$d\left(\frac{\mu_a^{s}}{T}\right) = -\left(\frac{h_a^{os}}{T^2}\right) dT + \left(\frac{V_a^{os}}{T}\right) dp_1 + kd \ln x_a^{s}\, Ce_a^{s} \qquad \text{VIII-21}$$

on the other hand, at micellar state we have

$$d\left(\frac{\mu_a^{m}}{T}\right) = -\left(\frac{\mu_a^{m}}{T^2}\right) dT + \left(\frac{d\mu_a^{m}}{T}\right) \qquad \text{VIII-22}$$

The relation (VIII-22) can be defined in terms of $T, p, \bar{N}$ as follows

$$d\mu_a^{m} = - S_a^{m}\, dT + V_a^{m}\, dp + \left(\frac{\partial \mu_a^{m}}{\partial \bar{N}}\right)_{T,p} d\bar{N} \qquad \text{VIII-23}$$

where

$$S_a^{m} = \left(\frac{\partial \bar{S}}{\partial \bar{N}}\right)_{T,p} = - \left(\frac{\partial \mu_a^{m}}{\partial T}\right)_{\bar{N},p}$$

$$V_a^{m} = \left(\frac{\partial \bar{V}}{\partial \bar{N}}\right)_{T,p} = \left(\frac{\partial \mu_a^{m}}{\partial p}\right)_{T,\bar{N}}$$

The equation (VIII-23) can be rearranged taking into account the enthalpy per monomer of micelle, volume and average property of a small system (micelle)

$$d\left(\frac{\mu_a^m}{T}\right) = -\left(\frac{h_a^m}{T^2}\right) dT + \left(\frac{V_a^m}{T}\right) dp + \frac{1}{T}\left(\frac{\partial \mu_a^m}{\partial \bar{N}}\right)_{T,p} d\bar{N} \qquad \text{VIII-24}$$

where

$$h_a^m = \mu_a^m + TS_a^m$$

Substituting equation (VIII-21) into equation (VIII-24) it takes the form

$$-\left(\frac{h_a^m - h_a^{os}}{T^2}\right) dT + \left(\frac{V_a^m - V_a^{os}}{T}\right) dp + \frac{1}{T}\left(\frac{\partial \mu_a}{\partial \bar{N}}\right) d\bar{N} = k d \ln x_a^s Ce_a^s \qquad \text{VIII-25}$$

first term of equation (VIII-25) can be defined in terms of the temperature dependence of activity coefficient of monomer at pressure p, the variation of chemical potential of monomer depending on $\bar{N}$ at T,p and the temperature dependence of the average property of micelle at pressure p by means of the relation,

$$\left(\frac{h_a^m - h_a^{os}}{T^2}\right) = -k\left(\frac{\partial \ln x_a^s Ce_a^s}{\partial T}\right)_p + \frac{1}{T}\left(\frac{\partial \mu_a}{\partial \bar{N}}\right)_{T,p}\left(\frac{\partial \bar{N}}{\partial T}\right)_p \qquad \text{VIII-26}$$

on the other hand the second term of equation (VIII-25) can be introduced in the same way taking into account the pressure (p) dependence of above quantities mentioned in equation (VIII-26)

$$V_a^m - V_a^{os} = kT\left(\frac{\partial \ln x_a^s Ce_a^s}{\partial p}\right)_T - \left(\frac{\partial \mu_a}{\partial \bar{N}}\right)_{T,p}\left(\frac{\partial \bar{N}}{\partial p}\right)_T \qquad \text{VIII-27}$$

VIII-28

If an equation $\mu_a = \mu_a^{os} = kT \ln x_a^s Ce_a^s$ is substituted into equation (VIII-26) the following relation is obtained

$$S_a^{m} - S_a^{os} = - kT \left(\frac{\partial \ln x_a^{s} Ce_a^{s}}{\partial T}\right)_p + \left(\frac{\partial \mu_a}{\partial \bar{N}}\right)_{T,p} \left(\frac{\partial \bar{N}}{\partial T}\right)_p - k \ln x_a^{s} Ce_a^{s} \qquad \text{VIII-29}$$

Alternatively with the relation given for the small systems in a solvent,

$$0 = - \bar{S}\, dT + \bar{V}\, dp - \sum_{a=1}^{c} \bar{N}_a\, d\mu_a^{m} - d\varepsilon_m \qquad \text{VIII-30}$$

and with equation (VIII-29) the following relation can be given by an equation for a single component micelle

$$d\mu_a^{m} = - \left(\frac{\bar{S}}{\bar{N}}\right) dT + \left(\frac{\bar{V}}{\bar{N}}\right) dp - \frac{d\varepsilon_m}{\bar{N}} \qquad \text{VIII-31}$$

$$\frac{d\mu_a^{m}}{T} = - \frac{\mu_a^{m} dT}{T^2} - \frac{\bar{S}}{\bar{N}T}\, dT + \frac{\bar{V}}{\bar{N}T}\, dp - \frac{d\varepsilon_m}{\bar{N}T} \qquad \text{VIII-32}$$

The average enthalpy, entropy and free energy relation of the small system can be defined in terms of average properties of micelles and subdivision potential of micelles, such as

$$\bar{H} - T\bar{S} = \bar{F} = \bar{N}\mu_a^{m} + \varepsilon_m \qquad \text{VIII-33}$$

$$\frac{\bar{H}}{\bar{N}} - \frac{\varepsilon_m}{\bar{N}} = \mu_a^{m} + \frac{T\bar{S}}{\bar{N}} \qquad \text{VIII-34}$$

substituting this expression into equation (VIII-32) the following equation is obtained

$$d\left(\frac{\mu_a^{m}}{T}\right) = - \frac{\bar{H}}{\bar{N}T^2}\, dT + \frac{\bar{V}}{\bar{N}T}\, dp - \frac{1}{\bar{N}}\, d\left(\frac{\varepsilon_m}{T}\right) \qquad \text{VIII-35}$$

puting $\bar{H}/\bar{N} = h_a^{+}$, $\bar{S}/\bar{N} = S_a^{+}$, $\bar{V}/\bar{N} = V_a^{+}$ and $\bar{F}/\bar{N} = F_a^{+}$ and equation equation (VIII-35) with equation (VIII-21) the following relation is obtained

$$- \left(\frac{h_a^{+} - h_a^{os}}{T^2}\right) dT + \left(\frac{V_a^{+} - V_a^{os}}{T}\right) dp - \frac{1}{\bar{N}}\, d\left(\frac{\varepsilon_m}{T}\right) = kd\, x_a^{s} Ce_a^{s} \qquad \text{VIII-36}$$

and substituting $\varepsilon_m/T = - k \ln x_m$ into equation (VIII-36) it takes the form

$$-\Delta H_a = -(h_a^{+} - h_a^{os}) = kT^2 \left(\frac{\partial \ln x_a^s \, Ce_a^s}{\partial T}\right)_p - \frac{kT^2}{\bar{N}} \left(\frac{\partial \ln X_m}{\partial T}\right)_p \qquad \text{VIII-37}$$

$$\Delta V_a = (V_a^{+} - V_a^{os}) = kT \left(\frac{\partial \ln x_a^s \, Ce_a^s}{\partial p}\right)_T - \frac{kT}{\bar{N}} \left(\frac{\partial \ln x_m}{\partial p}\right) \qquad \text{VIII-38}$$

$$\bar{N} = \left(\frac{\partial \ln x_m}{\partial \ln x_a^s Ce_a^s}\right)_{T,p} \qquad \text{VIII-39}$$

and the entropy and free energy of micellization can be defined by an equations

$$\Delta F_a = (F_a^{+} - F_a^{os}) = kT \ln x_a^s \, Ce_a^s - \frac{1}{\bar{N}} kT \ln X_m \qquad \text{VIII-40}$$

$$\Delta S_a = (S_a^{+} - S_a^{os}) = -kT \left(\frac{\partial \ln x_a^s Ce_a^s}{\partial T}\right)_p + \frac{kT}{\bar{N}} \left(\frac{\partial \ln X_m}{\partial T}\right) \qquad \text{VIII-41}$$

$$-k \ln x_a^s \, Ce_a^s + (k/\bar{N}) \ln X_m$$

Since V_a^{os} and h_a^{os} are functions of T,p any changes in the left side of equations (VIII-37) and (VIII-38) at constant T,p can be defined by the corresponding changes in h_a^{+} and V_a^{+}. The variation of enthalpy and volume of micellization with mole fraction of micelles is defined by the relation

$$\left(\frac{\partial \Delta H_a}{\partial \ln X_m}\right)_{T,p} = \frac{k\,T^2}{\bar{N}^2} \left(\frac{\partial \bar{N}}{\partial T}\right)_{X_m,p} \qquad \text{VIII-42}$$

$$\left(\frac{\partial \Delta V_a}{\partial \ln X_m}\right)_{T,p} = \frac{kT^2}{\bar{N}^2} \left(\frac{\partial \bar{N}}{\partial p}\right)_{T,X_m} \qquad \text{VIII-43}$$

At constant T and p, at equilibrium from equation (VIII-30) the variation of chemical potential of monomer of component (a) with $\bar{N}$ can be defined in terms of the reciprocal relation of the average property of micelles and the variation of subdivision potential of micelles with $\bar{N}$ such as,

$$\left(\frac{\partial \mu_a}{\partial \bar{N}}\right)_{T,p} = - \frac{1}{\bar{N}} \left(\frac{\partial \varepsilon_m}{\partial \bar{N}}\right)_{T,p} \qquad \text{VIII-44}$$

and on the other hand the chemical potential of monomer can be given in terms of chemical potential of monomer at standard state and its mole fraction

$$\mu_a^{s} = \mu_a^{os} + kT \ln x_a^{s} \qquad \text{VIII-45}$$

and this relation (VIII-45) can be rewritten by means of

$$\left(\frac{\partial \bar{N}}{\partial \mu_a}\right)_{T,p} = \left(\frac{\overline{N^2} - \bar{N}^2}{kT}\right) \qquad \text{VIII-46}$$

an equation is obtained

$$\left(\frac{\partial \bar{N}}{\partial \mu_a^{s}}\right)_{T,p} = \frac{\overline{N^2} - \bar{N}^2}{x_a^{s}} \qquad \text{VIII-47}$$

and it takes the following form with equation (VIII-23)

$$\left(\frac{\partial x_a}{\partial x_a^{s}}\right)_{T,p} = \frac{x_m \bar{N}}{x_a^{s}}$$

If $xt = (x_a^{s} + \bar{N}_{x_m})$ is total concentration of surfactant then the fraction of total surfactant (fa) goes into monomeric form can be defined by

$$fa = \left(\frac{\partial x_a^{s}}{\partial x_t}\right) ; \quad 1\text{-}fa = \left(\frac{\partial \bar{N} x_m}{\partial x_t}\right)_{T,p} \qquad \text{VIII-48}$$

If above expressions are combined, the following relation is obtained

$$\frac{1\text{-}fa}{fa} = \left(\frac{\partial x_m \bar{N}}{\partial x_a^{s}}\right)_{T,p} \qquad \text{VIII-49}$$

The approach mentioned in this section on small systems in a solvent, concerns solutions which are so dilute that they do not interact. But in view of this observation a question arises as to how a small system can be defined. In fact it is purely a matter of convenience whether the aggregate formation can be considered explicitly. As has been discussed above, the non-ionic surfactant system can be treated as a two component solution consisting of non-ionic surfactant plus water in terms of activity coefficients.

In view of this treatment, the change in the thermodynamic properties of micelles can be discussed with aggregation number, and the concentration of monomer.

VIII.If - Thermodynamics of micellization of polyoxyethylene mono hexadecyl ethers in waters.

Benjamine(315) has measured the partial molal enthalpy values of a series of dimethyl-n-alkylamine oxides in water. He has found that the partial molal free energy decreases with increasing chain length, and the partial molal enthalpy of the micellization is positive, and it decreases with chain length studied. The positive values ofenthalpy have been interpreted in terms of hydrophobic bonding present during the micellization. The positive entropy increase has been introduced with the concept of releasing of order of water molecules associated with the monomer during the micellization process. The enthalpy and entropy contributions to the micelle formation has been estimated as -140 cal/mole of $-CH_2-$ group + 2.9 e.u.

Hermann(323) has studied the heat of micellization of n-dimethyl-dodecylamine oxide from the temperature variation of C_0 determined by light scattering. He has observed that the heat and entropy of micellization are positive, and remain positive over the temperature range 1-50°. The positive entropy change has also been discussed with the change in solution. The value for enthalpy of micellization (1.9 K cal/mole) is lower than found by Benjamine (2.6 K cal/mole).

Corkill et al.(319) have investigated the thermodynamics of micellization of the alkylsulphinylakanols. They have shown that the additional methylene group away from the head group contributes a decrement in enthalpy as the additional methylene group in the head group gives an increase in enthalpy. The increment in entropy has been interpreted by the solvation of head group causing the losses of ordered water molecules. They have also observed that the extent of the hydration of the head group decreased as the temperature increased.

Corkill et al.(304) have shown,that the free energy, and enthalpy of the micellization of alkyltrimethyl ammonium alkyl sulphates are linear functions of the total alkyl chain length. The increment in enthalpy per $-CH_2-$ group has been discussed in terms of the major contribution to the free energy increment. According to their view, the process of micellization is promoted due to the cohesive forces between water molecules, which extrude the hydrocarbon chain, and the heat and entropy changes are due to solvent reorientation.

The increment in free energy of micellization per $-CH_2-$ group has been interpreted(304) by means of the elimination of a fraction of the monomers hydrocarbon-water interface which causes the minimization of interfacial free energy. Although the electrical contribution to the free energy of micellization is a second order effect, the minimization in interfacial energy has been discussed as the driving force for micellization.

Corkill et al.(319) have also examined the thermodynamics of a homologous series of polyoxyethylene surfactants. They have shown that the positive heat of micellization increases with increasing ehtylene oxide chain length, and the micellization is governed by the gain in positive entropy associated with the transfer of the monomer from an aqueous environment to the micelle.

Schick(324) has investigated the thermodynamics of micellization of non-ionic surfactants (ethylene oxide condensates of n-dodecanol and n-hexadecanol) in aqueous solution. The partial molal entropy change which occurs on micelle formation has been attributed to the desolvation, or increment in the configurational entropy of surfactant moonomers. The enthalpy contribution to the free energy increment in the micellization of n-alkylhexaoxyethylene glycol monoethers has been discussed in terms of the change in cohesional energy of the hydrocarbon chain on micellization, and the release of energy associated with the reformation of hydrogen bonds in solvent molecules.

Elworthy-McDonald(325) have shown that the positive differential entropy is due to a mixing process of water molecules around the polyoxyethylene chains. They have also concluded that the mixing process is considerable at higher temperatures.

Moroi et al.(326) have investigated the contributions of hydrophobic, and hydrophilic groups to the enthalpy of micellization of sodium alkyl sulphates with the chain length from C_8 to C_{14}, and polyoxyethylene oxide surfactant containing different numbers of ethylene oxide units. They have shown that although the hydrophilic group has a major contribution at low temperature, it gives a minor contribution at higher temperature. The hydrophilic part of enthalpy is positive and it shows a minimum at 35°C, while the hydrophilic part of enthalpy is negative. It decreases with increasing temperature. They have also discussed that the water molecules around the hydrophilic group have a great effect on C_0. In the case of non-ionic surfactants, the hydrophilic part of enthalpy makes a major contribution to the enthalpy of micellication resulting in a positive enthalpy change. The positive partial molal enthalpy and entropy have also been discussed(129) as being concerned with water structure surrounding the monomer hydrocarbon chains.

The thermodynamics of micellization of polyoxyethylene hexadecyl mono ethers were studied using micro calorimetry at 25°C as described in the previous section. The free energy of micellization decreases with increasing exthylene oxide units (-8.2 K cal/mole, -9.0 K cal/mole for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively Table VIII.I.1,

Fig.VIII.3). The free energy change involved in the micelle formation has an entropy origin rather than the potential energy, and it also has a contribution from the enthalpy of micellization.

The enthalpy of micellication increases with decreasing free energy (7.2 K cal/mole and 8.85 K cal/mole for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively). The enthalpy contribution to free energy change 34 cal/mole Table VIII.I.1 while the entropy contribution is 50 cal/mole the decrement in free energy per (CH_2-CH_2-O) group is -20 cal/mole which is smaller in magnitude compared with-0.5 K cal/mole per CH_2 group. This is due to the opposing effects of the alkyl and ether units in the head group. On the other hand the hydrocarbon free energy was derived from the extra polation of the enthalpy - EO unit curve to zero, which is-6.86 K cal/mole Fig.VIII.3.

The increase in entropy which occurs on micellization can be discussed in terms of water molecules surrounding a hydrocarbon chain, and aggregation of the monomers. The structure of water molecules increases near nonpolar groups. In this stage water molecules are more highly hydrogen bonded than in bulk water having a state of lower entropy. The aggregation of nonpolar groups causes the melting of water clusters, consequently the entropy of the system increases. This process is typical hydrophibic interactions because it is an entropy derived process. The release of energy due to reorientation of water molecules, the decrement in solvation because of minimization of water hydrocarbon interface contributes an increase in entropy. At this state, the removal of aggregated monomers to a nonpolar environment micelles are formed. Enthalpy and entropy of micelle formation are positive, showing that the micellization is governed by the gain in entropy.

VIII.Ig - Conclusions.

Thermodynamic properties of micelle formation in aqueous solution of alkylammonium bromides and polyoxyethylene monohexadecyl ethers were examined at 25°C using a microcalorimeter. In this work it has been observed that ΔG_M decreases with a decrease in enthalpy. The decrement in ΔG_M has been discussed in terms of hydrophobic interactions between monomers, and water icebergs. The reduction in structural order of water molecules due to a minimization of hydrocarbon water interface, and transferring of monomer from aqueous region to nonpolar environment reduce the free energy of system.

However, according to this observation a decrement in ΔH_M accompanied with the standard free energy change, has been attributed to the change in translational energy of monomer, water molecules, and the effect of charged hydrated head groups. Micelle formation appears to be an exothermic process due to a high enthalpic contribution.

The change in entropy during micelle formation is not significant. It is believed that the entropic contribution to the micellization, is due to the increment in flexibility of monomer in nonpolar region, the decrement in hydration of monomer when it enters in to the micelle, and the interactions between hydrocarbon chains and structured water molecules.

In the case of non-ionic surfactants the free energy of micellization decreases with increasing ethylene oxide chain length. The enthalpy of micellization is positive, and it increases with decreasing free energy. On the other hand the entropy of micelle formation increases. The increment in entropy is due to the release of water molecules around the nonpolar groups, the decrement in solvation because of the minimization of water-hydrocarbon interface, and the removal of aggregated monomers to a nonpolar environment. The positive entropy of micellization indicates that the micelle formation is an entropy derived process, which is governed by the presence of hydrophobic interactions during the micellization.

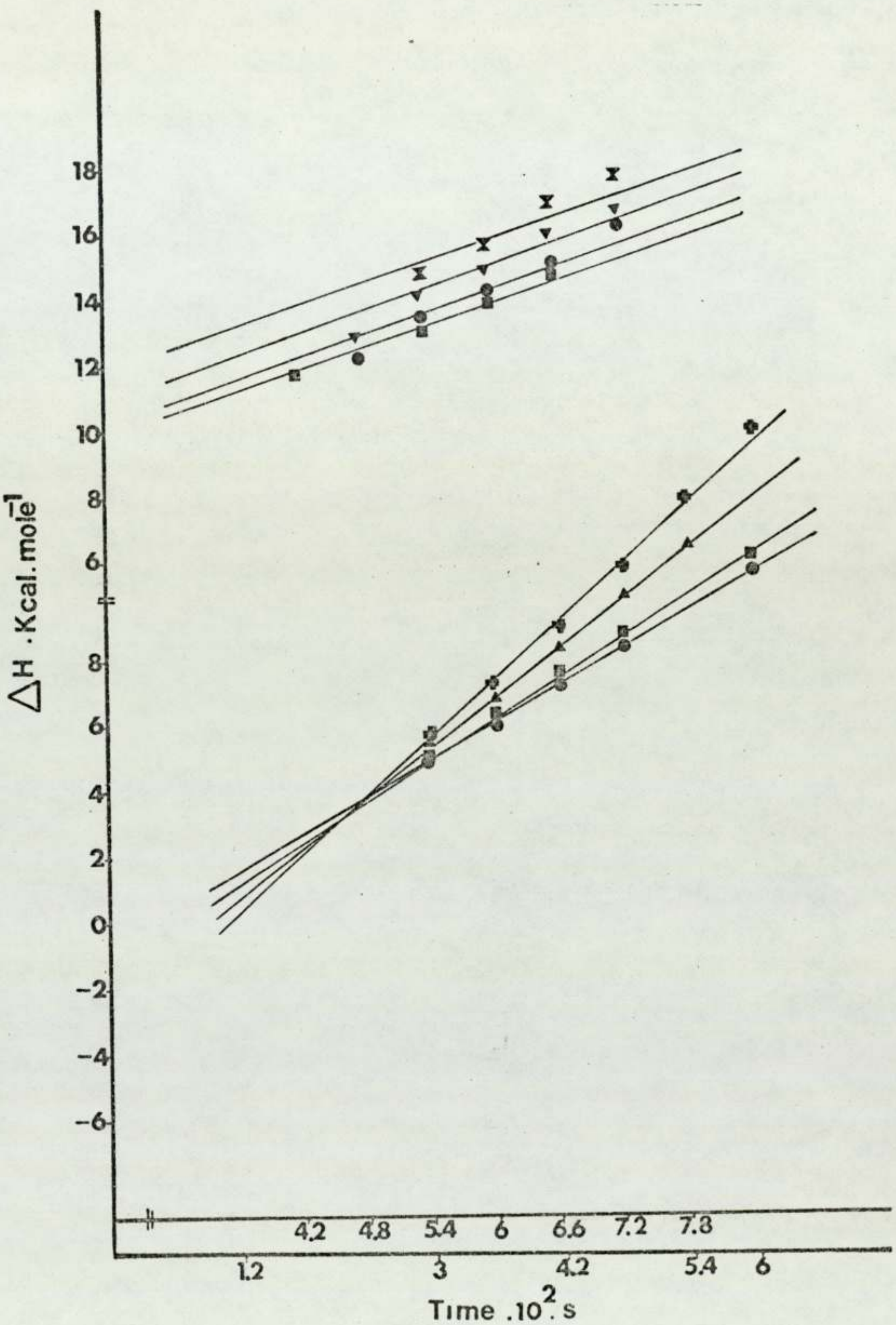


Fig.VIII.1 Heat of solution variation with time in seconds for the alkyltrimethyl ammonium bromides and the polyoxyethylene mono hexadecyl ethers; ● C_{10}, ■ C_{12}, ▲ C_{14}, and ✚ C_{16}: ■ EO_{10}, ● EO_{18}, ▲ EO_{30} and ⧗ EO_{60}

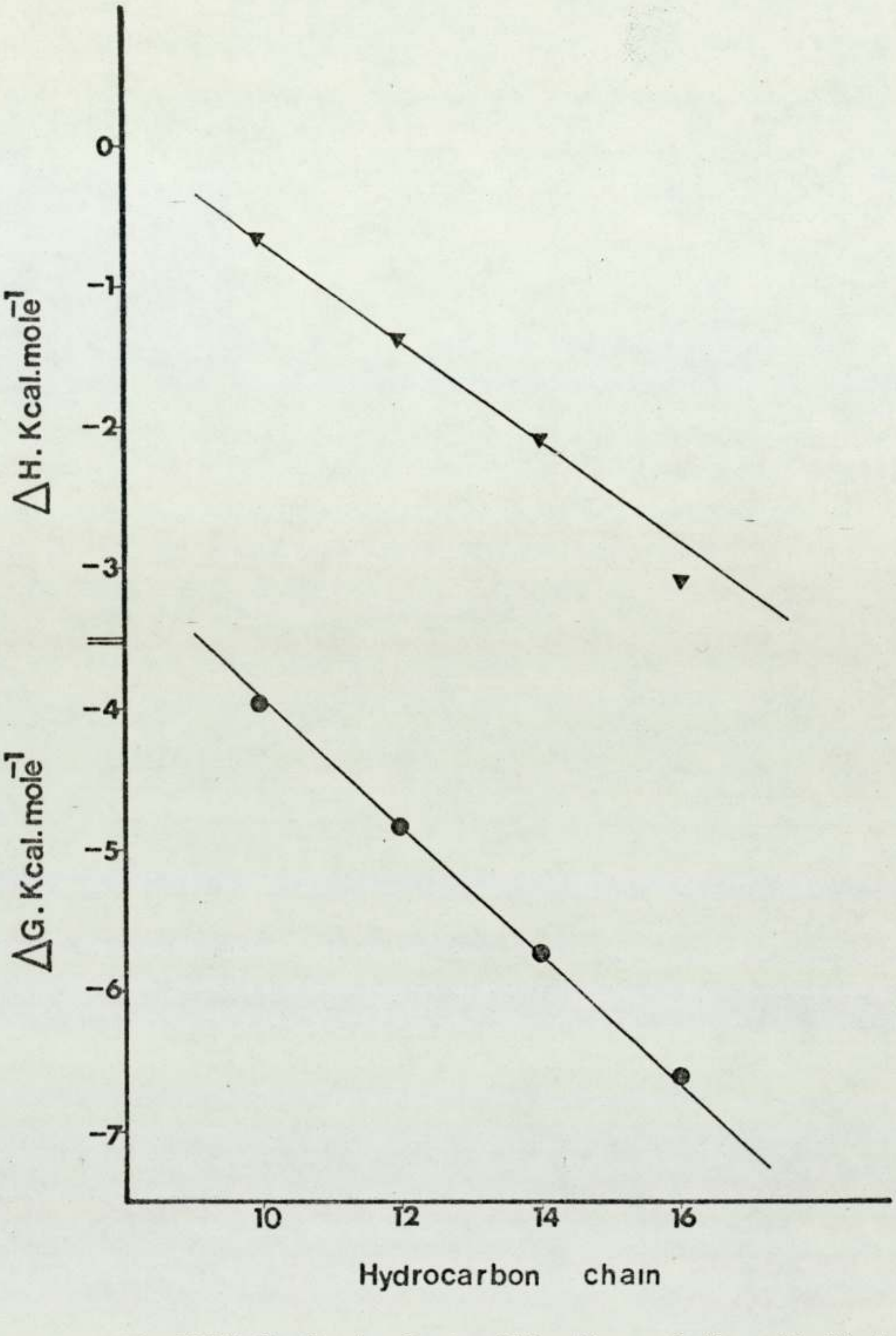


Fig.VIII.2 Heat of micellization of the alkyltrimethyl ammonium bromides as a function of hydrocarbon chain length; Relation ship between free energy of micelle formation for the alkyltrimethyl ammonium bromides and the alkyl chain length at 25° C;

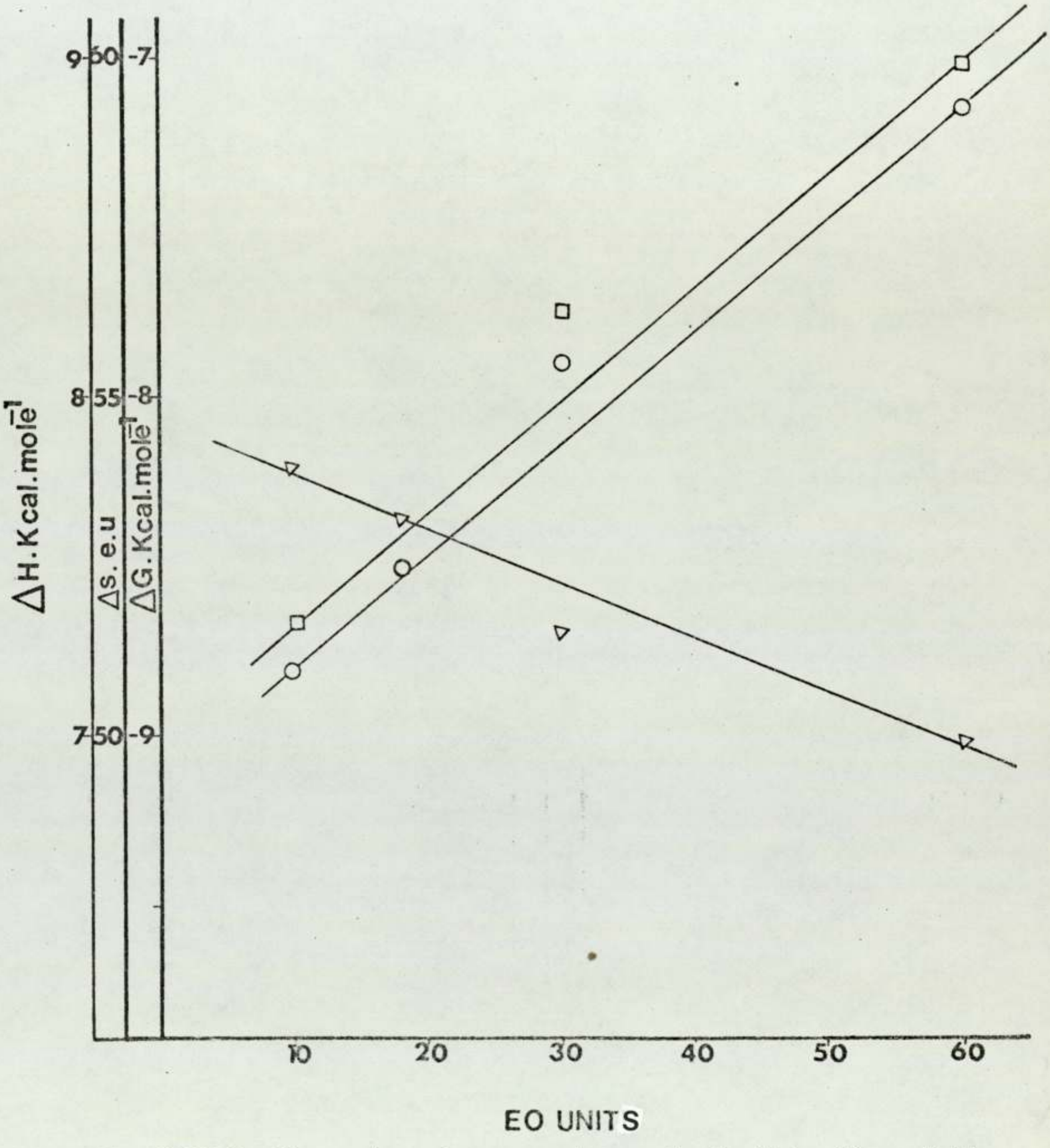


Fig.VIII.3 Thermodynamic parameters of micellization of the polyoxyethylene mono hexadecyl ethers in Water as a function of the alkyl chain length at 25° C;

THERMODAYNAMIC DATA FOR THE MICELLIZATION OF .ALKYAMMONIUM BROMIDES

AND POLYOXYETHEYLENE ETHERS IN WATER AT 25° C

TABLE VIII.I.1

S.A.A	ΔG Kcal.mole^{-1}	ΔH Kcal.mole^{-1}	TΔS Kcal.mole^{-1}	ΔS Cal.mol.deg^{-1}	C_0 mol.dm^{-3}	ΔG change per CH_2	ΔH Contr. to ΔG
				CATIONICS			
C_{10}	-4.0	-0.65	3.35	11.23	6.5 x10^{-2}	-0.5 Kcal.mol.$^{-1}$	-0.34 Kcal.mol^{-1}
C_{12}	-4.8	-1.4	3.4	11.40	1.68x10^{-2}		
C_{14}	-5.7	-2.1	3.6	12.07	3.7 x10^{-3}		
C_{16}	-6.6	-3.2	3.4	11.40	8.0 x10^{-4}		
				NON-IONICS			
EO_{10}	-8.2	7.2	15.4	51.65	5.6 x10^{-5}	ΔG per $-CH_2-CH_2-O-$	ΔH Contr. to ΔG
EO_{18}	-8.4	7.5	15.9	53.32	3.89x10^{-5}	-20 cal. mole^{-1}	34 Cal.mol.$^{-1}$
EO_{30}	-8.7	8.1	16.8	56.34	2.4 x10^{-5}		
EO_{60}	-9.0	8.85	17.85	59.87	1.4 x10^{-5}	Hydrocarbon Cont to Micellization -6.86 Kcal.mole^{-1}	

<

C_{10}	ΔH Kcal.mole^{-1}	C_{12}	ΔH Kcal.mole^{-1}	C_{14}	ΔH Kcal.mole^{-1}	C_{16}	ΔH Kcal.mole^{-1}
t s.		t s.		t s.		t s.	
300	5.3	300	5.2	300	5.4	300	5.5
360	6.24	360	6.3	360	6.9	360	7.2
420	7.3	420	7.4	420	8.4	420	9.1
480	8.4	480	8.5	480	10.5	480	10.9
600	10.7	600	11.1	540	11.67		

<

Eo_{10}	ΔH Kcal.mole^{-1}	Eo_{18}	ΔH Kcal.mole^{-1}	Eo_{30}	ΔH Kcal.mole^{-1}	Eo_{60}	ΔH Kcal.mole^{-1}
420	10.6	480	12.0	480	12.6	540	17.4
540	12.8	540	13.7	540	13.4	600	15.5
600	14.1	600	14.2	600	14.9	660	17.1
660	15.4	660	15.5	660	16.4	720	17.9
		720	17.0	720	17.3		

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SYMBOLS.

$\breve{A}$ = A parameter which depends on the properties of the solvent, Anstrom.

$A_{N+2}(R_1,R_2)$ = The quantity which is in effect a function of the distance $R_{12} = [R_1-R_2]$

AHl (R_1,R_2) = Hydrophobic interaction between two solute particles at fixed positions (R_1,R_2)

A = The intercept (light scattering),constant
$A_{a,b}$ = Equatiorial radius, Semi-axis of revolution
A_o, E_L = Effective length
A_R = Axial ratio
a = The radius of the micelle = $\sqrt[3]{3M/4\,Nod}$

a_o = Hydrodynamics radius

a_i = Coefficient of friction of ions

$\bar{a}_2$ = The partial molal expansibility of infinite dilution

$\Delta\bar{V}^o_{1A}$ = Increment in $\bar{V}_1$ per $-CH_2-$ group of alkyl chain length

B = Constant for the particular homog series and temperature (158) second virial coefficient

B_1,B_2 = Experimental constants

b = κa

be = Effictive bond length

b_i = The functions of the properties of the double layer

$\bar{V}^o_{1B}$ = Increment in $\bar{V}_0$ per $-CH_2-$ group of alkyl chain length

C_A = Concentration of the alcohol

C^o_A = Concentration of alcohol equilibrium with the imaginary alcohol micelle at a given temperature and pressure

C_a = Initial concentration of the electrolyte in the syringe
Λ_c = Conductance
C_i^- = Counter ion

(C_i^-) = Respective equilibrium concentration of C_i

C_i, c_i = Concentration of ion (i), molarity of ion (i) at C_o

Ceq = Unit equivalent concentration

C_o = Critical micelle concentration

Ce^s_a = Activity coefficient of component (a)

$\bar{C}p^o$ = Vapour heat capacity

C_s = Concentration of the surfactant

C_s° = Concentration of the monomer equilibrium with the micelle at a given temperature and pressure

Csp = Chart speed

C_t = The concentration of the electrolyte in the titration vessel at time t

$\overline{V}_c$ = Crystal molar volume of the surfactant

$\overline{V}_{1C}^\circ$ = Increment in $\overline{V}_0$ per $(-CH_2-CH_2-O)$ group

ΔCp = The heat capacity

ΔCp° = Heat capacity of the hydration

D = Dielectric constant of the solvent

D_i = Diffusion coefficient of ion (i)

D_L = The density of the reference liquid
D_R = Dissymmetry
D_s = The density of the solid (surfactant)

d = Density of the micelle

da = The density of the solution

dw = Density of the solvent

ΔD = Chart distance from t_0-t_1

$\overline{V}_{1D}^\circ$ = Increment in $\overline{V}_1$ per $(-CH_2-CH_2-O)$

E = Electric intensity, a correction term for electro viscous effect
Λeq = Equivalent conductance
e = Electronic charge, electrical charge

F = Faraday constant, the intensity of a homogeneous electric field

Fa = Free energy of micellization

$\overline{F}$ = Average free energy

fa = The fraction of total surfactant goes into monomeric form

$f_\pm$ = The mean ionic activity coefficient

F_m, F_{S_i}, F_{C_i} = Activity coefficients of S_i, micelle, and C_i

ΔF = Rate of flow

ΔG = Free energy

ΔG_H^{θ} = Hydration free energy

ΔG_{iel}^{θ} = Electrostatic contribution to the hydration free energy

ΔG_{inel} = Non electrostatic i to the hydration free energy

ΔG_{Mp} = Free energy of micellization (phase separation model)

ΔG_{Mb} = " " " " (mass-action model)

ΔG_{soln} = Free energy of the solution

H = The magnetic intensity, optical constant

Ha = Enthalpy of micellization

h_a = Mean entropy value of component (a)

h_a^{os} = Enthalpy per monomer component (a) at standard state

ΔH = Enthalpy

ΔH_h = Enthalpy of the hydration

$\Delta H_{Mp}, \Delta H_{Mb}$ = Enthalpy of micellization (phase-separation and mass-action models)

ΔH_{soln} = Enthalpy of the solution

ΔH_t = Enthalpy of the aqueous binary mixture

I = The intensity of light
ΔI = Refranctive indiex increment of the solution
i = The various ion species present in solution at C_o including unassociated detergent

Λi = Initial conductivity in the titration vessel

K = Shape factor of the particle depending on the axial ratio

k = Boltzmann constant

L = Length of the conductor

M = The micelles (phase-separation model)

M = The number of the moles of the solvent per 1000g of solvent, molecular weight of the surfactant, corrected micellar molecular weight

M = Equilibrium concentration of the micelles

M' = The apparent micellar molecular weight

M_1 = The molecular weight of the monomer

M_o = Molecular weight of water molecule, molecular weight of the statistical element

M_2 = The additive molecular weight

M^{+z} = The micelles (mass-action model)

m = Dipole, molarity and mass

N = Aggregation number, number of molecules

NA = The uncorrected degree of association of micelles, number of particles (solvent)

$N_A/(N_s+N_a)$ = The molecular fraction of the alcohol

No = Avagadro number

$\bar{N}$ = Average property of a small system or micelle

$\bar{N}^2$ = As in $\bar{N}$ refers to an average property of a small system or micelle

Nc = The corrected degree of association of micelles

N^{-z} = The number of bound counter ions

(N+1) = Number of particles in a system

$N_S/(N_S+N_A)$ = The molecular fraction of the surfactant

n = Number of the particles, molar number of alkylammonium bromides, number of the components in the system, number of the volent molecules in the cosphere

n_1, n_2 = Number of the moles of components 1 and 2 respectively

n_o = Number of moles of water

n^{-2}, n_s = Refractive index of the solution

$\bar{n}_o, n_o$ = Refractive index of the solvent

O = Oxygen

P = Pressure

p = The effective charge (corrected) pressure, axial ratio

p' = The apparent ratio (uncorrected)

p_1 = Density of the solution

p_1H_2O = Density of water

pt = Dilution factor at time t

Q = Space charge

q = Conductivity coefficient

R = Gas constant, resistance of the conductor

R_1, R_2 = The fixed positions of the simple two solute particles

r = Distance

r_1 = Radius of ion (i)

r_1, r_2 = Location of ρ_1, ρ_2 ...

2R in M = Cratic term (cratic portion of the conventional partial molal entropy of the solution)

S = Cross-section of the conductor

Sa = Entropy of the micellization

Sa^m = Entropy of component (a) at micellar state

S_a^{os} = Entropy of " (a) at standard state

S_a = The electrostatic contribution to the stress

S_b = The stress between the solvent molecules.

S_i = Ionic space

$\bar{S}$ = Average entropy

$Spv, \bar{\nu}$ = Specific volume of the monomer at C_0

ΔS = Entropy

$\overline{\Delta S}$ = The partial entropy of the solution

ΔS_h = Entropy of hydration

$\Delta S_{Mp}, \Delta S_{Mb}$ = Entropy of micellization (phase-separation and mass-action models)

Λsp = Specific conductance

ΔS_{soln} = Entropy of the solution

ΔS_t = Entropy of the aqueous binary mixture

$\Delta S_{unitary}$ = Unitary entropy

Λ_{sp} = Specific conductivity

T = Temperature

t = time

ta = Flow time of the solution at 25°C

Λt = Recorded conductivity at time t

U_i = Mobility of ion (i)

$U_{12}(R_1, R_2)$ = The interation potential for the pair solute particles at R_1 and R_2 positions

U_{N+1} = Potential of the interaction of the N+1 particles in the specified configuration

U_+, U_- = Mobility of positive and negative ion

$U^{\circ}_{+,-}$ = Limiting ion conductivity

V = Molar volume of the polar liquid, volume

v = The angle of solution containing (n) particles in 1 cm^3

$\overline{V}$ = Average volume

Va = Anhydrous volume of the micelle, volume of the micelle

Va_m^+ = Mean volume quantity of component a

Va^m = Volume of component (a) at micellar state

Va^{os} = Volume of single component (a) at standard state

Vh = Hydrated volume of the micelle

V_i = Initial volume in the titration vessel

Vp = The volume of the pycnometer

V_t = The volume delivered by the syringe at time t

$\overline{V}$ = Partial molal volume of the particular concentration

$\overline{V}_o$ = Partial molal volume at infinite concentration

$\overline{V}_1$ = Partial molal volume of the micelles in aqueous solution partial molal volume of the component 1.

$\overline{V}_2$ = Partial molal volume of the component 2, partial molal volume of the surfactant in mixed systems

$\overline{V}_2^{\circ}$ = Partial molal volume of the mixed micelle

$\Delta\overline{V}_1$ = $\overline{V}_1 - \overline{V}_o$

$\Delta\overline{V}_2$ = $\overline{V}_2^{\circ} - \overline{V}_1$

$\overline{V}^{op}_1$ = Excess limiting partial molal volume

$\overline{V}_2(x_2)$ = Partial molal volume - molfraction curve

$\partial\overline{V}_2/\partial T$ = " " " - temperature slope

$\partial\overline{V}_2/\partial X_2$ = " " " - molfraction "

$\partial\overline{V}_2^E(X_2)$ = Concentration dependence of partial molal volume

$\frac{\partial V_X}{\partial y}$ = The relative rate of deformation

Y = An extensive property of a given system

Y_1, Y_2 = Partial moal quantities

Z = Degree of polymerization, a function of b evaluated by Booth(43,44)

z_i = Valency

Z_{ie} = Charge of ion (i)

Wd = The weight of the dry pycnometer

Ww = The weight of the pycnometer filled with water

W_S = The weight of the solid

W_T = The weight of the pycnometer filled with the liquid and solid

W = Weight of water hydrating one gram substance

x = Electrolytic conductivity, the mole fraction of the alcohol in the micelle

X_m = Mole fraction of micelle

X^z = An ion where z is positive or negative charge

X_a^s = Mole fraction of component a

X_1, X_2 = Number of moles of component 1 and 2

X Fo(X) = Hydrodynamic-draining parameter

$X-X'$ = m'w = cohesive energy change per one alcohol molecule

Xt = Total concentration of surfactant

ϵ = The dielectric constant of the solution electronic charge, average dielectric constant of the medium

ϵ = The dielectric constant of the solvent

ϵ' = The dielectric constant of the region exhibiting the fluctuation

ε_m = Subdivision potential of micelle

α = Degree of dissociation, polarizibility of the particle

β = The viscosity increment

βs = The adiabatic compressibility

δB = The zeta potential of the micelles from their size and electrophoretic mobility in terms of an equation proposed by Booth(43,44)

δ = $6\pi n\mu/D$

$(\delta a')^2$ = The mean square of the excesspolarizability

$(\delta d)^2$ = " " " " " fluctuation in density

$(\delta\varepsilon)^2$ = The mean square of the dielectric constant of the medium

$(\delta m)^2$ = " " " " " concentration fluctuations

δV = The volume element

η_o = The absolute visoosity of the solvent

η_1 = " " " of water at 25°C

η_2 = " " " of 20% sucrose solution at 25°C

η_k = Kinematic viscosity of water at 25°C

μ = Electrophoretic mobility of the micelles extrapolated to the C_o

μa^{s} = Chemical potential of component (a)

μ_1 = Electrophoretic mobility of the micelles estimated from conductivity data

μ_a^{m} = Chemical potential of component (a) at micellar state

μ_a^{os} = Standard chemical potential of component (a)

μ_o = Dipole moment of the molecule

$\bar{\mu}_o$ = Average dipole moment per molecule

v_1 = The velocity of light in a vacuum

p = The polarization or dipole moment per unit volume of a continuous material

ρ_1, ρ_2 = Each set of moment a

τd = The turbidity due to density fluctuations

τE = " " " " concentration "

ϕ = Volume fraction, apparent molal volume

λ_o = The wave length in vacuo

λ^o = Limiting ion conductivity

λ_i^{o} = " conductivity of ion i

ω = The frequency of light vibrations

σ = The specific conductivity of the solution at C_o

R_H = Resistance of heating coil

Rs = Resistance of standard coil

E_p = Potential difference between resistances when current is turned on to the heating coil in solution.

HYDROPHOBIC INTERACTIONS IN MODEL SYSTEMS

BY

DOGAN EMIN GUVELI

A dissertation submitted for the
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in the
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PREFACE.

This dissertation, which is being submitted for the degrae of Doctor of Philosophy of the University of Aston in Birmingham, is an account of the work carried out under the supervision of Dr.J.B.Kayes in the Department of Pharmacy of the University of Aston in Birmingham, from October, 1972 to June 1976.

Except where acknowledged by reference in the text, the work described herein is claimed to be original and has not been submitted for any other award.

Dogan E.Guveli

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To Ywette Emile Wichner

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Hydrophobic Interactions in Model Systems

SUMMARY

Hydrophobic interactions in model systems have been studied. Cationic and non-ionic aqueous surfactant systems were used as model systems. The physico-chemical properties of surfactant solutions studied, in order to evaluate hydrophobic interaction, were critical micelle concentrations, hydrodynamics, conductance, partial molal volumes, light scattering and the thermodynamic data of micellization.

The observed hydrodynamic micellar properties of cationic surfactants indicate that the intrinsic viscosity of micelles is affected by hydration, the electroviscous effect and the micellar shape by means of hydrophobic interactions. The micellar properties are changed when aliphatic alcohol is added to the system. The intrinsic viscosity of the micelles does not increase significantly, although the relative viscosity of the solution is higher compared with the aqueous surfactant solution.

The increase in viscosity has been discussed in terms of hydrophobic interactions and the change in micellar shape. The observed decrement in intrinsic viscosity shows that the hydration and electroviscous effect decreases with increasing concentration of alcohol.

The critical micelle concentrations of cationic surfactant solutions containing alcohols were discussed considering the structure promoting effect of alcohols at low concentration, the reverse effect at higher concentration; solubility; hydrophobic interactions between possible orientated configurations, and their effect on the surface charge of the micelles.

The positive B coefficients of alkylammonium bromides confirm the structure maker effect of the nonpolar groups of the surfactants. This behaviour is considerably influenced by the addition of alcohol to the system. At low concentration of alcohol the B coefficient is positive, but as the concentration of alcohol is increased it shifts to a negative value. This is due to destruction of water clusters around the nonpolar groups, and the breaking of structured water molecules in the bulk liquid.

The volumetric properties of cationic surfactants below the critical micelle concentration, and above the critical micelle concentration show that the partial molal volume of the surfactant increases with increasing alkylchain length. The micelle formation is accompanied by an increase in volume. When aliphatic alcohol is added to the system, it contributes to the volume change and increases the partial molal volume of the micelles.

The effect of aromatic alcohols, ureas and urethane on micellar properties of cationic systems has been examined by measuring the conductance of the micelles. The observed conductance of the micelles indicate that the critical micelle concentration increases, when 0.01M alcohol is added to the system. As the concentration of alcohol is increased the critical micelle concentration value shifts to lower values. The increment in critical micelle concentration has been discussed in terms of hydrophobic interactions between alcohol, surfactant and water molecules, taking into account the solubility of alcohols and their structure promoting behaviour at low concentration.

However the decrement in critical micelle concentration has been attributed to the structure breaking behaviour of alcohol at high concentration. On the addition of urea and urethane the critical micelle concentration increases. The increment in specific conductance at the critical micelle concentration has been attributed to the cooperative effect of the solutes on water structure. It is believed that ureas and urethane behave as structure promoting, since they take an active part in mixed cluster formation, which are big enough to accommodate nonpolar groups.

Light scattering data on micelles of cationic surfactants indicates that the micellar molecular weight increases as the chain length increases. The addition of aliphatic alcohol to the system, first increased the apparent molecular weight, then it decreased with increasing concentration. The aliphatic alcohols decreased the scattering intensity, and the turbidity of the solution in terms of the density, and concentration fluctuations in refractive index of the solution near the surfactant molecule. The effective charge on the micelles increased, then decreased with increasing concentration of the alcohol.

Hydrophobic interactions in non-ionic surfactant systems of the polyoxyethylene n-alkanol type were also studied in terms of the hydrodynamic, volumetric, light scattering and thermodyanmic data of micellar properties. The intrinsic viscosity of the micelles increases as the ethylene oxide chain length increases. The increment in relative viscosity, and in intrinsic viscosity of the micelles is due to the hydration of micelles, micellar size and shape.

The observed critical micelle concentrations indicate that the critical micelle concentration decreases as the ethylene oxide chain length increases. This behaviour has been discussed by means of the decrement in solubility of non-ionics in aqueous solution, when the ethylene oxide chain length is increased, and the increment in degree of coiling as the hydrophilic chain length increases. It is likely that the hydrophilic chain coils tightly at the end of the hydrocarbon chain, this is entropically favourable allowing hydrogen bonded water molecules to be released, this type of configuration will increase the hydrophobic surface area of the molecule. Consequently the critical micelle concentration decreases with increasing hydrophobic character of the non-ionic surfactant. The volumetric properties of micelles show that a volume change occurs during the micelle formation. The partial molal volume change decreases with increasing hydrophilic chain length.

The addition of aromatic alcohols to the system shows
[illegible]
similar behaviour to that observed with cationic systems. The critical micelle concentration is increased when 0.01M aromatic alcohol is added to the system, then the effect of additive on critical micelle concentration tends to the reverse direction as the concentration increases.

The observed phenomen is due to the selective adsorption of additive on the surfactant molecule, the change in density, and concentration fluctuations in the refractive index of the solution near the surfactant molecule, and a complex type of association of surfactant with alcohol through hydrophobic interactions. The scattering intensity, and turbidity of the solution containing alcohol is higher compared with the aqueous surfactant solution.

The change in micellar properties of non-ionics in aqueous urea, and urethane, show that the critical micelle concentration increases. The increases arise from the active participation of urea, and urethane in mixed cluster formation in terms of hydrophobic interactions. The increment in scattering intensity and turbidity of the solution also supports the idea that these substances behave as structure makers inaqeuous surfactant solution.

The thermodynamic investigation of cationic and non-ionic micellization shows that micelle formation is an entropy directed process. The free energy of micellization decreases as the chain length, and ethylene oxide chain length increases. This decrement is due to the reduction of structural order of water molecules, which arises from the minimization of hydrocarbon water interface, this causes the transference of monomers to the nonpolar environments.

The decrement in enthalpy (cationics) is caused by the change in the translational energy of monomers, in water structure and the effect of hydrated head groups. The observed entropy change is governed by hydrophobic interactions between nonpolar, polar and structural water molecules.

The enthalpy and entropy of micellization of non-ionic surfactants is always positive showing that micelle formation is governed by the gain in entropy. Entropy increases during the micelle formation, which contributes largely to the free energy.

The increase in entropy is due to the hydrophobic interactions between nonpolar groups, and structured water molecules which is accompanied by a release of energy, due to the structural melting of water molecules, when the nonpolar groups move to the nonpolar environment. The reorientation of the solvent molecules contributes also to an increase in entropy.

CHAPTER I Theory

I.Ia - Role of Hydrophobic Interactions

I.Ib - Theories of Hydrophobic Interactions

I.Ic - Structural Models of liquid water

I.Id - Models for the Study of Hydrophobic Interactions

I.Ia - Role of Hydrophobic Interactions

The features of various molecules in aqueous solutions, have been studied for some 50 years. The nature of such solutions have been introduced in terms of conceptual models. Various solute-solvent interactions have been observed in aqueous solutions, in order to evaluate physio-chemical parameters of solution behaviour.

Among solute-solvent interactions, one special type of interaction, so called Hydrophobic interactions, have been paid much attention, and it is necessary to understand its role, in different aqueous systems.

The term Hydrophobic Interactions is simply long range interactions of apolar groups, causing association in aqueous environment, decreasing the degree of nonpolar-polar (water) contact.

This tendency is derived from a favourable Entropy effect, since the structural order of liquid water decreases due to removal of apolar solutes, from aqueous solution to nonpolar regions. Hydrophobic interactions play a unique role in Biological systems, aqueous, non-aqueous solutions of low molecular weight substances and macromolecules.

The features of molecular interactions in different systems such as:

Binding of biologically interesting molecules to each other, the binding of some pharmacologically active molecules to their substrates, binding of drugs to the receptors of such biological macromolecules as proteins and polypeptides, stabilization of double helical form of DNA and certain conformations of proteins and protein aggregation, formation of micelle-like structures in aqueous and non-aqueous systems, conformational changes of enzymes, related to the effects of subtrates, activators or inhibitors, stacking processes in polynucleotides and in nucleic acids, small-molecule binding to polymers in vitro and in vivo, specific aggregation of polymers to form supra molecular structures, enzyme catalytic processes, lipid bilayers. Cell membranes, local and general anasthesii have been discussed in terms of Hydrophobic Interactions.

I.Ib - Theories of hydrophobic interactions.

To understand the role of hydrophobic interactions, extensive theoretical and experimental investigations have been made(1,2,3)with hydrocarbon-aqueous sytems, in order to evaluate thermodynamic parametersof intermolecular interactions of hydrocarbons and liquid water structure.

In the study(3) of solubility of some hydrocarbons,unitary entropy has been found, with a decrease of the order of 20 e.u. The reason for this has been attributed to the structural restrictions involved on the water structure(4) surrounding the apolar solute, when transferring a mole of solute from nonpolar environment to aqueous region. Hydrophobic interactions in this approach are introduced by this structural restriction effect of the water molecules around the nonpolar moiety.

This attention towards molecular interactions of hydrocarbon moieties inaqueous solutions, has been centred by another theory(5) on the theoretical derivation of the thermodynamic parameters of liquid water and the thermodynamic behaviour of aqueous hydrocarbon solutions.

This theory is based on the flickering cluster model for liquid water(6). A derived partition function(7) for liquid water in the first layer of water around solute, has been used to obtain the contribution of structural changes of water to the total free energy of solution.

The contribution of the solute to the free energy is observed by means of changes of configurations of molecules, and Van der Waals interactions when solute transfers to the aqueous state.

Since aliphatic hydrocarbons exothermally dissolve in water by negative enthalpy counter balanced by a large entropy effect, hydrophobic interactions have been considered, as the partial or complete reversal of the solution process for hydrocarbons in water.

This theory has been developed by calculating hydrophobic interactions between nonpolar side chains of amino acid residues in polypeptides(8). This treatment has been constructed on the quantity of free energy observed, per water molecule in the first layer of solvation shell, around the side chains and the energy involved with the exclusion of water molecules from this solvation shell, when the side chains transfer to the nonpolar region.

Also the entropy change is introduced as a main driving force, for the hydrophobic interactions. But with the aqueous aromatic hydrocarbon solutions, positive enthalpy and negative entropy effect is obtained due to the stronger association of the water molecules with the π electron orbitals of benzene ring than with aliphatic groups.

The total free energy ΔF_H° of hydrophobic interactions is given by

$$\Delta F_H^\circ = \Delta F_W^\circ + \Delta F_S^\circ \qquad \text{I-1}$$

ΔF_W° = contributions from the change of the water structure to the ΔF_H°

ΔF_S° contributions from the change in the states of the side chains themselves.

(9,10,11,12) A different view of hydrophobic interactions, has been given by considering the ordering of water in a lattice around nonpolar groups as a stabilizing effect, in analogy with gas hydrates.

The magnitude of hydrophobic interaction has also been examined within the framework of classical statistical mechanics, by considering a system consisting of N solvent molecules and two solute particles at fixed positions R_1 and R_2 in aqueous solution(13).

Various solute-solute distances and related strength of hydrophobic interactions are discussed in this approach. Helmholtz free energy is given by three terms for such a system as follows:

$$A_{N+2}(R_1,R_2) = A^\circ + U_{12}(R_1,R_2) + A_{H1}(R_1,R_2) \qquad \text{I-2}$$

and the hydrophobic interaction has been defined as a indirect part of the work by the equation:

$$A_{H1}(R_{12}=\infty) - A_{H1}(R_{12}) \qquad \text{I-3}$$

when two solute particles are brought from infinity to the distance R_{12}. This statistical approach has been extended by taking into account a system, consisting of a number of identical, spherical nonpolar particles and number of solvent molecules(14).

Solute particles tend to adhere each other, and the process involves bringing the solute particles from infinity to close configuration has been examined in various solutions(14).

A different view(15), involving the degree of overlap of solvation cospheres about solutes, has also been given for evaluation of some features of hydrophobic interactions.

Hydrophobic interactions, based on the solubility parameters of hydrocarbons in water, have also been discussed(16) in terms of the structure theory of the liquids(17,18,19). This theory successfully applied to water(20). The obtained free energy, entropy and internal energy, except low heat capacity values(16) which agree well with the values given in literature.

This approach has been extended, by taking into account, the solvent cavity surface area(21), considering the water molecules in the first layer of water, used as being a factor(5) for the hydrocarbon solubility in aqueous environment.

The above approaches(16,21) have been developed by application of the first-order liquid state pertubation theory(22). In order to apply the usual form of liquid pertubation theory(23,24) to the gaseous hydrocarbon water interactions, the energy of the non-spherical cavity, that accommodates the solute molecule, has been assumed to be equal to the energy of the spherical cavity of equal area.

The Lennard-Jones potential has been used(22) to derive the hydrophobic interaction energy which has been given as the difference between the sum of cavity energy and solute-solvent interaction energy when hydrocarbon molecules come close to each other and when they are apart.

Some of well known theories of hydrophobic interactions in different systems have been summarized to introduce some information about their nature.

I.Ic - Structural Models of liquid water.

From the earliest theories(25), water has been recognized as an associated liquid. However these theories were not able to explain many observed properties. Bernal and Fowler(26) and later Morgan and Warren(27) showed by X-Ray diffraction measurements on liquid water that it is to be characteristic of tetrahedral water coordination, and suggested that the observed structure of liquid water should be similar to that of ice.

A number of theories of water structure have emerged from the above observations, these can be classified into two groups, in terms of obtained characteristics$^{(28)}$.

I.Ic1 - continuum models

I.Ic2 - mixture models

I.Ic1 - Continuum Models, treat water in terms of a continuous distribution of interactions of an uninterrupted, three dimensional lattice of tetrahedrally coordinated hydrogen bonded molecules. Bernaland Fowler$^{(26)}$ proposed a model for liquid water, on the basis of a broken-down ice structure, with most of the hydrogen bonding still in existence. The existence of highly hydrogen bonded regions and the gradual breakdown of hydrogen bonding, with increasing temperature appear as main features of the model. Pople$^{(29)}$ used a statistical mechanical approach to get the average degree of hydrogen bond bending, taking into account the harmonic restoring force constant. With this view, the obtained radial distribution function for relative positions of molecules, agreed well with the results introduced by Morgan-Warren$^{(27)}$ from X-Ray scattering. Also it is assumed that each bond bends independently of all others.

Bernal$^{(30)}$ developed a picture of water, considering the liquid water, as an intrinsically irregular structure. Rahman-Stillinger$^{(31)}$ employed molecular dynamics to obtain the dynamic properties of the molecular assembly of liquid water. Barker-Watts$^{(32)}$ used Monte-Carlo procedure to calculate the radial distribution function of water structure.

The small number of water molecules included in the sample and the nature of the pair potential function chosen resulted in only moderate agreement, with X-Ray radial distribution function.

Stevenson$^{(33)}$ suggested that the monomeric water molecules in liquid water, should be small at ordinary temperature. He introduced his concept of water structure, using IR and UV spectra data of liquid water.

I.Ica - Mixture models in which the water is considered as a collection of differently hydrogen bonding species where each water molecule can fluctuate through the states where the molecules are involved in hydrogen bending.

By Raman spectrum analysis, Cross(34) concluded that the liquid has considerable amounts of molecules, with four, three and two hydrogen bonds as seen in a broken-down ice-lattice. Eucken(35) introduced a model that has two four and eight molecules in the liquid state.

Adjusting the mole fractions of the aggregates he obtained the values that agree well with experimental values of compressibility and thermal expansion. Grjotheim-Krogh-Moe(36) gave a different view assuming that liquid water consists of an ice like species of density identical to that of ice and of a non-hydrogen bonded close-packed species.

Haggis-Hasted-Buchanan(37) considered the dielectric properties of aqueous solutions and they derived simultaneous equations, for the probability of transition between the systems that have been treated as reacting species which consist of different hydrogen bonded molecules. Frank-Wen(6,38) have centred their attention on the partially covalent character of the hydrogen bond. They postulated that the formation of the hydrogen bonds in the liquid is a cooperative phenomenon and involves a contribution from delocalization energy, due to electron overlap. This approach assumes that the formation and dissolution of flickering clusters that are short-lived highly hydrogen bonded molecules is governed by local energy fluctuations.

Pauling(39) has taken the structure of solid gas hydrates, formed by small size tetrahedrally hydrogen bonded water molecules and nonpolar substances, as a basis of his qualitative model for liquid water. He suggested similar type of structure for pure water considering the structure of gas hydrates.

Forslind(40) represented a lattice-point model, treating liquid water as an extended crystalline system, similar to ice and assumed this crystalline system has sufficient size cavities to accept the monomeric water molecules.

Nemethy-Scheraga(7) constructed a structure partition function, taking into account the treatment of (0.1.2.3.4) hydrogen bonded water molecules and derived a number of model details, such as cluster sizes and relative numbers of molecules of different bondedness.

Walrafen(41) in his model of liquid water structure, deals with Raman scattering spectra in the valency-stretching region and the analyses of these into bands of related to bonded and unbonded O-H and O-D motions.

As it can be seen these are a number of competing models each of which gives useful details of some of the features of water but not for the others.

I.Id - Models for the Study of Hydrophobic Interactions.

Amphiphilic substances are very suitable materials, as they have strong molecular interactions, with solvent molecules in solutions. These interations are operated between nonpolar, polar sides of amphiphile and water structure in aqueous solutions. Also they have distinctive features, such as molecular dispersion, depression of surface and interfacial tension due to the absorption and orientation of molecules at interface, micelle formation above a certain concentration due to free energy decrease of system.

Hence amphiphilic systems can be used as model systems, to investigate hydrophobic interactions which can be assessed relatively easily through measurements of critical micelle concentration and mentioned properties.

To examine the physico-chemical properties of hydrophobic interactions in aqueous solutions, two types of model systems have been employed. These systems can be divided into two categories, in terms of their physico-chemical nature, which are:

A. Ionic systems (Cationic)

B. Non-Ionic " (Polymeric)

These two kind of systems will be used, to obtain some information about the unique role of the phenomenon, which is known as hydrophobic interactions.

CHAPTER II Hydrodynamic Properties of Alkylammonium Bromides in water and alcohol solutions.

II.Ia - Electroviscous Effect

II.Ib - Hydration

II.Ic - Dielectric Effect

II.Id - Thermodynamics of Solute-Solvent Interactions

II.Ie - Effect of Aliphatic alcohols

II.If - Relative, Reduced and Intrinsic Viscosities of Aqueous solutions of Alkyltrimethyl ammonium bromides

II.Ig - Experimental Procedure

II.Ih - Micellar Properties from Hydrodynamic Data

II.Ii - Conclusions

II.Ia - Electroviscous Effect.

It has been observed that the viscosity of a colloidal system increases, when the dispersed particle is charged. This increase in viscosity, is due to the charge of the particle and is called the "Electroviscous Effect", which is connected with the existence of an electrical double layer around the particle.

Hence, the electrokinetic phenomenon known as the electroviscous effect occurs, when the outer part of the electrical double layer is drawn away from the particle in a laminar field flow. Consequently the electrical double layer tends to restore itself by conduction. The dissipation energy in the process of conduction effect, is the cause of the increase in viscosity.

The micelles of surface active agents carry an electric charge in aqueous solution, and an electroviscous effect is always included, as a part of the measured intrinsic viscosity $[\eta]$(42).

The intrinsic viscosity and the electroviscous effect can be obtained theoretically from the Booth modification(43,44) of the Einstein's theory, taking into account the size and electrophoretic mobility of the micelle.

$$[\eta] = 2.5 \left[1 + \pi \, \bar{\rho} \, \bar{\mu} \, b^2(1+b)^2 \, Z \, \gamma \, \zeta \, B^2\right] \qquad \text{II-1}$$

where

$$\bar{\rho} = \sum_i c_i z_i^{\,2} \, \mu_i^{-1} \Big/ \sum_i c_i z_i^{\,2} \qquad \text{II-2}$$

$$\bar{\mu} = \sum_i c_i z_i^{\,2} \, \mu_i \Big/ \sum_i c_i z_i^{\,2} \qquad \text{II-3}$$

$$\gamma = D^2/4\pi^2 \sigma \eta a^2 \qquad \text{II-4}$$

Smoluchowski(45,46), Krasny-Ergen(47) and Finkelstein-Cursin(48) also have introduced similar equations for the spherical particle, considering the intrinsic viscosity, size and electrophoretic mobility of the dispersed particle in aqueous sytems. In the evaluation of the following three equations, the thickness of the double layer has been assumed smaller than the radius of the particle.

$$\eta = 2.5\left[1 + \gamma\zeta^2\right] \qquad \text{(Smoluchowski)} \qquad \text{II-5}$$

$$\eta = 2.5\left[1 + \frac{3}{2}\gamma\zeta^2\right] \qquad \text{(Kransny-Ergen)} \qquad \text{II-6}$$

$$\eta = 2.5\left[1 + \frac{77}{25}\,\bar{\rho}\,\bar{\mu}\,\gamma\zeta^2\right] \qquad \text{(Finkelstein-Cursin)} \qquad \text{II-7}$$

The increase in the intrinsic viscosity values of the micelles of n-alkylbromides in aqueous solutions, and in aqueous solutions containing added solutes, is due to one of the operating phenomena , which is the dissipation energy effect in the conduction, which restores the electrical double layer situation of the particle, that has been disturbed in the laminar field flow, because of the internal friction of the particle with the solvent molecules.

II.Ib - Hydration.

An ionic solution has three components, solvent, cations and anions, in which the interactions between the ions and solvent molecules, can be termed as solvation, and in the case of water, hydration(49,50).

In the ionic solution, water molecules become attached to the ion, with loss of their own translational freedom but remain in activated exchange equilibrium with the rest of the solvent.

Ionic hydrations have been extensively studied, by using model systems. A simple model has been given by Born(51). In his model, the ions are introduced as charged hard spheres, and the solvent is considered as a fluid, which has a uniform dielectric constant, even in the presence of the ionic fields. The concept that the major part of the hydration free energy is related to the respective ionic charge and size, has met with great acceptance.

Another approach(52,53) is concerned with the spherical distribution of rigid spherical ions of radius r_i, and charge $z_i e$, in the solution, where the dielectric constant of the medium varies in the neighbourhood of the ion. It has been proposed that the accurate view of the electrostatic part of the ionic hydration, can be derived by taking into account the contributions of the discharge ions.

The ionic hydration free energy, is given(50) by an equation such as

$$\Delta G_H^\theta = \Delta G_{iel}^\theta + \Delta G_{inel}^\theta \qquad \text{II-8}$$

Noyes(54,55) applied a model to investigate the ionic hydration, and he has extended it for studying the thermodynamic coefficients of the hydration. Booth(56) has employed Kirkwood's(57) theory of the dielectric constant of an assembly of polar and polarisable molecules to the highfield state, and found that the theoretical results for water compared with the values given in the literature(58,59).

A further model which uses the Hamiltonian function(50), describing the interactions between nonpolar solutes, and water molecules and distribution of water molecules around an ion is given by:

$$H_{N+1}(\rho_1,\ldots,\rho_{N+1},\ r_1,\ \ldots\ r_{N+1}) = \sum_{i=1}^{N+1} (\rho_i{}^2/m_i) + U_{N+1}(r_1,\ldots,r_{N+1}) \qquad \text{II-9}$$

In order to investigate the ionic hydration in view of this approach, a definite functional form for the Hamiltonian is derived, in terms of the exact statistical approximations. In the light of this treatment, an analytical solution has been used(60) to observe the ion-solvent iterations in an assembly of hard spheres with the electric multipoles of the various orders, and this study has been extended(61,62,63) by using the pertubation methods of statistical mechanics, in order to obtain the thermodynamic coefficients of the hydration.

The process which involves the calculation of the interaction of an ion with its first nearest neighbour solvent molecules, in terms of the intermolecular forces, is known as the Hybird type model.

A modal particle which has the same dipole moment, as an isolated real water molecule, has been used(64) as a water molecule, in order to obtain the complex $(X.n\ H_2O)^z$.

The observed ΔG_H^θ is the summation of the three terms such as, (1) the interaction of the charge on X^z with the charges on n water molecules, (2) the London dispersion force acting between an ion and each of the n-water molecules, including nearest neighbour water molecules, and (3) the repulsive force operating between an ion and each of the n-water molecules in the complex.

This view has been subjected to several investigations, in order to evaluate the binding energies and force constants of the complexes, which relate to the $(X.n\ H_2O)^z$, that were formed with X^z or other ions.

Burton and Daly(65,66) applied a quantum mechanical treatment to a system, in which the water-ion distance varies. The calculations have been constructed, on the basis of fixed relative configurations of the nuclei of water molecules, and a series of configurations of fixed symmetries.

On the relation of the thermodynamic properties of the molecules, the additive contributions of the chemical bonds to the energies, has been also introduced to describe the chemical models of the ion-solvent interactions(50). In view of a chemical model, it is assumed that each solute particle X^z has a region around it, and it is called cosphere which has the thickness of one solvent molecule, in which the solvent property is affected by the presence of the neighbour molecules, and it has been characterized by an equation, such as

$$n\left[\text{Solvent(pure bulk liquid)}\right] \rightarrow n\left[\text{Solvent(in cosphere state next to } X^z)\right] \qquad \text{II-10}$$

Robinson and Stokes(67,68) studied the excess free energies of aqueous solutions of the strong electrolytes, in terms of the complexes of the solute species, which have fixed numbers of the solvent molecules. The solvation models have been introduced by Gurney(69) and Samilov(70) for examining the ion-solvent interactions.

Frank and Evans(4) proposed a chemical model for the investigation of the hydration phenomena, which has introduced very successful information , and they showed that there is something like a double cosphere around each ion.

The Barclay-Butler rule(71), its applicability to the solvation phenomena, and the basis of the rule have been extensively studied, in terms of the molecular interactions(72,73). The chemical approach has been developed(4,74), on the basis of the configurational treatments of the interactions, between hydrogen-bonded assemblies of water molecules and the cospheres of the ions.

II.Ic - Dielectric Effect.

When two parallel conducting plates have on their surface electric charges of densities $+\sigma$, $-\sigma$ respectively, in a parallel plate condenser(68), the field intensity between the plates in vacuo is given by an equation

$$E_v = 4\pi\sigma \qquad \text{II-11}$$

The field intensity of the condenser is altered with the displacement of the medium by another insulating medium, and consequently the field strength drops to a value:

$$E = 4\pi\sigma/\varepsilon_s \qquad \text{II-12}$$

where ε_s is called the static dielectric constant of the medium. The static dielectric constant of a polar liquid arises from the electrical distorsion of the molecules, and the orientations of the permanent electric dipoles (μ) in the static electric field(28). Both effects can be expressed by an equation:

$$\rho = (N_0/V)\bar{\mu}_0 \qquad \text{II-13}$$

In a steady uniform electric field, the orientated permanent dipole is distributed according to a Boltzmann distribution. The populations in different energy states are governed by thermal fluctuations, which are originally different orientations. The permanent dipole orientation polarizibility, in such distribution is given by

$$A_{or} = \mu_0^2/3kT \qquad \text{II-14}$$

The average orientation polarization has been calculated by Debye(75,76), in terms of the molecular electric dipole moment effect, on the assumption that the energy of the orientated dipole is distributed according to Boltzmann distribution.

Onsager(77) has interpreted the local field effect on a molecule in a liquid, by considering a model molecule, which has polarizibility α and a point dipole at the centre cavity of radius a_1 in continuous dielectric constant field. He proposed that only the cavity field orientates the dipoles, and the remaining part of the electric field has been termed a 'Reaction field'. According to Onsager's theory, this field should be parallel to the dipole moments of the dipoles.

Oster and Kirkwood(78) examined the directions of the neighbour molecules of a given molecule, in terms of the direction of the central molecule. The number of nearest neighbour molecules, has been calculated by taking into account Morgan-Worren's(27) X-Ray diffraction distribution function. The dielectric of the homogeneous static electric field, in the vicinity of the molecule, has been discussed by Kirkwood(57) in terms of the hindering of rotations of the neighbouring molecules. He proposed that the average dipole moment of an H_2O molecule, surrounded by the neighbouring molecules is the vector sum of the dipoles moments of all the neighbours, which are at fixed orientations for a given molecule.

The liquids which are completely miscible with water are polar in nature, and they possess correlation parameters, which are the measure of the mutual hindering rotations of the neighbouring dipoles, and the orientational correlations. Consequently he concluded that the mixtures of the polar liquids with water, can be examined along the same lines.

Pople(29,79) employed Kirkwood's Theory to his own hydrogen bond bending model. Haggis(37) investigated the static dielectric constant, in terms of the statistical analysis of hydrogen bond breaking, neglecting the bond bending.

The orientational(80) correlation is governed by the molecular dipole, and the location of the permanent charge distribution, in the interior of a polar molecule, which has been interpreted by means of the energy of the hydrogen bonding.

The dipole is affected by the static electric field of the continuous medium, and it relaxes to its equilibrium state of random orientation by taking a finite time. The lag between the motion of the dipoles, and the static electric fields introduces a dielectric loss. The contribution energy arising from the field is dissipated as heat in the medium.

The principal(28) relaxation time of pure water is often interpreted, in terms of the breakage of a hydrogen bond. The water molecule is supposed to reorient with rotational Brownian motion, and a water molecule bonded with one bond to one neighbour, can rotate without involving an activation energy. But a molecule bonded to two neighbours needs for reorientation an activation energy.

The relaxation process of the alcohol-water mixture, has been studied by Cole(81) in terms of breakage of the hydrogen bonds, and he obtained an activation energy for the relaxation process in the monohydroxylic alcohol system, which is of the order of the hydrogen bond energy.

This result has been attributed to the reorientation of a molecular OH moment, by breaking of its hydrogen bond, and subsequently forming a bond to the oxygen of another molecule. In view of this approach, the relaxation is supposed as a cooperative process in the entire medium.

Hassion and Colc(82) discussed the small quantities of water in various alcohols. They observed that the relaxation time is affected by the addition of water. Pottel-Kaatze(83) investigated cospheres of the ions, in a static electric field. They concluded that water molecules in each hydration sheath, have different relaxation times to that of the pure water in the solution, and they contribute a certain fraction of entire static permittivity of the solution.

The static dielectric constant, and dielectric relaxation time, decreases as the concentration of electrolyte is increased. The reason for the changing of the dielectric properties of the medium, has been attributed to the structure breaking effect of the solute(80).

The electric field of an ion polarizes the neighbouring solvent molecules. The electric field near an ion is quite intense enough to cause a marked dielectric saturation in surrounding water molecules.

At the water-ion interface, a water molecule carries bound charge(50), (i.e. a polarization charge) which is opposite to that of the ion charge. This polarization charge becomes assymetric with respect to the ion, due to the orientational relaxation of water, in the applied electric field(84).

The ion-pairs have smaller reorientational times than water molecules. They reduce the principal dielectric relaxation time, in terms of their contributions to the total orientational polarization. Only the small cations such as Li$^{(+)}$ and Na$^{(+)}$, are saturated dielectrically towards their inner hydration layers by the strong ionic electric field. The small cations have the highest number of moles of water, without orientational polarizability per mole of electrolyte, which is smaller for the large cations.

Ritson and Hasted(85) calculated the dielectric constant of water as a function of the distance from a point electronic charge, and concluded that the difference between dielectrically saturated positive and negative ions, is due to the ionic size.

Macroscopic electrical property of a disperse system, can be characterized(86) by the static dielectric constant of the dispersed medium. The dielectric increment effects of the particles arise from their polarizibility, the orientational relaxations, and their correlation parameters.

The static dielectric constant of a colloidal solution is different from that of the pure dispersion medium. In the colloidal system, the molecules of the dispersion phase are replaced by the particles, which have lower dielectric effects. Consequently the dielectric constant of the medium is lowered.

The orientations of permanent dipole moments of hydrophilic colloids by the electric field change the polarization, and the dielectric constant of the medium(87). The electrical double layer influences the static dielectric constant of the disperse system. The particles possess dipole moment which are directed opposite to the field, due to having electrical double layers. This process changes the orientations of the particles, their polarizibilities, and the dielectric constant of the dispersion medium.

The solute which dissolved in dispersion medium lowers or increases the correlation parameter, which governs the static dielectric constant, and it raises or decreases the relaxation time.

The correlation factor is lowered by the added solute, due to 'structure breaking' effect, and is increased by the iceberg formation (i.e. structure-making), which contributes the largest contribution to the correlation factor.

II.Id - Thermodynamics of Solute -Solvent Interactions.

Various thermodynamic quantities have been employed, in order to obtain thermodynamic properties of the systems. Some of them are most important, and the commonly evaluated properties of the systems, are the Enthalphy(H), Entropy(S), and Free energy(G)(88). These are related by the equation

$$\Delta G = \Delta H - T\Delta S \qquad \text{II-15}$$

The other quantities which are frequently measured are the change in heat capacity ΔC_p, where

$$\Delta C_p = \left[\partial\ (\Delta H)/\partial T\right]_P \qquad \text{II-16}$$

and the partial molal volume, a quantity used to observe solute-solvent interactions.

$$\bar{V} = \left(\frac{\partial v}{\partial n_1}\right)_{T,P,n,n_2} \qquad \text{II-17}$$

The solutes can be classified(80) into two groups, in terms of their thermodynamic magnitudes of ΔH and $T\Delta S$. The solutes where $T/\Delta S > \Delta H$ are called aqueous in nature, whereas those for which $T/\Delta S < \Delta H$ are the nonaqueous. In other words, the characteristic of an aqueous nature solute is entropy control of the solution thermodynamics. The series of apolar solutes have been examined. It has been postulated that the hydrocarbons have low solubility in water, hence have a positive ΔG soln. The ΔH_{soln} is negative for the lower hydrocarbons. The low solubility is due to the negative ΔS_{soln}.

Butler(1) calculated the entropy of nonelectrolytes in dilute solution, and showed that ΔS_h plays a unique role in determining the free energy of hydration of the alcohols. In addition to this view Barclay-Butler(71) introduced a plot of ΔH_h against Δh, for the rare gases in the nonaqueous solvents, which is a straight line.

Frank -Evans(4) explained that the negative ΔS_h is due to the formation of hydrogen bonded clusters around the apolar solute, in terms of hydrophobic interactions. The structural effect of the liquid water has been examined by Nemethy-Scheraga(5). They employed the Frank-Wen(6) model for water of the flickering cluster, and based their calculations with statistical mechanical basis, on the assumption that a water molecule possessing four hydrogen bonded water neighbours,could accommodate neighbour solute molecule by lowering the energy of the water molecule. According to the Aranow-Witten(89) model the chain mobility is restricted when a hydrocarbon molecule or the chain length of the alcohol or amine transfer from vapour state to the aqueous environment. As a result, the internal entropy is reduced. This behaviour has been attributed to the loss in entropy rather than any formation of hydrogen bonded configurations.

Miller-Hildebrand(90) proposed a different view for the behaviour of the apolar solutes in aqueous solution considering the bent hydrogen bond.

Krishnan-Friedman(91) studied the thermodynamic transfer properties of hydrocarbons from water to dimethylsulfoxide (DMSO), and to propylene carbonate (PC) environments. They have observed that there is no structural increase of water, which gives a positive entropy change for the transfer as pointed out by Frank-Evans(4).

The view which is related to the structural properties of the water in the presence of apolar solutes, has been extensively studied in order to evaluate the thermodynamic properties of the hydration of apolar solutes in aqueous systems(92,93,94,95).

In recent years, new results concerning the heats of the solutions of the alcohols at various temperature, ranging from methanol to the butanol have been introduced.

Butler(96) was able to evaluate enthalpy, entropy and the free energy of the hydration, in terms of the heat of vaporization of the alcohol. In this process it is apparent that the apolar region of the alcohol behaves the same as an apolar solute.

Arnett-Kover-Carter(97) have determined the heat capacities of the solutions of lower alcohols. They also found large positive values of ΔC_p. This observaton indicates that the apolar part of the alcohol molecule controls the solution behaviour, and the lower ΔC_p value being due to the branching of the chain. The heat capacity of the solution from the vapour phase was compared with the entropy of hydration. This treatment supported the idea that the heat capacity reflects also the solvent structuring character of the apolar side of the alcohol molecule.

The solvent-structuring concept has been extended for measuring the ΔH_{soln} of the alcohols in water and the other solvents. The enthalpies of transfer of the molecules from one state to another, has been calculated(91) by taking into account the contributions of the groups to the solvation enthalpies. This approach has enabled the evaluation of group contributions, and the magnitude of the solvent structuring in water. It is reasonable to consider that ΔH_h and ΔS_h of the apolar group hydration of the alcohol up to C_6 is not affected by the presence of the C-OH(4,71,80) group.

Another study has been carried out by Konicek-Wadsö(98). The most interesting conclusion arising from their results, is the independent nature of the polar group in the increment of vapour heat capacity per -CH_2- group. In this process it appears that the water structure around the apolar group is only slightly affected by the polar group.

Similar behaviour has been observed in the solution of the tetraalkylammonium ions(6,99). The obtained heat capacities are large and positive, due to effects of the apolar groups on water structure, and depend on the nature and size of the alkyl groups of the ions, (i.e. Bu_4N^+ ion has more positive heat capacity $\Delta C_p{}^\circ$ than the Pr_4N^+ ion). It can be concluded that the apolar groups govern the interactions of the ions, in terms of the electrostrictive structure making and breaking effects.

Considering the solvation enthalpies, Krishnan-Friedman suggested(91,100) that Me_4N^+ is a net structure breaker, while Pr_4N^+, Bu_4N^+ and AmN^+ ions are net structure makers. This conclusion has been confirmed by other investigators(101,102). The volumetric properties of ions are also interesting. In the case of simple ions there is a volume decrease on solution, and it decreases with increasing ion size, due to the apolar group of the ion(103).

Hepler(104) studied the relationship between the structure-making and structure-breaking solutes, and the thermal expansion of the aqueous solutions.

He introduced the relationship:

$$\left(\partial \bar{C}_p{}^\circ / \partial P\right)_T = -T\left(\partial^2 V / \partial T^2\right)_P \qquad \text{II-18}$$

and concluded that structure-breaking solutes should have negative $\partial\bar{a}_2/\partial T$ and structure-making solutes positive $\partial\bar{a}_2/\partial T$.

The ultrasonic velocity measurement method has been employed by Conway-Verrall(105) for the investigation of solution properties of a series of tetraalkyl ammonium salts. They obtained negative values of the apparent molal adiabatic compressibilities of the ions, which decreased as the apolar groups increased.

Frank-Wen(6) introduced the idea that the partial molal heat capacity of the solution, in the presence of the ionic solute is negative, due to "freezing out" of a degree of freedom in the region of immobilization of water molecules, and destroying the ice-likeness region around the ion. They have also studied the apparent molal heat capacity of the solute $(n\text{-}C_4H_9)_4N\ Br$ in aqueous solution.

The observed large value of ϕ_{cp} which is about 270 Cal/deg.mole, has been interpreted in terms of the increased ordering of the water molecules around the apolar side of the alkylhalide ion, and according to their postulation the hydrogen bonded water configurations around the solute decrease with increasing temperature, consequently it melts due to the adsorbed extra heat.

The activity and osmotic coefficients of the tetraalkylammonium salts, have been investigated by Lindenbaum-Boyd(106). They have shown that at low concentration the coefficients of the chloride salts increase with the size of cations,

$$Me_4N^+ < Et_4N^+ < Pr_4N^+ < Bu_4N^+ \qquad \text{II-i.1}$$

bromides and iodides show the reverse order. At high concentration the osmotic coefficient of the salt decreases with increasing ion size. This behaviour has been attributed to the structure making ability of the chlorides, and the enforcement of the bromides, and iodides for ion-pairing.

Lindenbaum has extended(107,108,109) his investigation by examining the apparent molal heat contents of one molar aqueous solutions of the sodium salts of butyric and valeric acides. The results follow a similar pattern to those of cationics, except inorganic cationics which decrease with increasing cation size. On the other hand, the exothermic heats of tetrabutylammonium carboxylates, have been discussed in terms of hydrophobic interactions, under the influence of both cationic and anionic hydrophobic groups.

The effect of apolar groups on the entropies and enthalpies of theaqueous salt solutions, have been also examined in order to explain the solvent-solute interactions.

The order of decreased heat of the solution of a given halide can be defined such as,

$$Bu_4N^+ > Pr_4N^+ > Et_4N^+ > Me_4N^+ \qquad \text{II-i.2}$$

Timasheff-Fasman$^{(110)}$ have introduced the partial molal unitary entropy of the solution, in order to characterize the effects of a given solute on the solution property.

The entropy related to the solute, and its cosphere in the solution, has been termed the cratic portion of the conventional partial molal entropy of the solution. He has shown that the partial molal unitary entropy of the solution is related to $\overline{\Delta S}$ as,

$$\Delta S_{unitary} = \overline{\Delta S} - 2R \ln M \qquad \text{II-19}$$

Wen-Hung$^{(111)}$ measured the solubilities of lower hydrocarbons in water containing 0,1 to 1.0M solutions of ammonium bromides $(HOC_2H_4)_4NBr$ and R_4NBr at four temperatures. They explained that ammonium bromide salted out all the gases, while the large tetraalkylammonium ion had a salting-in effect. Both $(CH_3)_4NBr$ and $(HOC_2H_4)_4Br$ salted in the larger gas molecule, while salting out the smaller molecule. Their explanations have been based on two fundamental effects, a) indirect interactions between R_4NBr and RH, due to changes in the structure of the solvent molecules. b) direct hydrophobic interactions between two solutes. The salting out efficiency between 5° and 35° is,

$Bu_4N^+ > Pr_4N^+ > Et_4N^+$ 5°

$Et_4N^+ > Pr_4N^+ > Bu_4N^+$ 35°

The thermodynamics of electrolytes of aqueous binary mixtures have shown that ΔH_t and ΔS_t contain the structural contributions. It has been shown(112,113) that ΔH_t is positive, increases with the dilution of the solution. But ΔH_t becomes negative when the organic solvent concentration is increased. This behaviour has been examined by means of the solvent-organic solute interactions. Feakins(114) suggested that at low concentrations, organic solutes behave as structure making (i.e. increase solvent structure).

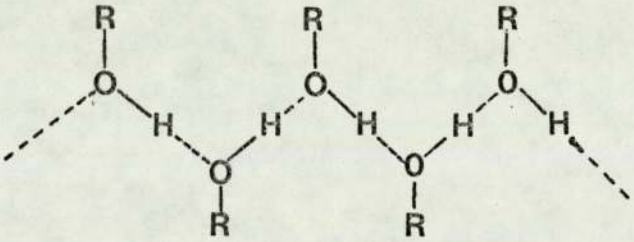
The standard partial molal heat capacities of sodium tetraphenylborons in the aqueous solutions from 0° to 90°, have been examined(115) in terms of the variations of the integral heats of the solutions with temperature. The relationship between heat and temperature shows two discontinuities, which corresponds to a minimum around 50°, and maximum around 70°. The minimum has been interpreted in terms of hydrophobic interactions, and the maximum is attributed to a reduction in structure makers capacity of the solute above 70°.

The thermodynamics of the mixed solutes in water at infinite concentrations provide valuable information about the solute-solvent interactions. In order to evaluate the solution properties, one must experimentally determine the thermodynamic parameters of the solution. No doubt, the obtained features will be the thermodynamic description of a system.

II.Ie - Effect of Aliphatic Alcohols.

The interactions between water and the alcohols are rather complex. An alcohol molecule has one oxygen atom which carries one proton, and two lone pairs of electrons. Therefore it acts as a proton donor, and as a proton accepter. It has been shown(116) that only two bonds are formed in the liquid state, due to the average coordination number of a molecule being two.

It has therefore been suggested(117,118,78) that the molecules are arranged in chains, in terms of hydrogen bonds as linear polymers or cyclic aggregates (most probably linear polymers as shown below)



II.i.4

The water behaves as a host to the molecules, which have a certain affinity for water. Since the alcohols possess both hydrophilic and hydrophobic functions, the alcohol-water-mixture reflects the strength of the intercomponent attractions.

In the alcohol-water mixture, the hydrogen bonded water molecules are endothermically destructed with the alcohol molecules, which interact with water by hydrogen bonding(116). Consequently this could be attributed to the bond breaking, and loss of order involved in the pseudo crystalline structure of water(26). Such breakdown increases with increasing concentration of the alcohol.

On the other hand, the water molecules depolymerise the cyclic or linear polymeric aggregates of the alcohol molecules in the mixture, by intercomponent hydrogen bonding, and preferential hydrogen bonding occurs between dissimilar species(119).

The molecule of the alcohol is able to 'build in' to the water structure. This is quite certain for the methanol-water mixture(120). It has been observed that, the alcohols have more 'basic character' than that of water in the alcohol-water mixtures, and they behave more as protons acceptors than donors(116). This interaction can be shown by a simple acid-base proton transfer of the kind(119).

$$H_3O^+ + RO^- = H_2O + ROH = OH^- + ROH_2^+ \qquad \text{II.i.5}$$

The order of increasing proton accepting facility has been given by Gerrad-Macklen(121);

$$\text{Me-OH} < \text{Et-OH} < \text{Pr-OH} < \text{t.Bu-OH} \qquad \text{II.i.6}$$

Eley observed(2) that a mole of water can accommodate nonpolar molecules, since it has 9 cm^3 of empty space provided by its ice like structure. So it is reasonable to assume that nonpolar parts of the lower alcohol molecules, could fit well into such cavities.

The lowering of the transition temperature in aqueous protein solutions containing aliphatic alcohols, has been interpreted(122) in terms of the binding of the nonpolar portions of the alcohol molecules, to the nonpolar sides of the denaturated proteins. This binding has been explained, by means of the formation of hydrophobic bonds between nonpolar sides of the molecules.

The polar end of the alcohol is considered to retain its hydrogen bonding to water. Herskowits et al.(123) introduced a similar type of interaction, in an aqueous solution of a protein containing the alcohol, taking into account the interactions between the water cluster and the alcohol molecule(123,124,125).

The addition of aliphatic alcohols to the aqueous solution of alkylammonium bromides, have increased the relative viscosities of the systems. (1.2148 and 1.3210 for 0.1M aqueous solution of C_{10} containing 1M and 2M, CH_3OH respectively. Table II.I.2). The observed viscosity is much higher than that of aqueous solution (1.0761. Table II.I.1). The intrinsic viscosity of micelles increases also nonlinearly with the increasing alcohol chain length (0.0415 $g.dl^{-1}$, 0.056 $g.dl^{-1}$ and 0.058 $g.dl^{-1}$ for C_{10} in addition to 1.M. CH_3OH, C_2H_5OH, and C_3H_7OH respectively (Fig.II.12 and Tables II.I.2, II.I.2,A,C).

It is reasonable to consider that the interactions of water molecules with the OH groups of the alcohols, hydrophobic interactions between nonpolar parts of the alcohol molecules and the aggregated alkyl groups, and the interactions mentioned in this chapter contribute to the viscosity increment of the aqueous solutions of n-alkylbromides containing alcohols.

II.If - Relative, Reduced and Intrinsic viscosities of Aqueous Solutions of n-Alkyltrimethyammonium Bromides.

The viscosity increases in aqueous solution which occurs with the addition of solute particles, has been explained by Einstein. When a particle is dispersed in a liquid, this disturbs the flow of the liquid. Consequently the internal friction of the system is higher than that of the pure liquid.

This disturbance was calculated by Einstein(126,127) by investigating how the energy dissipation of the system was changed by the presence of the spherical particle which carries no electrical charge.

The liquid was treated as a viscous continuum, with rigid spherical obstructions at the surface of which the liquid is at rest. He obtained a well known expression,

$$\eta = \eta_0(1+2.5\phi) \qquad \text{II-20}$$

which is valid at low concentrations. The equation is strictly applicable only to systems in which the particles are perfect spheres, which do not interact with one another.

In order to derive the relative viscosity, which is the ratio of the viscosity of the dispersion to that of the solvent the Einstein equation (II-20) can be written as,

$$\eta_{rel} = \frac{\eta}{\eta_o} = 1+2.5\phi \qquad \text{II-21}$$

The relative increase in the viscosity of the dispersion, over that of the solvent alone, is defined as specific viscosity, which is given as,

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \frac{\eta}{\eta_o} - 1 \qquad \text{II-22}$$

and the Einstein equation becomes,

$$\eta_{sp} = \frac{\eta}{\eta_o} - 1 = 2.5\phi \qquad \text{II-23}$$

The reduced viscosity is obtained from equation (II-23), dividing by the volume fraction ϕ,

$$\frac{\eta_{sp}}{\phi} = 2.5 \qquad \text{II-24}$$

Since the volume fraction ϕ is directly proportional to the concentration, the determined reduced viscosities of various concentrations are plotted versus concentrations in $g.dl.^{-1}$ The extrapolation of the obtained curve to c = o gives the intercept α, which is known as the intrinsic viscosity $[\eta]$ (Fig.II.5, Fig.II.10, II.10.A).

The relative viscosity which is relative to the solvent viscosity increases as the hydrocarbon chain length increases. The absolute viscosity of water at 25°C is 0,8949 CP(139). The lowest concentrationsused for the determination of viscosities of alkylammonium bromides are 1×10^{-2} $m.dm^{-2}$, 4×10^{-3} $m.dm^{-3}$ and

1×10^{-3} m.dm^{-3} for C_{10}, C_{12} and C_{14} respectively. (Tables II.I.1, II.I.1.A). The corresponding viscosities are 1.0027, 1.0035 and 1.003 respectively. This increase in relative viscosity as can be seen (Fig.II.1), is independent of the concentration, and molecular weight of the surface active agent.

The viscosity increases nonlinearly as the chain length and concentration increases. The obtained relative viscosities are larger than unity. This increase is mainly due to the solute-solvent interactions in the aqueous solution. In aqueous solutions of alkylammonium bromides, the structural order of liquid water increases near the nonpolar solutes, and forms hydrogen bonded water networks or clusters around the nonpolar groups(4).

The increased volume of liquid water, stronger associations of the polar head groups, and the ions with water can be given as possible reasons for the increased viscosities of the system.

An abrupt change occurs at a critical concentration on the viscosity-concentration curve (Fig.II.2). The viscosity gradually increases with the concentration. However at a critical concentration (6.5×10^{-2} m.dm^{-3} and 1.68×10^{-2} m.dm^{-3} for C_{10} and C_{12} respectively) the slopes of the curves change.

This is due to the release of ordered water molecules around the nonpolar groups(128), and transferring of nonpolar groups from the aqueous environment to nonpolar region. As a result of this process the free energy of the system decreases(129,130).

The hydrodynamic result of the distortion of stream lines by the particles in aqueous solution, and the electrical forces between the ions in adjacent layers of an electrolyte solution, could be also considered as possible effects, which play a unique role, for increasing the viscosities of systems(131).

In order to isolate the effect of solute, we can compute the value of the specific viscosity. This is found to be small compared with the relative viscosities. As it can be seen, the specific viscosity of particular concentration such as 0.06 $m.dm^{-3}$ and 0.01 $m.dm^{-3}$ for C_{12} are 0.09386 and 0.0081 respectively. (Table II.I.1). These values are very small compared with the respective relative viscosities (1.0938 and 1.0081). However the respective reduced viscosities 0.0507 $g.dl^{-1}$ and 0.0262 $g.dl^{-1}$ are relatively large. The reduced viscosity does not change much in the dilute solution. It would not change at all, if the specific viscosity was proportional to the concentration.

The reduced viscosity is an indication of the increase in viscosity due to the mentioned effects,for per unity concentration in the solution concentration, the intrinsic viscosity of micelles increases with the increasing chain length, (0.06 $g.dl^{-1}$ and 0.069 $g.dl^{-1}$ for C_{10} and C_{12} respectively Fig.II.6).

It is precisely the desired quantity needed, in order to measure the solute- solvent interactions, in terms of the hydro-dyanmic properties of micelles.

II-Ig - Experimental Procedure.

II-Ig1 - Materials.

Methanol, n-propanol and n-butanol were BDH A.R. material. Absolute ethanol was obtained from Fisons(132) as absolute grade material. The alcohols were dried by standing over anhdrous sodium sulphate for 24h, and then distilled from all Pyrex glass apparatus. n-decyl, n-dodecyl and myristyl bromide were Kochlight(133) purus grade and cetyltrimethylammonium bromide, trimethylamine (anhydrous) were BDH(134) grade. The distilled water used was doubly distilled from all Pyrex glass apparatus. It had a surface tension of 71.5 dyn cm^{-1}, and a conductance (Λw) of the order of $< 1 \times 10^{-6}$ $ohm^{-1}cm^{-1}$ at 25°C.

II-Ig2 - Preparation of n-Alkyltrimethyammonium bromides.

An homologous series of alkyltrimethylammonium bromides with 10 to 14 carbon atoms was prepared with trimethylamine (anhydrous);(135) the alkylbromide was added slowly to a cold solution of excess (anhydrous) trimethylamine in absolute ethanol, and the mixture stirred at 0° for one hour, then the mixture was heated under a reflux condenser, cooled and the solvent evaporated. The obtained salts were filtered and dried. These salts and the commercial cetyltrimethylammonium bromide were recrystallized several times from benzene-ethanol (20:1) mixture.

The purity of the compounds was checked by using Du Nouy tensiometer(136). The alkylammonium bromides were recrystallized until a fine intersection on the surface tension-concentration curve was obtained. The C_0 values for alkylammonium bromides (6×10^{-2} mol.dm^{-3} and 1.9×10^{-2} mol.dm^{-3} for C_{10} and C_{12} respectively. Table II.I.1, II.I.1A and Fig.II3) are very close to the C_0 values obtained by viscosity method (6.5×10^{-2} mol.dm^{-3} and 1.68×10^{-2} mol.dim^{-3} respectively. Fig.II.2). These reported C_0 values were in good agreement with the values given in literature(137) (6×10^{-5} mol.dim^{-3} and 1.5×10^{-2} mol.dm^{-3} for C_{10} and C_{12} respectively). The bromide content 28.50%, and 25.90% for C_{10} and C_{12} was found very close to the theoretical values (28.51% and 25.91% for C_{10} and C_{12} respectively).

II.Ig3 - Measurement and Instrumentation.

II.Ig3.A - Viscosity Measurement.

For the viscosity measurements a U-tube capillary viscometer (Size A Serial No.4857 B.S. U.S.A.Volac Fisons)(132) with a flow time of ca.291s. for double distilled water ($\Lambda w < 1 \times 10^{-6}$ ohm^{-1}cm^{-1}) at 25° was employed. The viscometer was calibrated by using double distilled water, and 20% sucrose solution according to BS.188.1957(138).

The viscometer was carefully cleaned, rinsed with distilled water, and dried before filling with the calibration solution, then immersed in a thermostat, and 15 minutes allowed for equilibrium with the temperature 25°C ± 0.005 deg C, then the flow times of the reference liquids were measured by using an electric stop clock (cap. $^1/_{50}$th sec). The procedure was repeated three times, then the average time was used as flow time of the liquid. (291 sec. and 513.22 sec. for double distilled water and 20% sucrose solution at 25°C respectively).

The values of B and C constants for the viscometer used were calculated by following equations, taking into account the viscosities (absolute) of the reference liquids (0.8949 cp and 1.701 cp for distilled water(139) and 20% sucrose solution(140) respectively)

$$B = \frac{t_1.t_2(\eta_2 t_1 - \eta_1 t_2)}{t_2^2 - t_1^2} \qquad \text{II-25}$$

$$C = \frac{\eta_2 t_2 - \eta_1 t_1}{t_2^2 - t_1^2} \qquad \text{II-26}$$

The obtained values of B and C constants are 30 and 0.00342 respectively. The kinematic viscosity of the double distilled water was calculated by using an equation(138) at 25°C

$$\eta_k = C.t_1 - \frac{B}{t_1} \qquad \text{II-27}$$

The obtained kinematic viscosity of the double distilled water is 0.8921 cp, which is in good agreement with the value (0.8975 cp) given in literature)(139).

After the calibration, the absolute viscosity of the solutions were calculated using an equation,(87) taking into account the density, and viscosity of the reference liquid (distilled water).

$$\frac{\eta_a}{\eta_1} = \frac{t_a \times d_a}{t_1 \times dw} \qquad \text{II-28}$$

II.Ig3.B - Density of the solutions.

The density of solutions were measured with a 10 ml pycnometer at 25°C ± 0.005 deg.C(141). In order to obtain the density of a solution, the weight of the dry pycnometer was determined (Wd), and was filled with double distilled water, then was thermostated at 25°C for about 10 to 15 minutes. After the equilibrium with temperature the stopper of the pycnometer was inserted. It was made certain that the outside of the pycnometer was completely dry, then the weight of the pycnometer filled with water was determined (Ww).

From the density of water at 25°C (dw = 0.9971 g/ml) the volume of the pycnometer was determined by the equation,

$$V = \frac{Ww - Wd}{dw} \qquad \text{II-29}$$

then the density of solutions were measured in the same way by using calibrated pycnometer at 25°C (1.0002 g/ml for C_{10} of 0.1 mol.dm^{-3} Table II.I.1.).

II-Ig3.C - Density of Solids.

A weighed amount of substance was introduced into a calibrated pycnometer, (known volume) then a suitable liquid (paraffin liquid B.P.) was added to the reference mark. The weights of the empty and filled pycnometer was used to calculate the density of the alkyl-ammonium bromides at 25°C, in terms of the following equation(142)

$$D_s = \frac{D_L \quad W_s}{V_p \; D_L + W_d + W_s - W_T} \qquad \text{II-30}$$

II.Ig3.D - Surface Tension measurement.

The surface tension measurements of the solutions were made using the Du Nouy Tensiometer according to the instrument manual(136).

II.Ig3.D.1 - Zero adjustment.

First the tension of the torsion wire was checked. After this procedure the pointer on the torsion head was set to zero on the scale by means of the knurled knob, then the other head at the other end of the wire was turned to adjust the boom until the line on the mirror appeared to be halfway between the boom and its image (zero point).

II.Ig3.D.2 - Calibration.

Calibration was made using a liquid (double distilled water) of known surface tension, and a weight. A piece of tissue paper was put on the ring, and the boom was adjusted to zero. After that a 0.5g weight put on the paper, then the pointer was adjusted until the boom was again at zero. Since the ring has a total contact of length of 8 cm, the corresponding surface tension is 61.3 dyne cm^{-1}. The obtained reading (61.2 dyne cm^{-1}) was very close to the above value.

On the other hand, double distilled water was used to calibrate the instrument. The obtained surface tension of water at 25°C (71.5 dyne cm^{-1}) is very close to the value given in literature (71.9 dyne cm^{-1})(139).

II.Ig3.D.3 - Measurement of Surface Tension by the Ring Method.

The ring was cleaned by heating in a bunsen flame before taking the measurement. The clock glass containing the solution was placed on the circular table, and the height was adjusted so that the liquid level was about 1 cm below the ring. The pointer, and the boom both were set to zero (as described), then the liquid was raised until it touched the ring. The torsion head was turned until the boom was again on zero.

After this procedure, the liquid was lowered slowly at the same time, turning the torsion head so that the boom remains on zero. The detachment of the ring from the surface of liquid corresponds to the pointer reading, which gives the surface tension.

The C_0 of surfactants with an alkyl chain from 10 to 16 carbon atoms in aqueous solutions, and solutions containing additives was determined by means of the viscosity, and surface tension methods, plotting $^1/\eta_{red}$ viscosity versus concentration (surfactant), and the surface tension against the concentration. (3.4×10^{-3} mol.dm^{-3}, and 3.7×10^{-3} mol.dm^{-3} for C_{14} by surface tension, and viscosity methods respectively. Figs II.3, II.2, II.8, II.8.A and Tables II.I.1, II.I.1.A). The partial specific volume at C_0 in aqueous solution and solution containing additives was calculated from corresponding partial molal volume of the micelles(88).

II.Ih - Micellar Properties from Hydrodynamic Data.

II.Ih1 - The aqueous solutions of n-Alkylammonium bromides.

The viscosities of surfactant solutions have been widely investigated for the determination of the hydrodynamic properties of micellar systems. Viscosity theory has developed sufficiently to provide valuable information about the particle size, shape, charge and the structural problems of the micelles.

The theory of micelle formation has been extensively studied(143,144,145,146) taking into account the energy changes associated with the process. Although small heat changes occur, the micelle formation is predominantly an entropy directed process. The entropy effect arises from the formation of structural regions (ice bergs) around nonpolar solutes(4,6) and the interactions between polar head groups and water molecules (hydrophobic interactions) which cause the nonpolar portions of the solute molecules to transfer from an aqueous environment to the nonpolar regions(4). By this process they increase their flexibilites.

At this stage there are abrupt changes in the colligative properties of the amphiphiles and at a critical concentration due to the discussed thermodynamic process micelles are formed.

It is found that there is a change at certain concentrations on the $^1/\eta_{red}$ - concentration curve of the n-alkyl bromide in aqueous solution and in the solutions containing aliphatic alcohol. When the hydrophobic tails leave the water energy is gained. Consequently the charged heads are brought to the certain configurations, in order to develop a basic micellar structure.

The polar head groups are located at the micelle-water interfaces while the hydrophobic parts of the aggregates form the interior of the micelle(147).

Various models have been proposed for the micelle structure. McBain(148) introduced two kinds of micelles, ionic spherical and neutral lamellar. Hartley(143) proposed only one type of micelle, a spherical one.Mattoon et al.(149) postulated a two layer sandwich micelle as another possible model.

Debye and Anacker(144,150) showed by light scattering experiments that the micelles are small in solutions of low ionic strength. They become large as the ionic strength increases. They concluded that in the aqueous solution of n-alkylbromide containing KBr, the micelles are rod-like. Trap-Hermans(151), Cohen-Vassiliades(152) and Hermann (153) by using light scattering, Reiss-Husson-Luzzati(154) applying small angle X-Ray scattering introduced also the idea of rod like micelles. Stigter(155,156) postulated spherical, Poland-Scheraga(145,157), Shinoda(158) discussed cylindrical models of the micelles.

The micelle interior generally has been treated as a liquid hydrocarbon state(159,160,161). However there have been some indications that the micellar interior could have some amount of water molecules(162,163,164,165). According to this approach water molecules could penetrate in to the micelle up to the distances of approximately three to six carbon atoms.

The structure of the interior of a micelle has been considered as quasi-crystalline hydrocarbon structure(158).

The number of carbon atoms in the hydrocarbon chains of homologous amphiphiles is one factor determining the critical micelle concentration. It has been shown that the C.M.C's decrease logarithmically with the increase in the number of carbon atoms (n) for various amphiphiles. The relation could be given by the equation(158)

$$\log_{10} C_0 = A - Bn \qquad \text{II-31}$$

The C.M.C's of the n-alkylbromides in aqueous solution decrease linearly obeying the above expression (Fig.II.4). The intrinsic viscosities of the micelles increase also with the increasing chain lengths (Fig.II.6). Since the intrinsic viscosity $[\eta]$ is the function of the size and shape of the particle, the relationship between density of the micelle and $[\eta]$ can be given by an equation(166)

$$[\eta] = \frac{K}{100d} \qquad \text{II-32}$$

The shapes of the micelles of the n-alkylammonium bromides in aqueous solutions are discussed in terms of Huggins constant, viscosity, dissymmetry and light scattering measurements. For the rigid spherical particle, the Huggins constant is equal $\simeq 2.0$. The relationship between concentration effect and the particle shape has been given by Huggins(167).

$$\frac{\eta_{sp}}{C - C_0} = [\eta] + H_k[\eta]^2 C \qquad \text{II-33}$$

where H_k is the Huggins constant. In our case the value of H_k of C_{16} has been calculated in terms of the slope of the curve $\left(\frac{\eta_{sp}}{C - C_0}\right)$ versus $\left(C - C_0\right)$ (0.004) divided by $[\eta]^2$[176]. The obtained H_k value (0.44) is much smaller than that of ≃ 2.0. The dissymmetry of the solutions measured by light scattering at 60° and 120°, are very close to unity, (1.010). In order to introduce the possible shapes of the micelles, it is necessary to expand our considerations for the other kind of shapes, which could be the possible shapes of the micelles in our systems.

Let us first consider the possibility of nonspherity. The other likely shapes of the micelles are disc and rod. The disc shapes of the micelles have been discussed by Harkins[149,167,168] and he concluded that they have a thickness of twice of the length of the surfactant molecule. If we assume the distance between $-\overset{|}{\underset{|}{N}}-CH_2-$ is approximately equal to $-CH_2-CH_2-$ distance, one can calculate from the bond lengths and bond angles a length (fully extended), close to 25Å for C_{16} in aqueous solution. So the thickness of the disc micelle will be 50Å. We can calculate the volume of a micelle, taking into account the macroscopic density of C_{16} (1.1423 g/ml), and the micellar molecular weight (M = 31250, N ≃ 86 from light scattering). Considering the volume of the micelle, one can calculate that each monomer occupies a volume of about 528 Å^3. The micelle then should have a volume about 45410 Å^3. In order for a disc of thickness 50Å, to have the required volume, it should have a radius of 17Å. This disc might approximate a prolate spheroid of revolution of axial ratio 1.47, which should give rise to an intrinsic viscosity 0.023 g/dl [169,170].

On the other hand, the rod like model should have the diameter of 50Å.

This model could approximate to an oblate spheroid of revolution of axial ratio $^1/AR = 2.2$ The micelle of such shape should have the intrinsic viscosity 0.026 g/dl (169,170). Neither model suffices to explain $[\eta] = 0.096$ g/dl for C_{16} that was found experimentally. However the above theoretical approximations indicate that the micelles are spherical. It is generally believed that the ionic detergent micelles with molecular weights in the region of $1 \times 10^4 - 1 \times 10^5$, contain 20-100 monomers and have average radii of 12-30Å (171,172) are spherical.Schick et al. (172) has shown that with molecular weights in excess of 5×10^5 the micelles are rod shaped, and are large compared with the low molecular weights aggregates(172).

In view of the treatment of the micelles, and the observations about the micellar shapes given in the literature, it is concluded that the micelles are spherical. Since part of the volume of the any shape of micelle is occupied by liquid hydrocarbon chains, it is reasonable to assume that the density of a micelle of n-dodecyltrimethyl ammonium bromide in aqueous solution, could be fairly close to that of the liquid dodecane which is 0.802 g/ml at 25°C(155,156).

Theoretically $[\eta]$, calculated from the equation (II-32) for C_{12} micelles is 0.0312 g/dl. Since the $[\eta]$ of the rigid, non-interacting sphere which has unity density is equal to $[\eta]$, 0.025 g/dl. The deviation from the Einstein expression(126,127) could be attributed to the ionic micellar nature of the colloidal particle. The existence of the charges on the kinetic units increase the $[\eta]$, due to the electroviscous effect which has been discussed in Section II.Ia.

Booth(44) showed that the viscosities of the suspension particles, which are noninteracting charged spheres with Gouy Chapman double layer, could be given by an equation such as(147)

$$\eta = \eta_0[1 + 2.5\phi E] \qquad \text{II-34}$$

The interaction between a charged sphere and its double layer is given by

$$E = 1 + \sum_{1}^{\infty} b_i (e\xi/kT)^i \qquad \text{II-35}$$

which includes a correction for the electroviscous effect. If we generalize the above equation to include particles of all shapes, then we have

$$[\eta] = E\beta/100d \qquad \text{II-36}$$

It is also reasonable to discuss $[\eta]$ of the micelle from the solvation point of view. As the micelles have hydrophilic surfaces this approach could give valuable information about the hydration phenomenon of the micelles.McBain et al.(173) have shown that potassium laurate molecules are hydrated, and he suggested that each monomer contains 10 bound water molecules.

In view of this fact, we assume that the micelles are hydrated. Consequently this hydration contributes to the increases in viscosity and $[\eta]$ due to increase of its kinetic volume in terms of hydration.

The intrinsic viscosity is related to the shape and volume of the micelle by an equation(174);

$$[\eta] = \frac{NoK\ Vh}{100M} \qquad \text{II-37}$$

Since the micelles are assumed to be spherical, one can calculate the hydrated volumes of the micelles. (Table II.I.4). It is also possible to estimate the anhydrous volume by using an equation such as (174)

$$Va = M\bar{\nu}/No \qquad \text{II-38}$$

From the above observations, the deviation from theoretically calculated value of $[\eta]$, can be postulated by a quantitative treatment such that one can calculate the weight of water hydrating one gram of surfactant[175,176] using

$$100 \times [\eta] = 2.5(\bar{v} + w\,dw) \qquad \text{II-39}$$

The values obtained are 1.458 g /g.surfactant and 1.841 g /g.surfactant for the anhydrous micelles of C_{10} and C_{12}, which correspond to 22 and 31 water molecules for each monomer of the micelles of C_{10} and C_{12} respectively. It increases with increasing chain length (Table II.I.4).

According to Oncley's[177] calculations, the maximum hydration w compatible with $[\eta] = 0.045$ is 0.6 g /g. surfactant, whereas the limiting w value for $[\eta] = 0.049$ is 0.74 g /g. surfactant. These maximum hydration values refer to spheres. Since we have higher $[\eta]$ than the values given by Oncley, the deviations from given values could be attributed to the heavily hydrated spherical micelles.

This is due to the stronger interactions of the water molecules with the hydrophilic polar head groups in the Stern layer, in terms of hydrophobic interactions. Consequently water molecules are bound to the head groups with possible covalent hydrogen bonds.

The degree of hydration of the micelle undoubtedly depends on the number of counter ions adsorbed in the Stern layer, and the possible interactions between hydrated ions and polar head groups and water molecules.

II.Ih2 - The effects of the aliphatic alcohols.

The nature of the effects produced by alcohols upon the critical micelle concentrations of aqueous solutions of surface active agents is a matter of some dispute. In aqueous solutions containing a certain alcohol concentration, if it is assumed that the alcohol molecule and the soap ion in the micelle dissolve each other according to regular solution theory, then we can write[178]

$$C_S = C_S{}^{\circ}\, N_S\, (N_S + N_A) \;\ldots\; N_S/(N_S + N_A) = 1 \qquad \text{II-40}$$

and

$$C_A = KC_A{}^{\circ}\, N_A/(N_S + N_A) \;\ldots\; N_A/(N_A + N_S) \ll 1 \qquad \text{II-41}$$

The alcohol molecules in bulk solution are in equilibrium with the alcohol molecules in the micelles. Hence we could express the concentration of the alcohol in the mixed micelle

$$C_A \propto N_A/(N_A + N_S)\ \exp\left[-\ (X-X')kT\right] \qquad \text{II-42}$$

if we substitute the molar fraction of the alcohol then we obtain,

$$x \propto C_A\ \ \mathrm{Exp}(m'w)/kT \qquad \text{II-43}$$

The molar fraction of the alcohol in the micelle increases as the bulk concentration decreases, and the equilibrium concentration of soap ion in the bulk decreases in terms of the molar fraction of the soap ion in the micelle. In this work methanol, ethanol, n-propanol and n-butanol have been used as additives to investigate their effect on the formation of micelles, and to study hydrophobic interactions in aqueous solutions of decyl and dodecyl trimethylammonium bromides.

On the addition of a series of alcohols to aqueous solutions of C_{10} and C_{12}, it was observed that the relative viscosities of the systems increased the same as in aqueous solutions, with the increasing concentrations of the alcohols. On the other hand, $[\eta]$ values of the micelles increased also with increasing chain lengths of the alcohol molcules. But it decreased with the increasing concentration of the particular alcohol. (FigsII.11, II.11.A).

The increase in relative viscosity (relative to the solvent) is due to hydrophobic interactions between apolar regions of the soap and alcohol molecules(4,6), OH polar groups and icebergs(123,124,125), the alcohol molecules and polar heads of the amphiphiles(124,125) and the possible binding of the nonpolar parts of the alcohols to the apolar sides of the monomers(122).

The clusters around the nonpolar groups are not much affected by the alcohols at low concentrations, due to their behaviour as structure promoters(97). When the concentrations of the alcohols is increased alcohol rich systems are obtained. Hence the structure of water molecules are destroyed by the alcohols molcules in such systems. Owing to their polymeric characters(118,78), the alcohols molcules increase the hydrogen bonding mechanism by the interactions of water molecules while they associate with polar-OH groups in the solutions.

As has been explained, the effect of the alcohol on the water structure increases with the increasing alcohol concentration. This situation directly affects the micelle formation mechanism, and the micellar shape, size and the structure.

It is universally accepted that the alcohol penetrates into the micellar core through the bulk solution and the Gouy-Chapman-Stern electrical double layer and it changes the electrokinetic property of the system(158,179) forming a mixed micelle.

In the case of asymmetrical particles(175), the specific viscosity of the system is affected by the particle shape and size.

The Einstein equation(126,127) can be rewritten by including rigid particles with non spherical shapes.

$$\lim_{C \to 0} \left[\left(\frac{\eta - \eta_o}{\eta_o} \right) \Big/ C \right] = [\eta] = V \times K/100 \qquad \text{II-44}$$

The ratio $\frac{\eta - \eta_o}{\eta_o} \Big/ C$ is strongly dependent on the axial ratio of the particles.

The axial ratio of the particle is defined as $a/b = p$ where b is the semiaxis of the revolution, and a is the equatorial radius.

If the ratio is less than 1 the shape is oblate ellipsoid, equal to 1 for sphere and greater than 1 is for a prolate ellipsoid.

For the large value of the axial ratio of the nonspherical rigid particle, Kuhn and Kuhn(181) introduced an equation to calculate the axial ratio for prolate or oblate ellipsoids

$$K = 2.5 + (32/15\pi)(p^{-1}-1) - 0.628(p^{-1}-1)/(p^{-1}-0.075) \qquad 0 < p \leq 1 \qquad \text{II-45}$$

$$K = 2.5 + 0.4075(p-1)^{1.508} \qquad 1 \leq p \leq 15 \qquad \text{II-46}$$

$$K = 1.6 + \frac{p^2}{5}\left(\frac{1}{3(\ln 2p-1.5)} + \frac{1}{\ln 2p -0.5}\right) \qquad p > 15 \qquad \text{II-47}$$

Other possible effects are the electroviscous effect and hydration. It is apparent that the hydration of the micelles is influenced by the solvation effects of the alcohol molcules. Hence the quantity of the hydration varies with the concentration of the added alcohol.

Since the frictional dissipation energy exists in the system due to the presence of the assymetrical particles, it is reasonable to introduce these two effects, shape and size of the micelle as driving forces to increase the $[\eta]$ viscosities of the micelles.

The results of measurements of C_{10} and C_{12} in aqueous solutions containing varying amounts of methanol show that the C_0 decreases up to a certain concentration (5.88×10^{-2} m.dm^{-3} and 1.2×10^{-2} m.dm^{-3} for C_{10} and C_{12} respectively. Tables II.I.2, II.I.3, Fig.II.9), then increases gradually as the concentration increases.

Brown et al.(182) showed that the C.M.C. of dodecylammonium chloride in methanol-water mixture first decreases, then the C.M.C. shows a marked shift on the equivalent conductance - $\sqrt{c}$ curve at the higher concentration. Similar effects have been observed by Evers(183) and Grieger(184) in aqueous solutions of hexadecyl and octadecyl quaternery ammonium salts.

It is apparent that methanol has a less hydrophobic group than the other lower alcohols. Hence it has a less structure promoting effect(97), which does not increase water structure, due to its proton acceptor(116) character. Consequently the hydrophobic interactions are weakened in the mixed solution. Since the methanol molecules are oriented with respect to water molecules, the solubilization involves penetration of the methanol molecules into the micelles. This(185) penetration phenomenon occurs with the polar groups orientated towards water and the hydrocarbon chain lying between those of the soap molecules in the micelles. However the lower dielectric constant might affect the dielectric distribution of the micelles and their kinetic properties.

At low dielectric constant, the stability of the micelle increases due to a decrease in the degree of dissociation of the micelle.

The micellar properties in the methanol-water systems could be attributed to those factors which have been discussed, ethanol behaves in the same way (Fig.II.9). Its dielectric constant lowering effect is greater than that of methanol. It has also higher hydrophobic side which favours hydrophobic interactions between various orientations of the molecules in terms of its higher proton acceptor capacity(116).

The behaviour of other alcohols are more complex. It is generally accepted that the additions of n-PrOH and n-BuOH even at low concentrations decrease the C_o(158,186). This decreasing effect in BuOH is higher than that of n-PrOH (Tables II.I.2,B,C,II.I.3.B,C, Fig.II.9). The decrease of the C_o is due to the decrease of free energy of the system, and the surface charge density, in terms of the entropy effect of the hydrophobic interaction in the mixed solution.

Those alcohols have longer chain lengths than that of previous alcohols and at low concentrations they increase water structure(97). On the other hand the hydrophobic interactions are more favourable between possible orientated configurations. They react more effectively because they are stronger proton acceptors. The lower dielectric constant causes ion-pair formation in these systems. The observed micellar molecular weight from light scattering shows an increase with the addition of 1M C_2H_5OH, then it decreases as the concentration increases. (Chapter VI).

The addition of alcohol to the system affects the hydrodynamic properties of micelles. The increase in relative viscosity (Fig.II.7, Table,II.I.2,1.2148 for C_{10} of 0.1 $m.dm^{-3}$ containing 1M CH_3OH) is higher compared with the respective viscosity (1.0761, Table II.I.1) of aqueous solution of C_{10}. This increase is due to solute-solute, and solvent-solute interactions. It shows an increase with increasing concentration of alcohol (1.321 and 1.4103 for C_{10} containing 2M and 3M CH_3OH respectively).

However the observed $[\eta]$ of micelles is less (0.0415 $g.dl^{-1}$ and 0.056 $g.dl^{-1}$ for C_{10} containing 1M CH_3OH and 1M C_2H_5OH Tables II.I.2, II.I.2.A) than that of aqueous solution (0.06 $g.dl^{-1}$ Table II.I.1). The solutions containing various concentration of C_3H_7OH and C_7H_9OH show a similar pattern (Tables II.I.2.B,C, II.I.3.B,C).

The decrement in $[\eta]$ of micelles is due to the effect of alcohols on the hydration of micelles, and the electroviscous(42,43,44) effect. In this work observations indicate that the number of water molecules bound to the micelles decreases as the concentration increases (decrement in hydration) and a similar effect is postulated for the electroviscous effect in the micellar system. As can be seen in Fig.II.12, $[\eta]$ increases non linearly as the chain length of alcohol molecule increases. After 1M C_2H_5OH, on the addition of 1M C_3H_7OH

the increment in $[\eta]$ is not significant (0.0495 g.dl^{-1} for C_{12}) compared with the same solution containing 1M C_2H_5OH (0.044 g.dl^{-1}).

The $[\eta]$ of micelles decreases when the number of carbon atoms in alcohol molecules is higher than three. (Fig.II.12). Hence, it is apparent that the dehydration effect of alcohols increases as the straight chain length increases. Although $[\eta]$ decreases with concentration, and alcohol molecules behave as a structure breaker at high concentration, the increment in relative viscosity can be attributed to the change of micellar shape, and size of the micelle. According to light scattering data the AMW of micelles first increases, (5.263×10^4 and 4×10^4 for C_{12} containing 1M C_2H_5OH and 0.5M C_3H_7OH respectively, Chapter VI) then decreases with increasing concentration.

The shape function of the micelles has been calculated using equation (II-44) (4.7 and 3.9 for C_{12} containing 1M and 2M C_2H_5OH respectively Table II.I.5). Then the axial ratio of the micelle (4.1 and 3.3 for the mixed micelle of C_{12} containing 1M and 2M C_2H_5OH respectively Table II.I.5) has been determined by substitution of the shape function into equation (II-46). The observed shape functions and axial ratios are comparable with the data given by Mehl et al.(169), and Scheraga(170) for oblate and prolate particles.

The obtained viscosity, and light scattering data for alkylammonium bromides introduce the idea that the micelles are of the prolate type rather than the other shapes. The stability of micelles has been discussed by Emerson-Holtzer(179) in terms of hydrophobic interactions, temperature effect, and the dielectric effect of the medium. They have concluded that as the temperature increases, the stability of micelles (DTAB and SDS) decreases. The lowering dielectric constant of the medium, and rise in temperature behave as micelle breakers since the repulsive forces between the head groups increase.

As has been discussed in this section, and in Section II.Ic, the effect of decreasing the dielectric constant of the medium increases as the alcohol chain length increases. The hydrophobic character of the alcohol molecule behaves as structure promoting at low concentration, due to an increase in structural order of water molecules.

The micellar properties at low temperature have been interpreted by means of the predominance of hydrophobic interactions over the dielectric effect of medium, and at high temperature the dielectric effect over the hydrophobic interactions(179). But at any particular temperature, two factors have been introduced for the stability of mixed micelles.

1) The effect of hydrophobic surface, through the contribution of free energy of the hydrocarbon chain to the micellization.
2) The increment in the effect of dielectric constant of the medium when it is lowered by the addition of alcohol molecule.

Due to these factors the mixed micelles are more stable than the ordinary micelles at low concentrations of alcohol. But the hydrophobic interactions between the hydrocarbon chains near the micelle surface is considerably changed.

The deeper penetration of alcohol molecules disrupt the contact of the monomers. The effect of alcohol molecules on the stability of the micelle increases with increasing concentration and chain length. Consequently at higher concentration they break the micelles, while they disrupt the hydrophobic interactions between water networks and monomers.

In the light of this observation, it is reasonable to assume that the effect of the dielectric constant of the medium on the dipole orientation and dielectric distribution(36) of molecules, causing a change in electrokinetic properties of micelles, and hydrophobic interactions play an important role in the stability of mixed micelles.

II.Ii - Conclusions.

The observed micellar properties of alkyltrimethyl ammonium bromides in aqueous solution, and such solutions containing aliphatic alcohols, have been investigated by a viscosity method, surface tension measurement and light scattering data.

It is apparent that micelle formation is an entropy directed process, which is directed by hydrophobic interactions, which operate between the possible orientated configurations, and highly structured hydrogen bonded water molecules.

The observations indicate that the intrinsic viscosity of the micelles increases as the hydrocarbon group increases.

The increment in $[\eta]$ has been discussed in terms of the electroviscous effect, hydration and hydrophobic interactions between non-polar-polar groups.

On the addition of aliphatic alcohol to aqueous solutions of surfactants, due to the penetration of alcohol into interior of the micelle, the micellar properties are altered. Although the increase in relative viscosity is higher compared with the aqueous solution, the increment in $[\eta]$ is not significant compared with $[\eta]$ in aqueous solution. This observation has been attributed to the decrement in hydration, and electroviscous effect. The decrement in $[\eta]$ increases as the alcohol concentration increases.

On the other hand, the increment in relative viscosity, and $[\eta]$ have been discussed in terms of the changed micellar shape, and hydrophobic interactions. Possible shapes have been examined for the mixed micelles in terms of shape function, and axial ratio of the micelles.

The combination of the hydrodynamic and light scattering data indicate that the mixed micelles are prolate shaped, while the micelles of surfactants in aqueous solution are spherical. However, the observed C_o on the addition of methanol and ethanol to the system differs appreciably from that found with propanol and butanol. The C_o decreases up to a certain concentration with addition of organic additive, then it increases (methanol and ethanol).

In the case of higher alcohols C_o decreases with increasing concentration. The effect of alcohols on C_o has been discussed by means of hydrophobic interactions between alcohol, surfactant and water molecules. Alcohols at low concentration have structure promoting effect while they behave as structure breakers at high concentration.

Dipole orientation of the molecules due to the decrement in dielectric constant of the solution also contributes to the effects found.

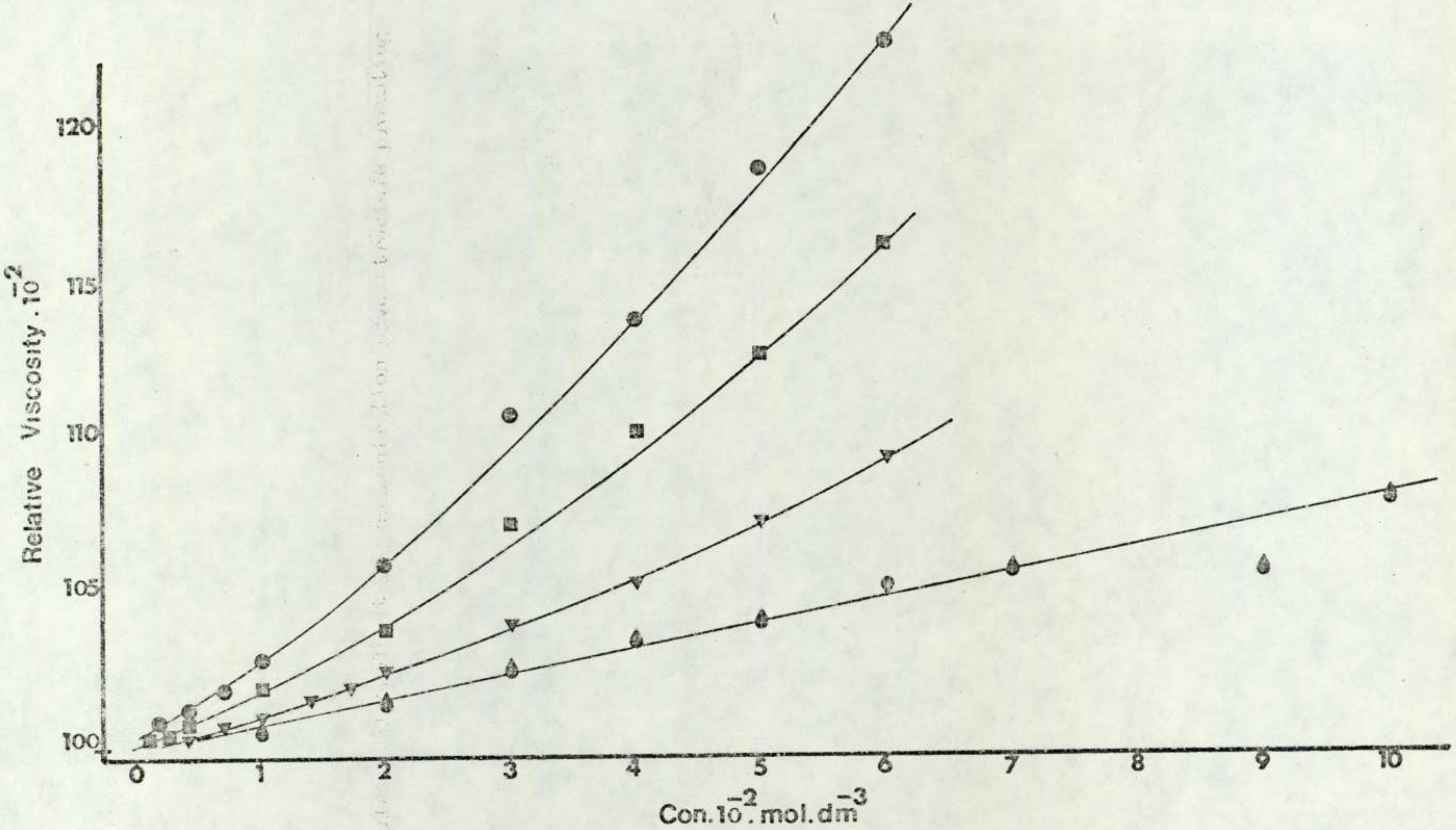


Fig. II.1 Plots of the relative viscosities versus concentration for the alkyltrimethyl ammonium bromides in water at 25° C; ♦ C_{10}, ▲ C_{12}, ■ C_{14}, and ● C_{16}

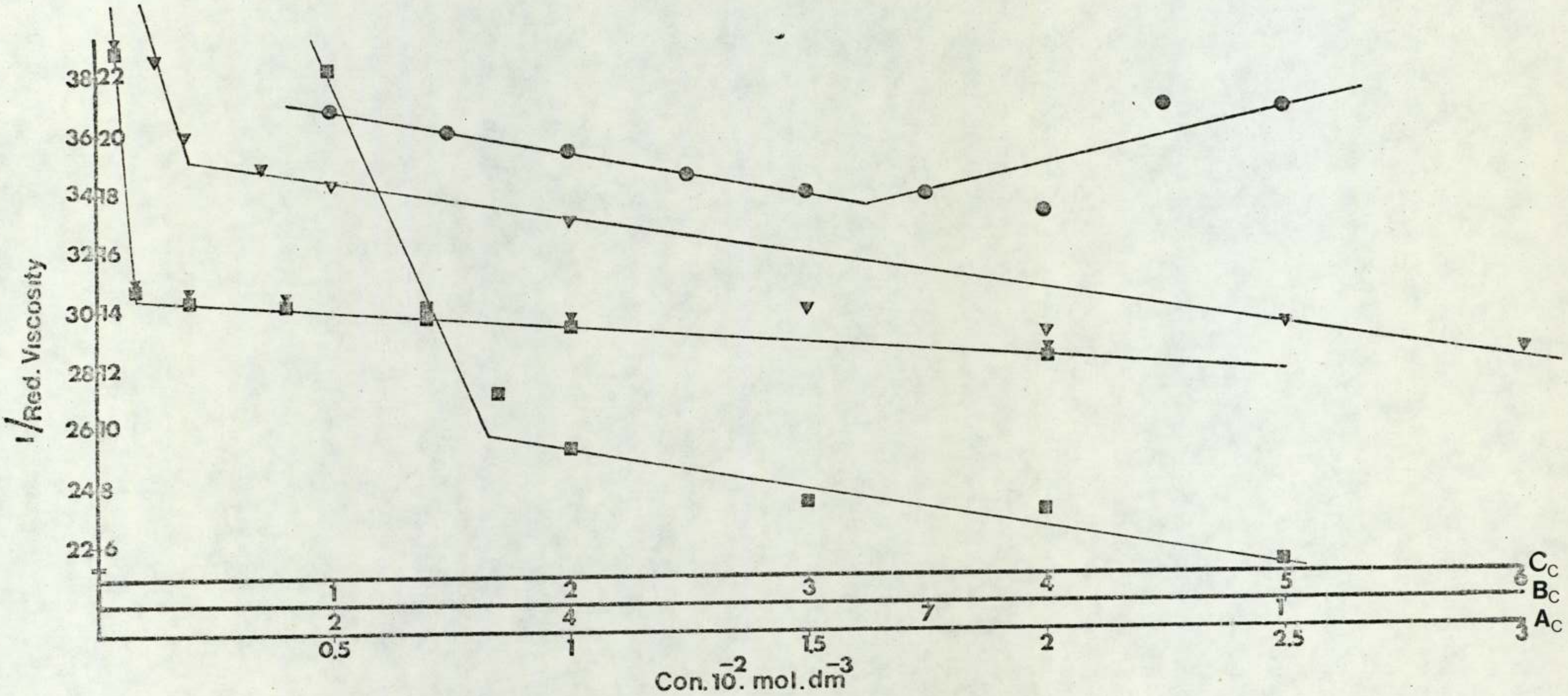


Fig. II.2 Reciprocal reduced viscosity as a function of the concentration of alkyltrimethyl ammonium bromide at 25° C; ● C_{10} , ■ C_{12} , ▲ C_{14} , and ▨ C_{16} ; B_c C_{10} , C_c C_{12}, and A_c C_{14} , C_{16}

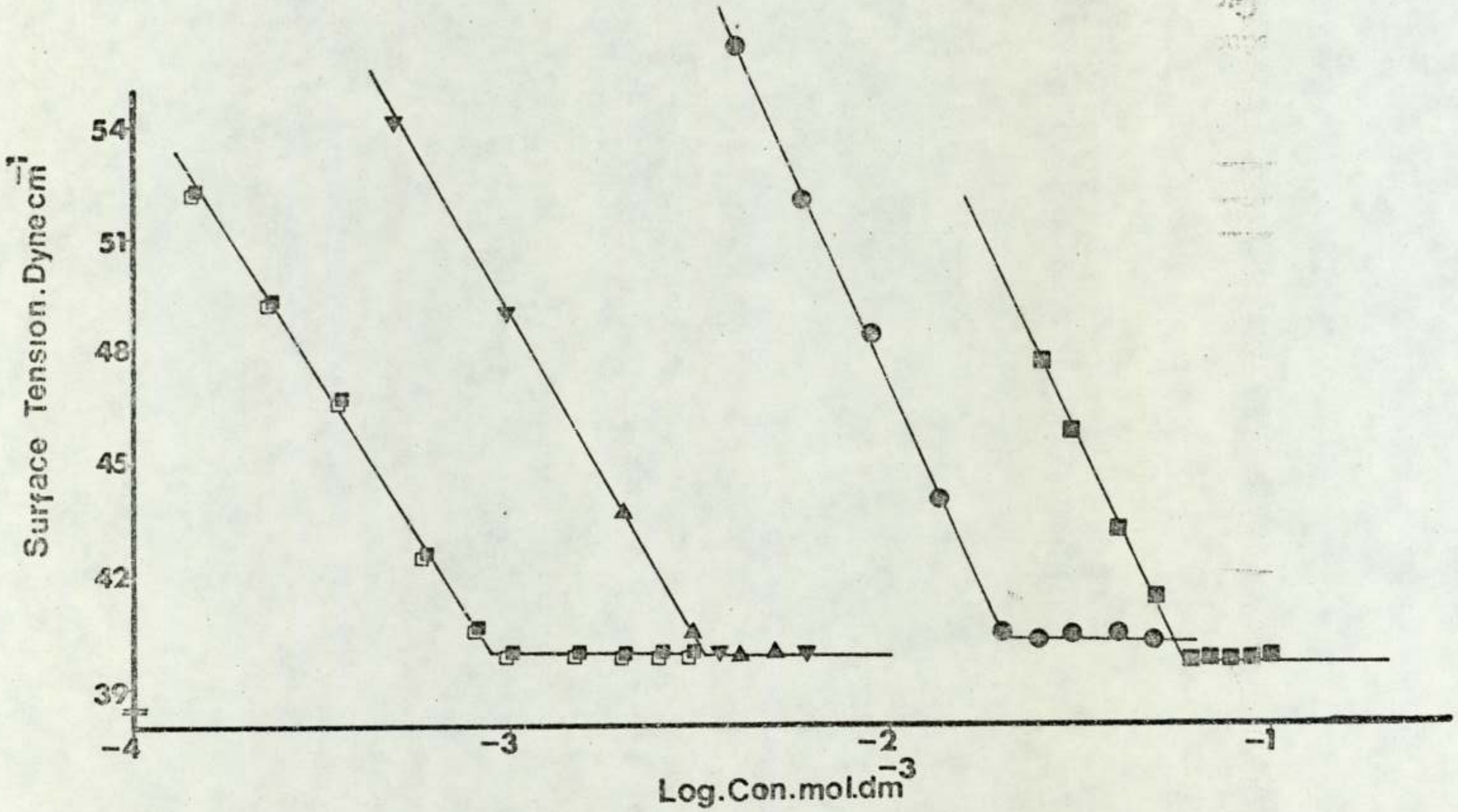


Fig. II.3 Surface tension versus log. concentration curves for the alkyltrimethyl ammonium bromides at 25° C; ■ C_{10} , ● C_{12} , ▲ C_{14} , and ▣ C_{16}

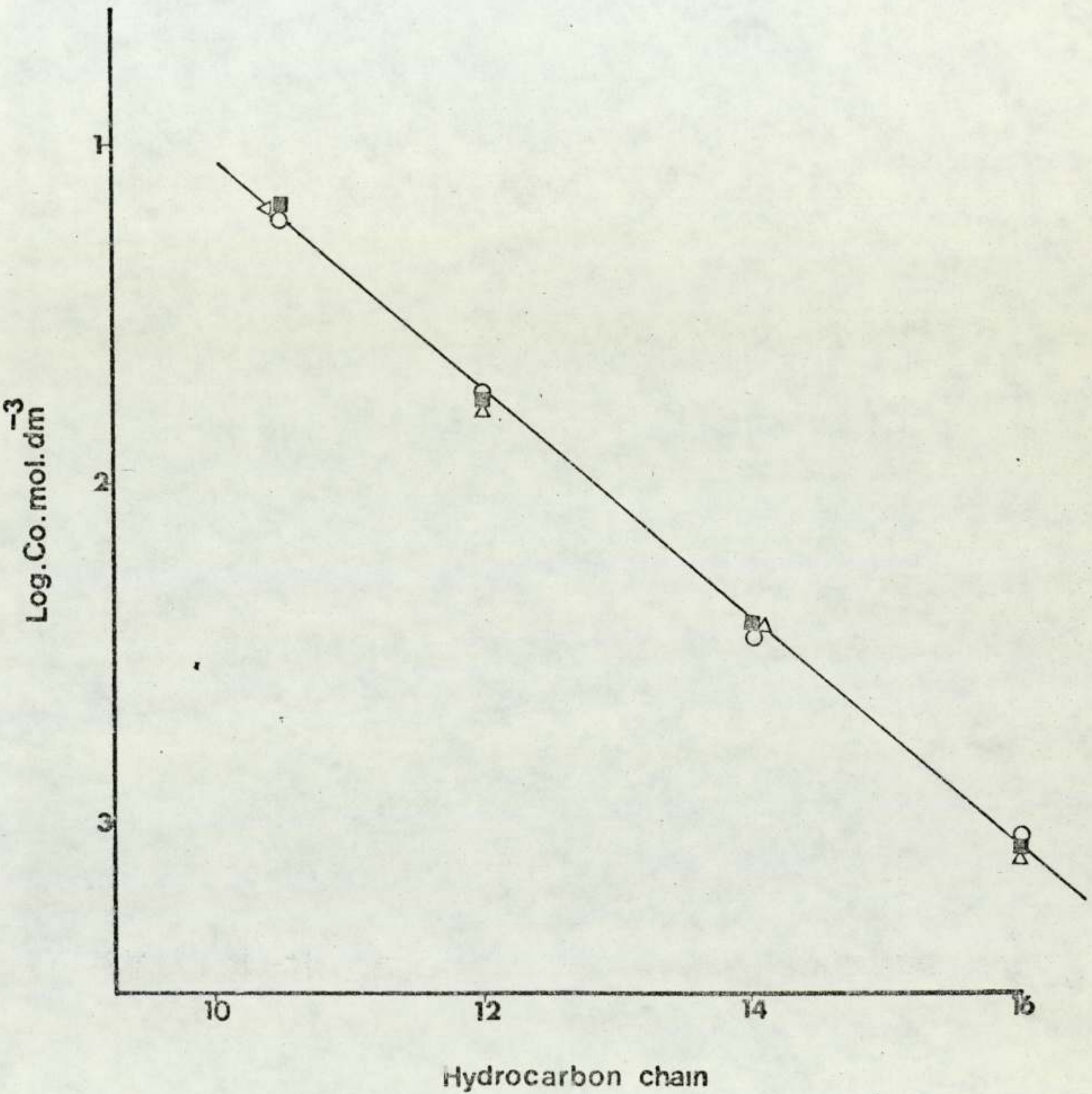


Fig.II.4 The variation of log. Co of alkyltrimethyl ammonium bromide with the hydrocarbon chain length at 25° C; ▨ Viscosity, ○ Surface Tension, △ Light Scattering

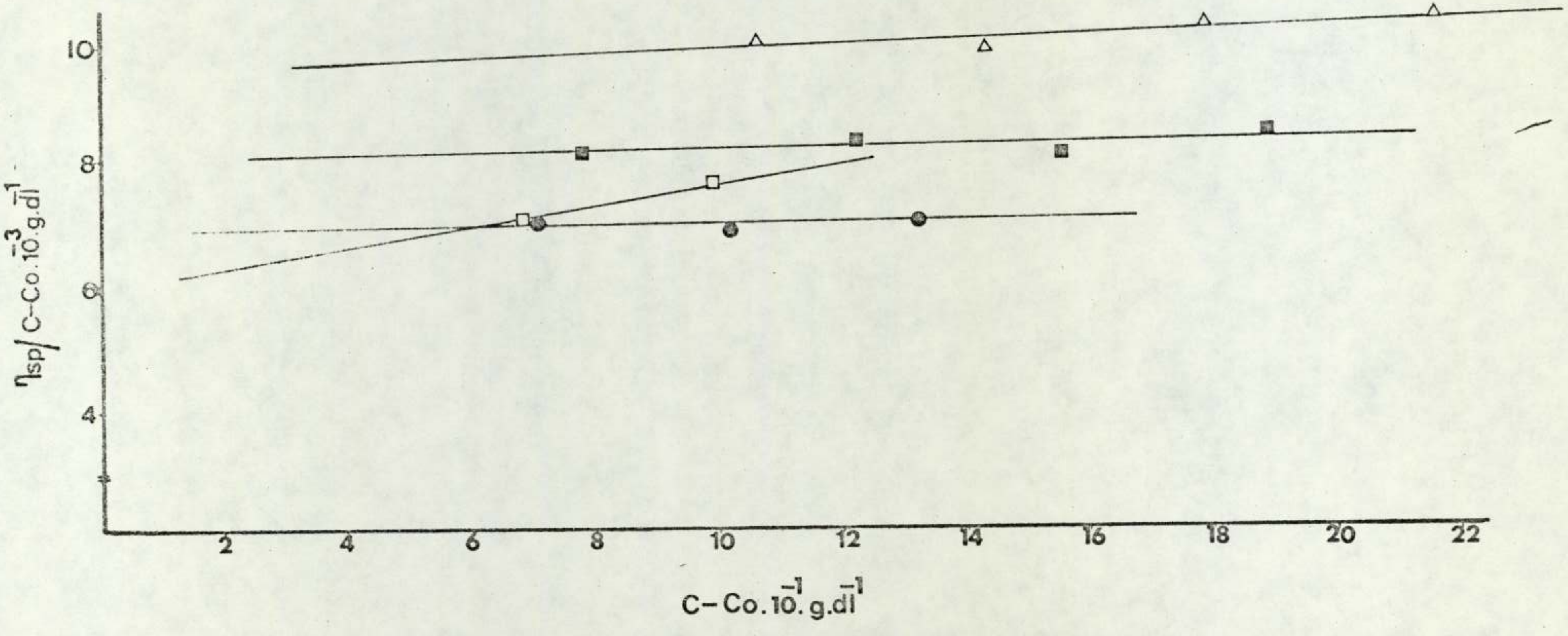


Fig. II.5 Plots of reduced viscosity versus concentration for the alkyltrimethyl ammonium bromides in water at 25° C; □ C_{10} , ● C_{12} , ■ C_{14} , and △ C_{16}

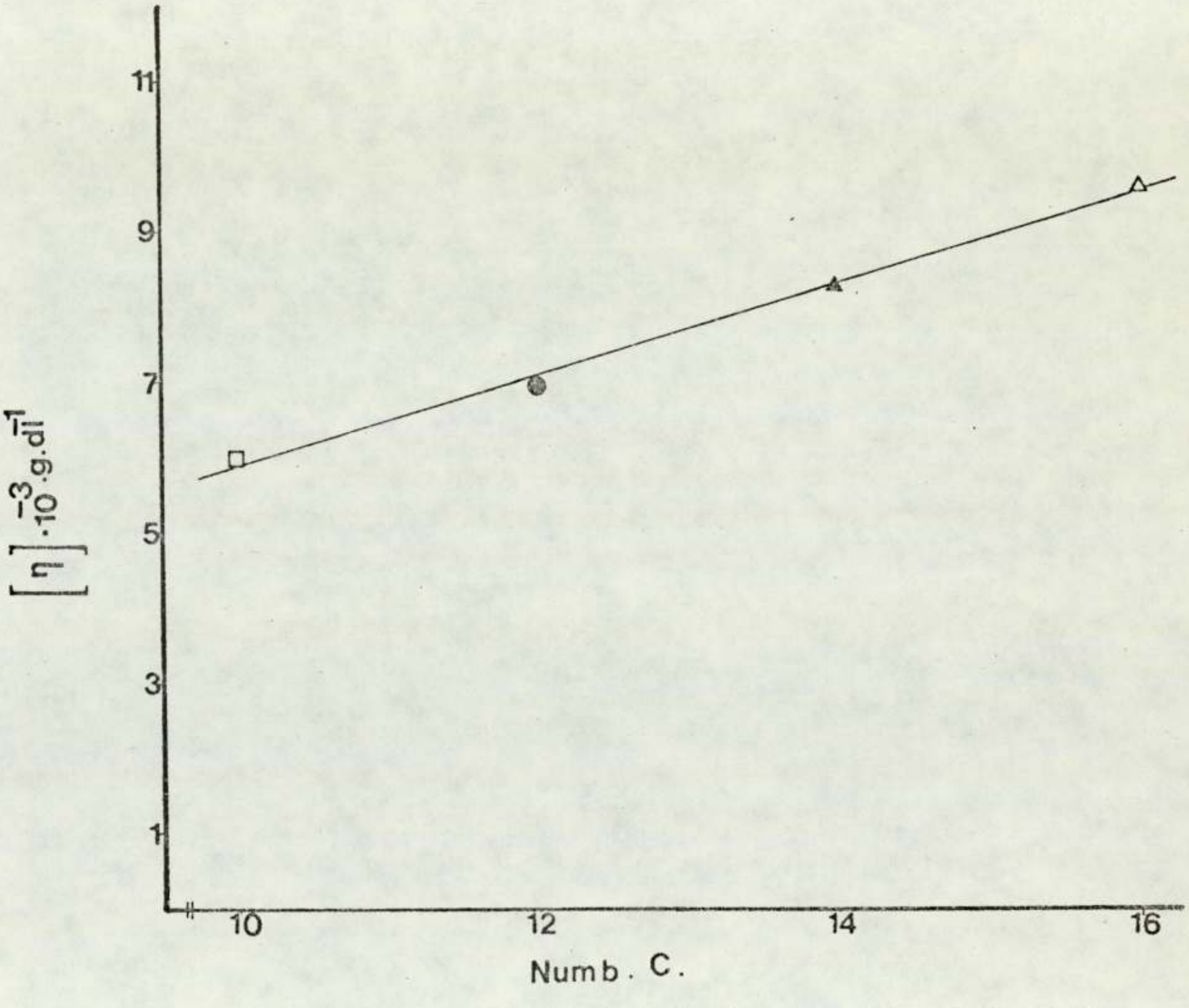


Fig. II.6 Dependence of the intrinsic viscosity of Co of the alkyltrimethyl ammonium bromide on the hydrocarbon chain length at 25° C;

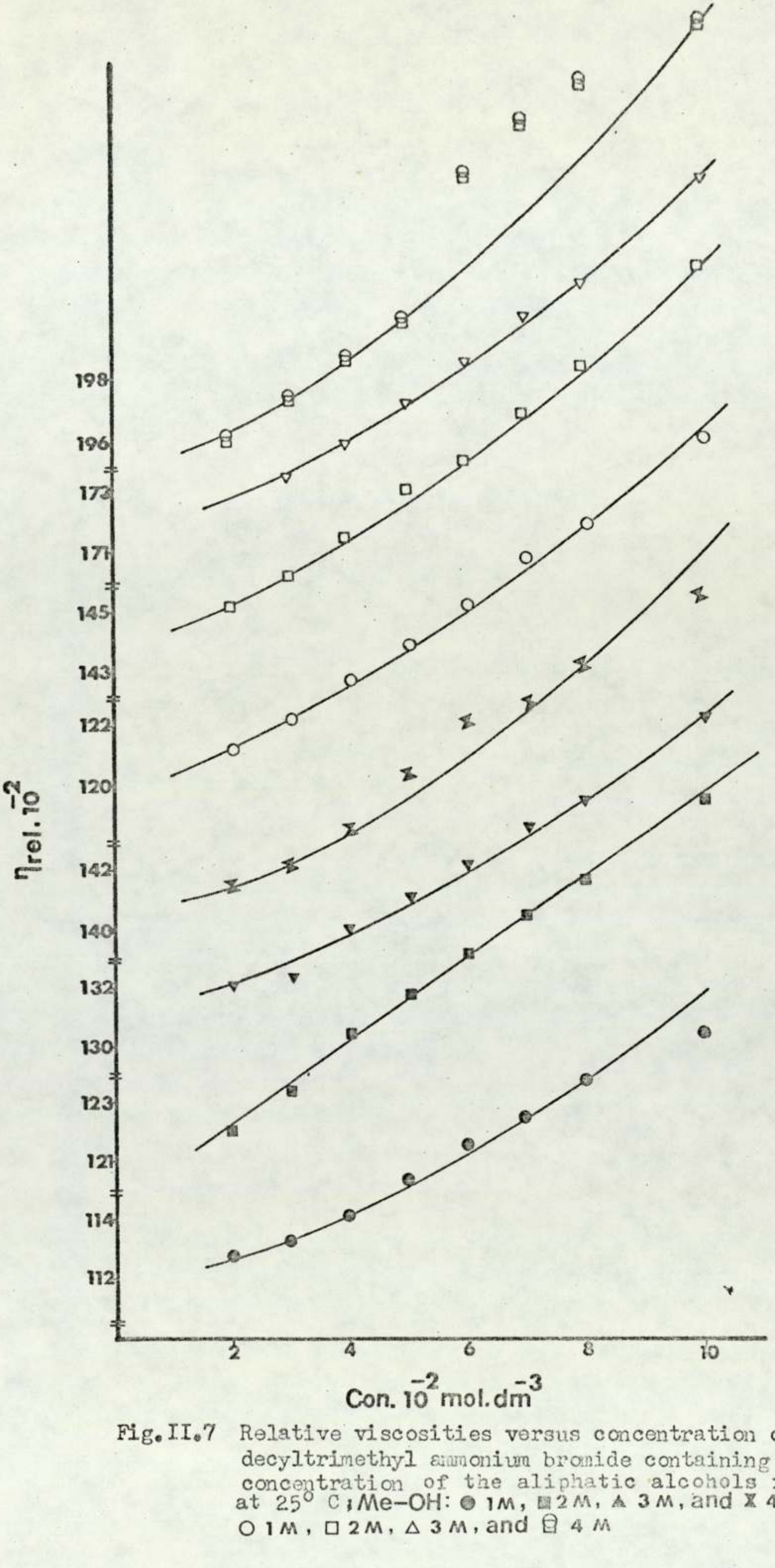


Fig. II.7 Relative viscosities versus concentration of the decyltrimethyl ammonium bromide containing various concentration of the aliphatic alcohols in water at 25° C; Me-OH: ● 1M, ■ 2M, ▲ 3M, and ⧗ 4M; Et-OH: ○ 1M, □ 2M, △ 3M, and ⊟ 4M

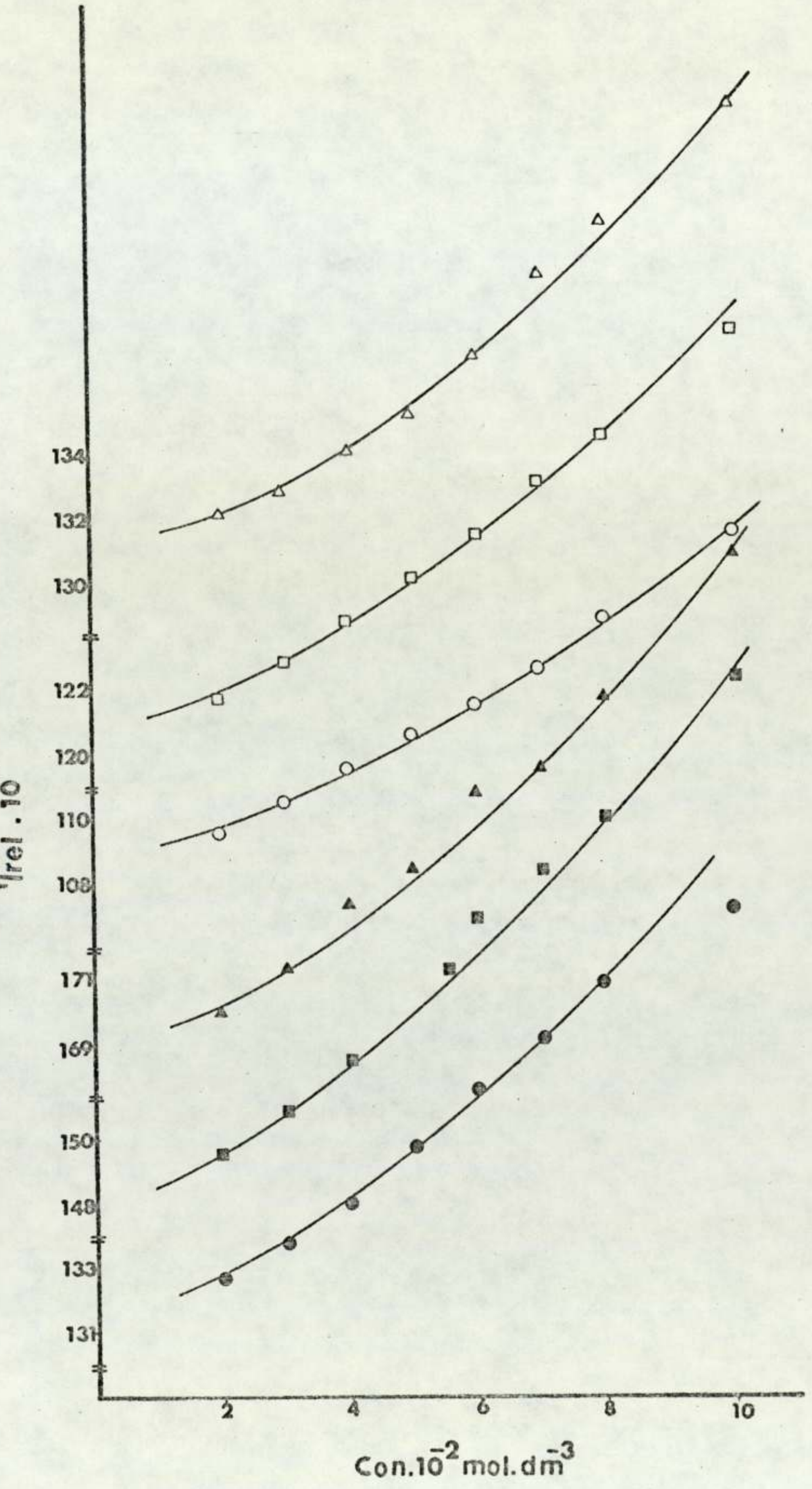


Fig. II.7.A. Relative viscosities versus concentration of the decyltrimethyl ammonium bromide containing various concentration of the aliphatic alcohols in water at 25° C; Pr-OH : ● 1 M, ■ 1.5 M, and ▲ 2 M; Bt-OH : ○ 0.2 M, □ 0.5 M, and △ 0.8 M

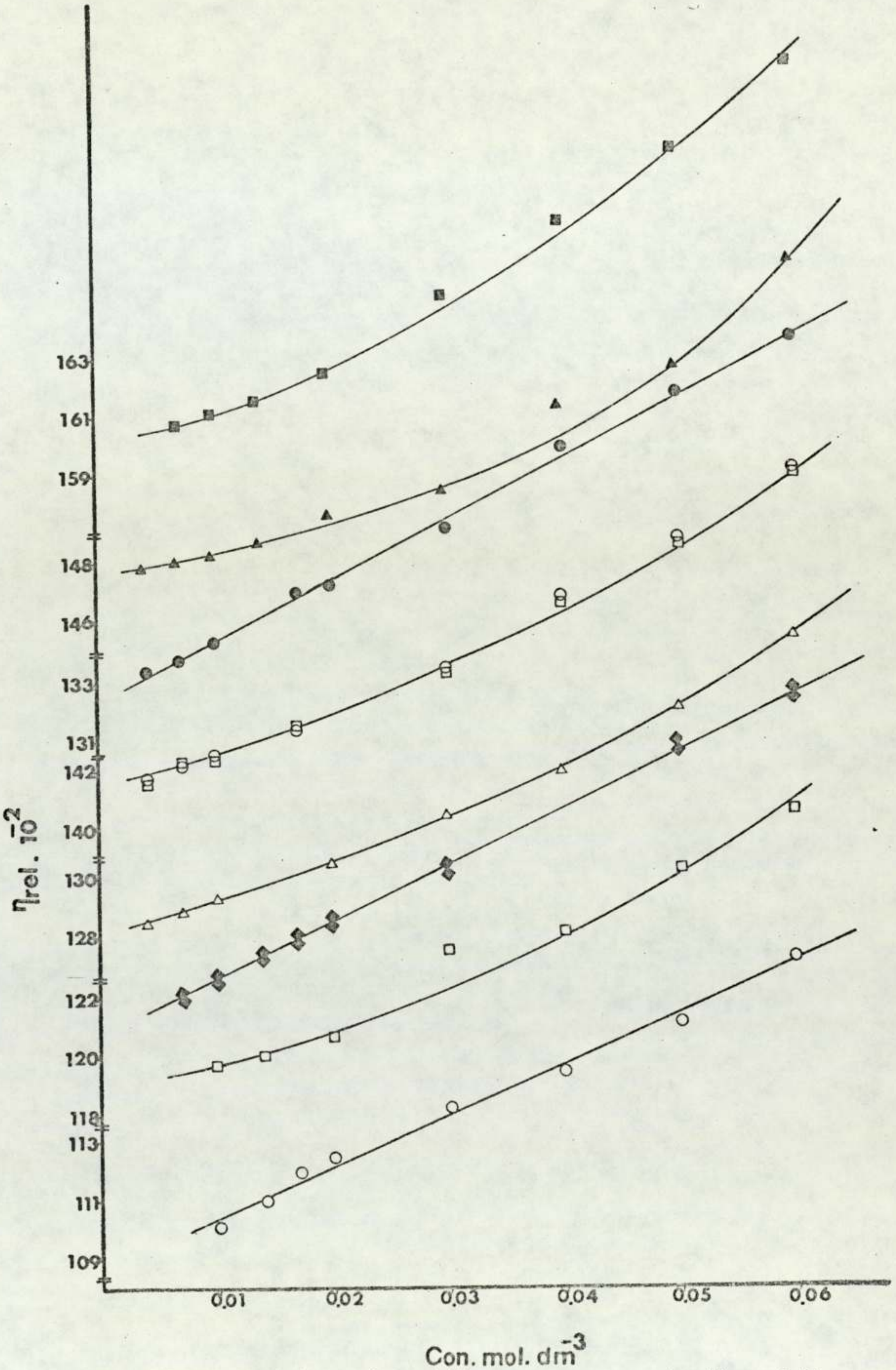


Fig. II.7.B Relative viscosities versus concentration of the dodecyltrimethyl ammonium bromide containing various concentration of the aliphatic alcohols in Water at 25° C; Me-OH: ○ 1M, □ 2M, △ 3M, and ⊟ 4M; Et-OH: ◆ 1M, ● 1.5M, ▲ 2M, and ■ 2.5M

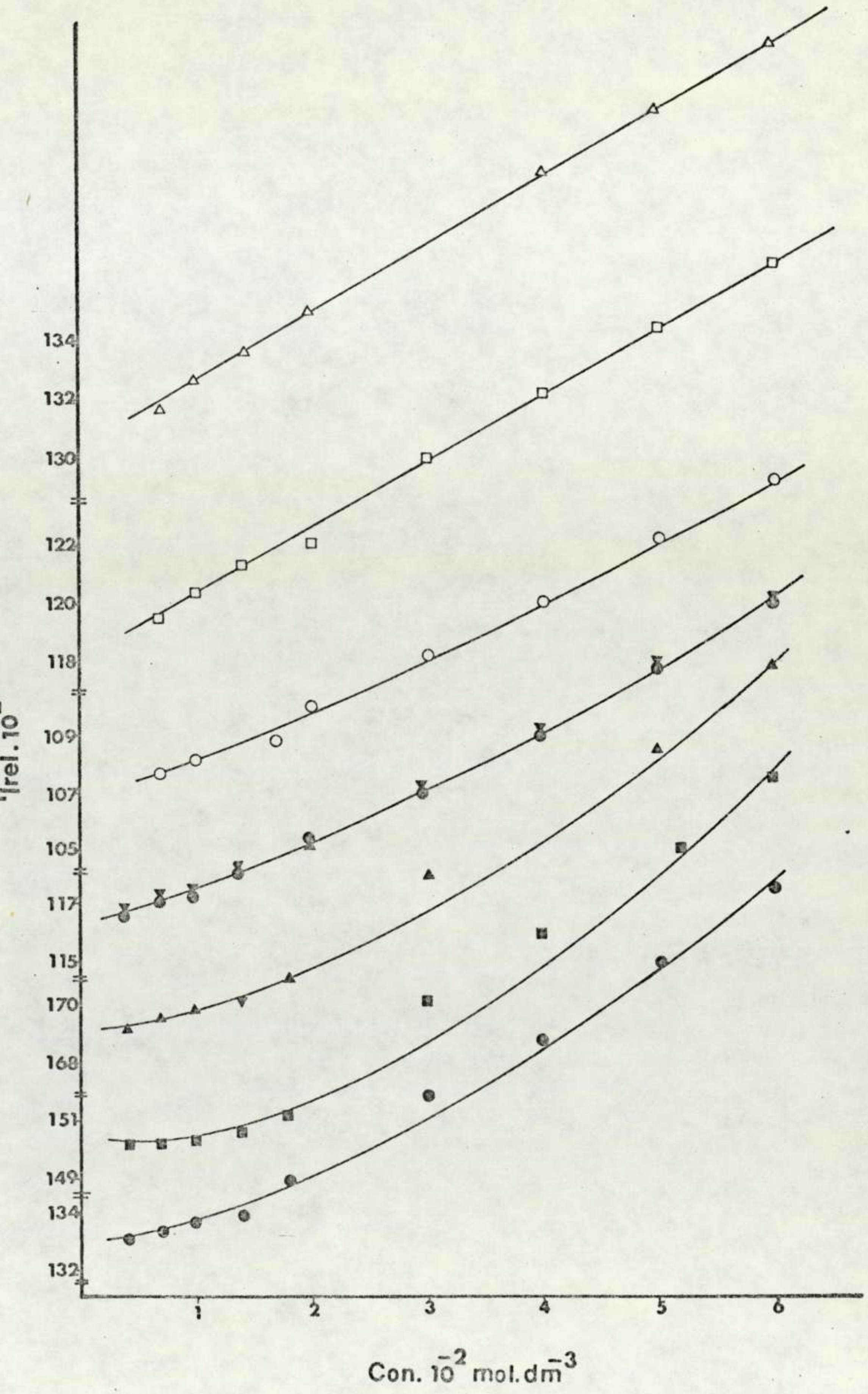


Fig. II.7.C Relative viscosities versus concentration of the dodecyltrimethyl ammonium bromide containing various concentration of the aliphatic alcohols in water at 25° C; Pr-OH: ● 1 M, ■ 1.5M, ▲ 2 M, and ⧗ 0.5 M Bt-OH: ○ 0.2M, □ 0.5 M, and 0.8 M

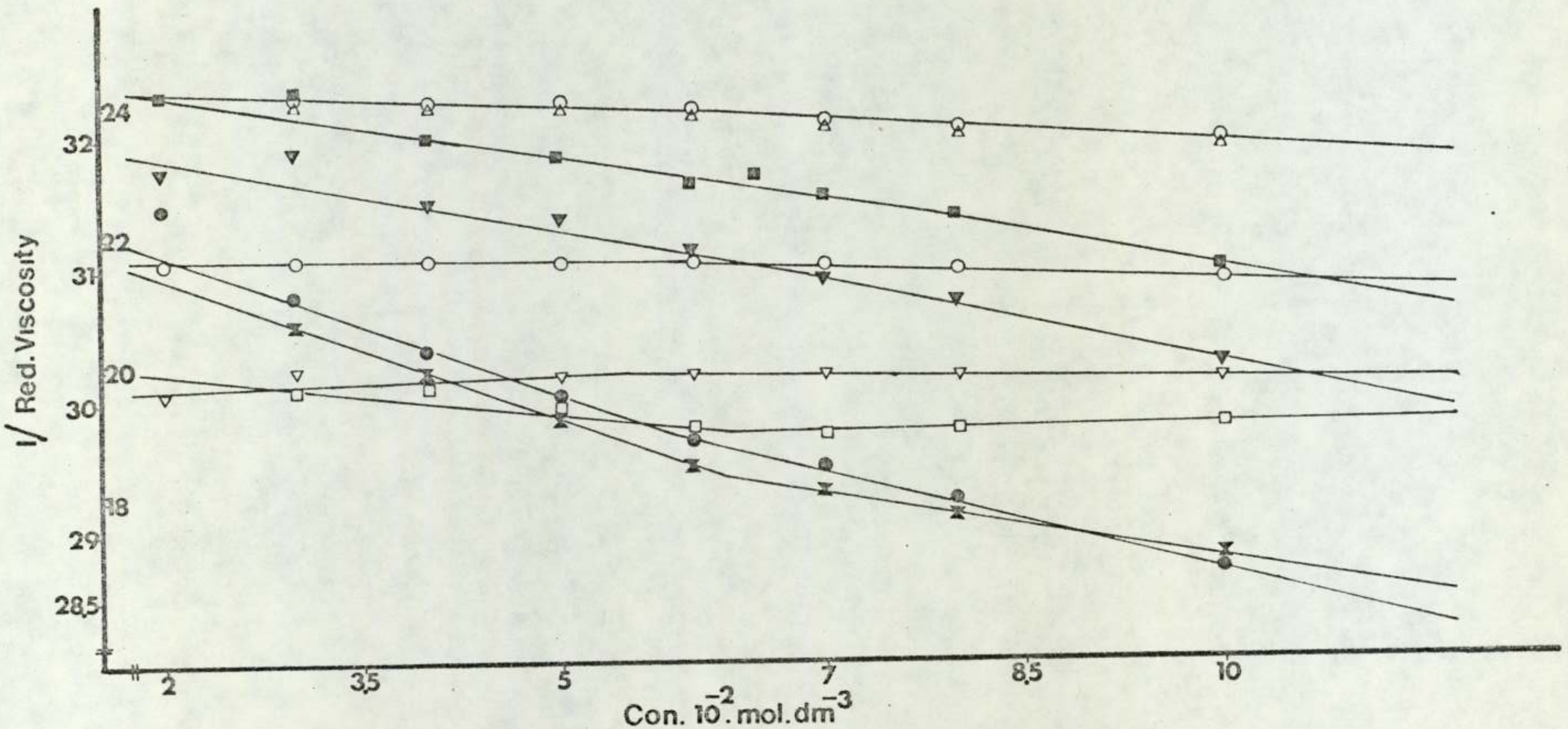


Fig. II.8 Reciprocal reduced viscosities as a function of the concentration for the decyltrimethyl ammonium bromide containing various concentration of methanol and ethanol in water at 25° C; Me-OH: ⧗ 1M, ● 2 M, ▲ 3M, and ■ 4 M, Et-OH: ⧖ 1 M, ○ 2 M, △ 3 M, and □ 4 M

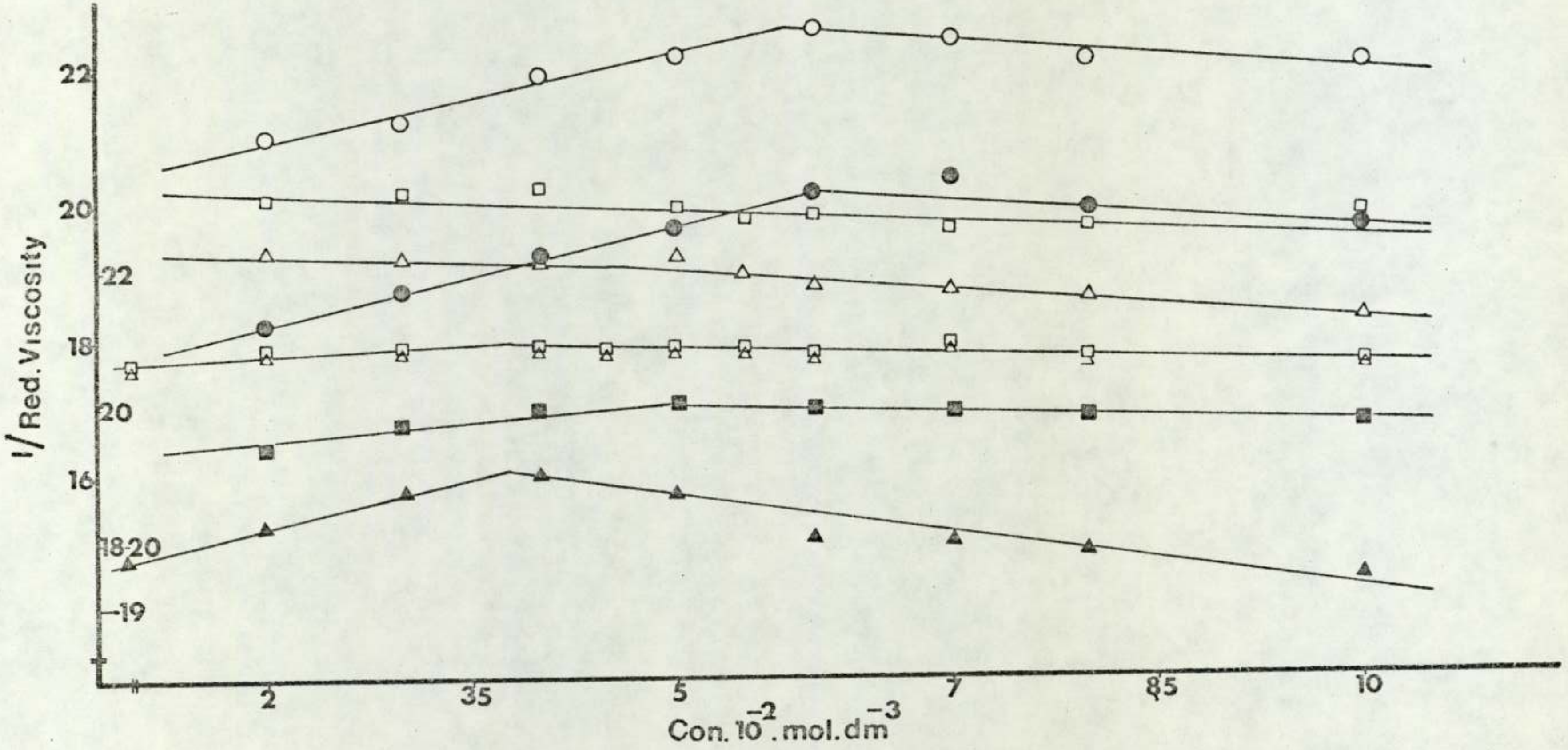


Fig. II. 8. A Reciprocal reduced viscosities as a function of the concentration for the decyltrimethyl ammonium bromide containing various concentration of propanol and butanol in water at 25° C;
Pr–OH: ○ 0.5 M, □ 1 M, △ 1.5 M, and ⊠ 2 M, Bt–OH: ● 0.2, ■ 0.5 M, and ▲ 0.8 M

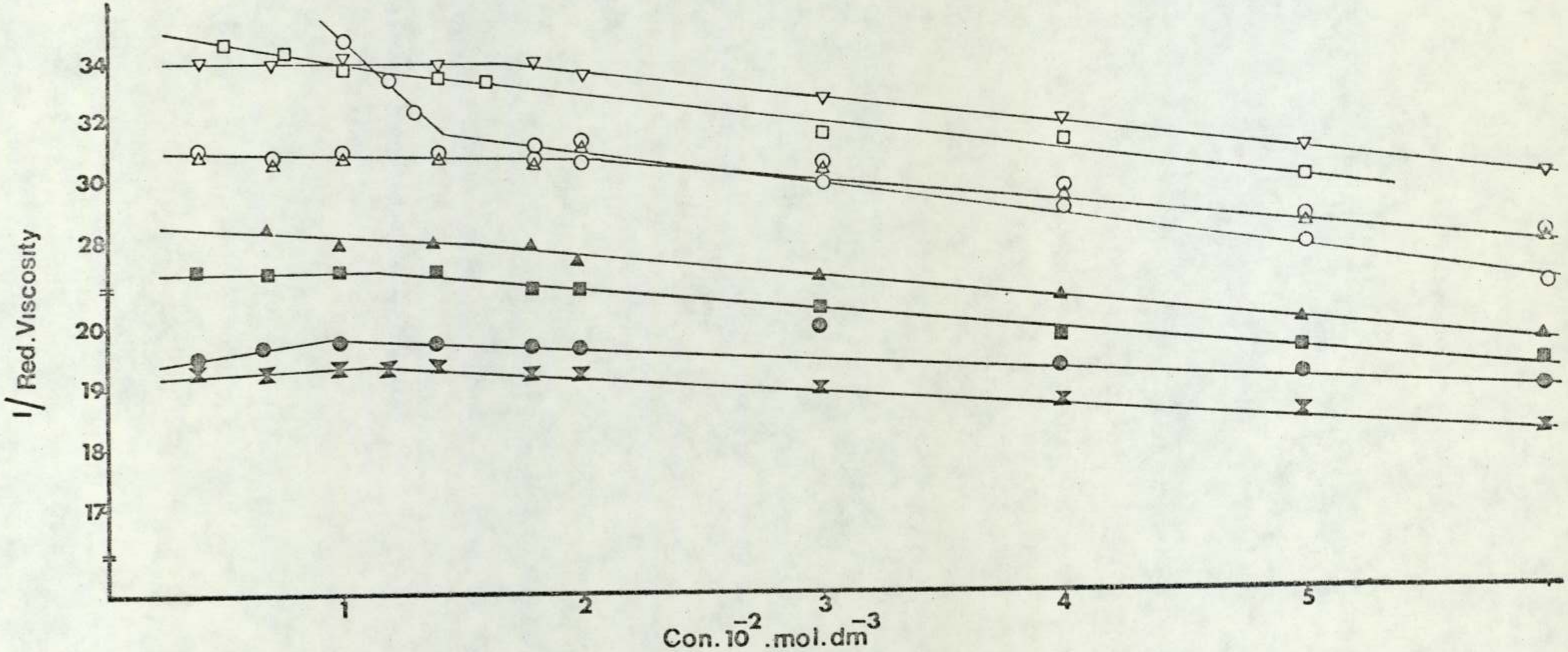


Fig. II.8.B Reciprocal reduced viscosities as a function of the concentration for the dodecyltrimethyl ammonium bromide containing various concentration of methanol and ethanol in water at 25° C;
Me–OH: ○ 1M, □ 2 M, △ 3 M, and ⊚ 4 M, Et–OH: ▲ 1 M, ■ 1.5 M, ● 2 M, and ⧗ 2.5

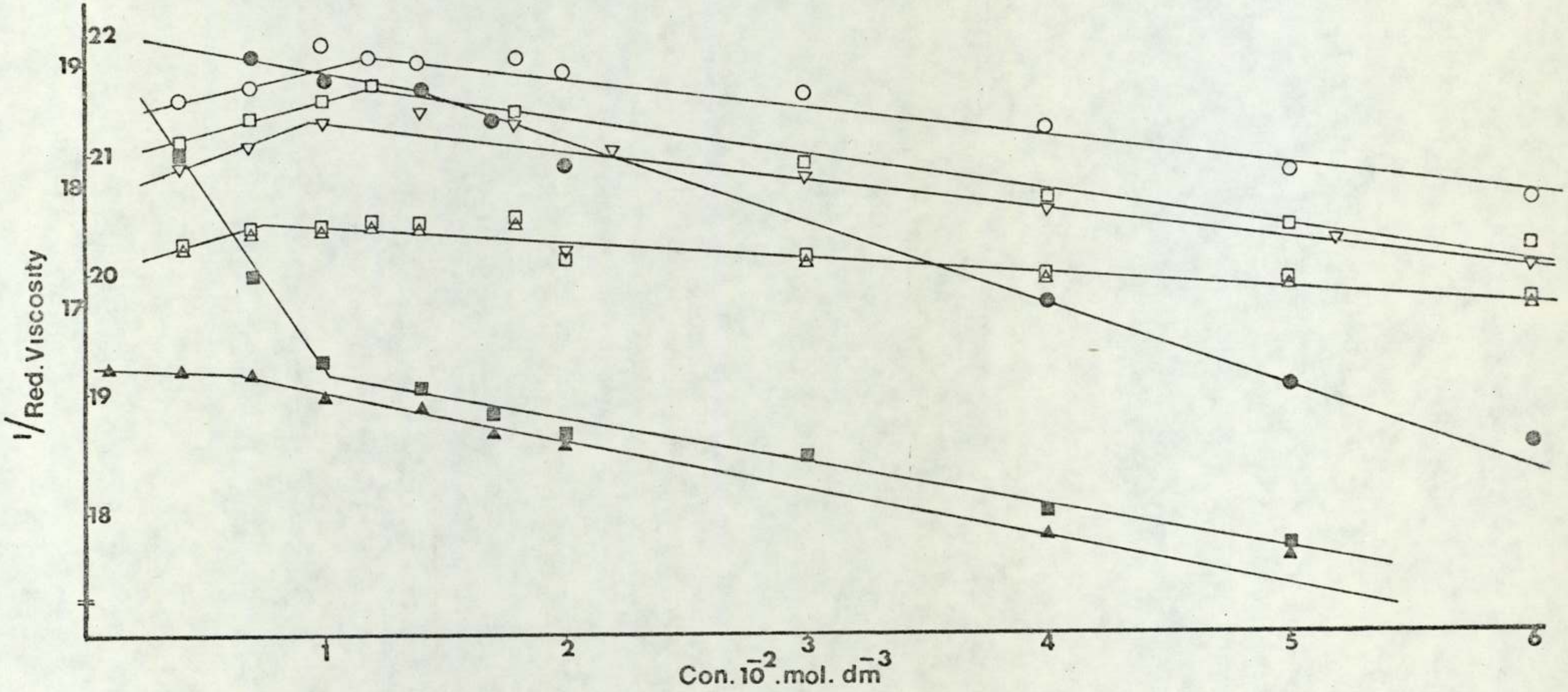


Fig. II.8.C Reciprocal reduced viscosities as a function of the concentration for the dodecyltrimethyl ammonium bromide containing various concentration of propanol and butanol in water at 25° C;

Pr-OH: ○ 0.5 M, □ 1 M, △ 1.5 M, and ⊠ 2 M, Bt-OH: ● 0.2 M, ■ 0.5 M, and ▲ 0.8 M

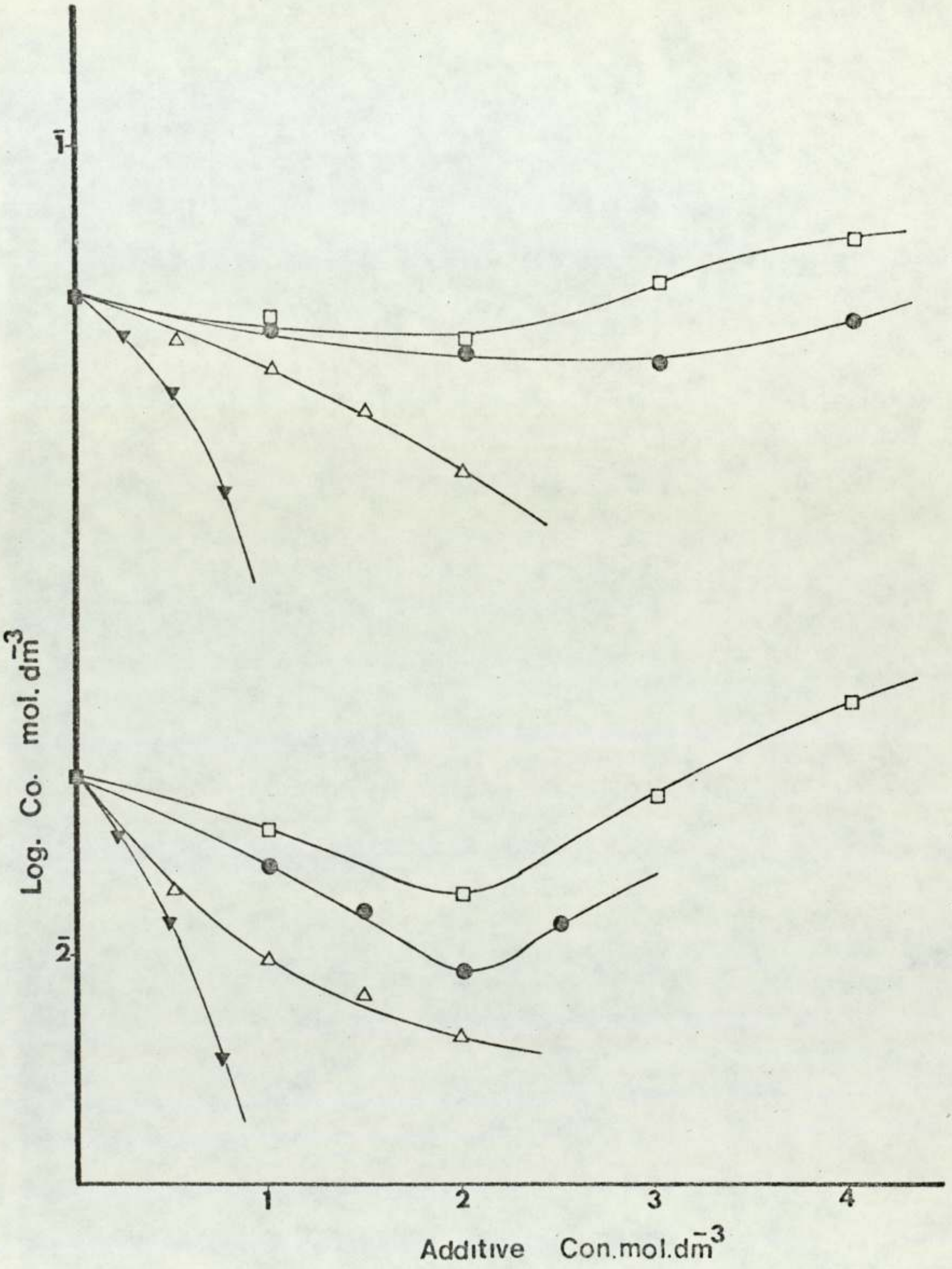


Fig.II.9 The effect of the various concentration of aliphatic alcohols on the Co of alkyltrimethyl ammonium bromides at 25° C; C_{10} : □ Me-OH, ● Et-OH, △ Pr-OH, and ▼ Bt-OH; C_{12} : □ Me-OH, ● Et-OH, △ Pr-OH, and ▼ Bt-OH

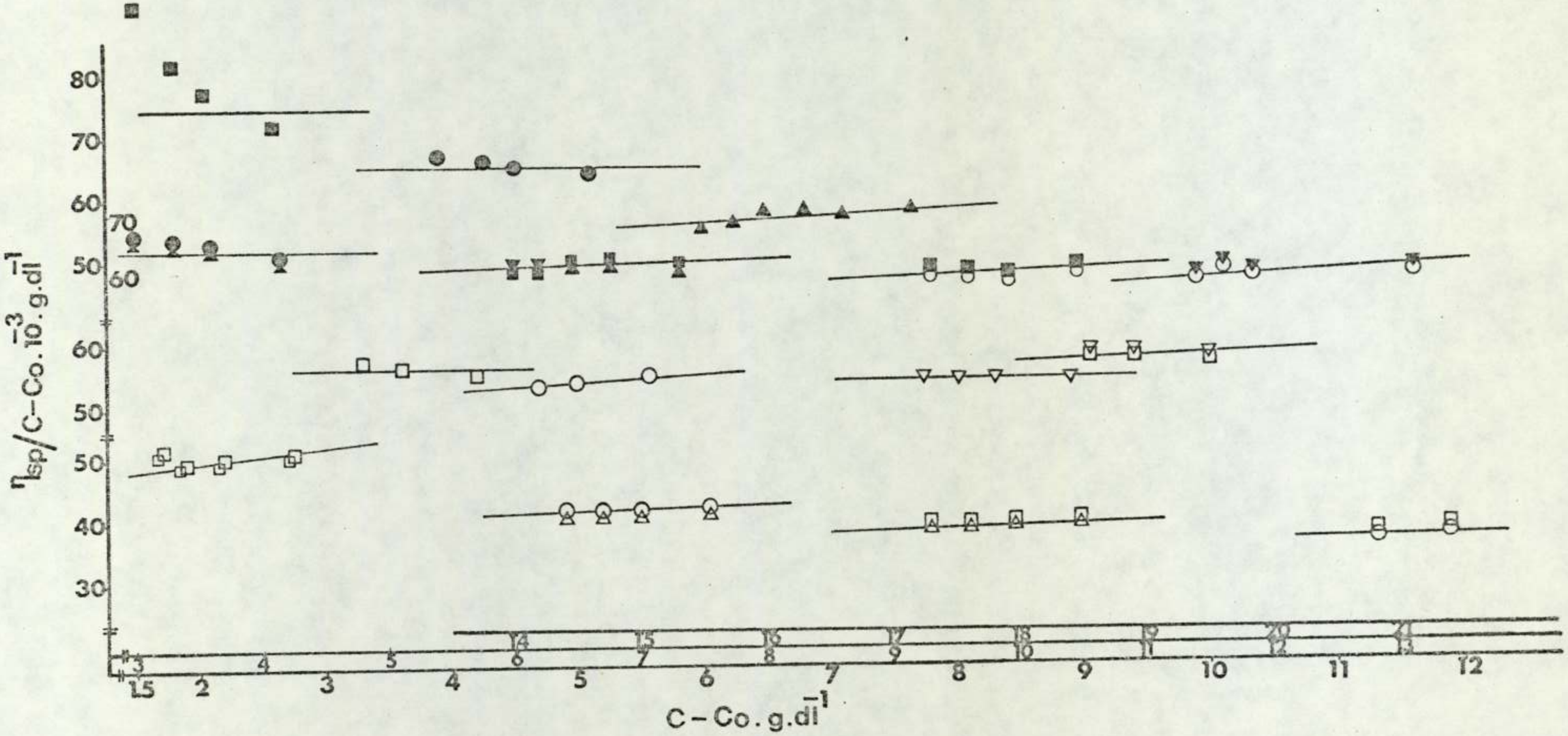


Fig. II.10 Dependence of the reduced viscosity of decyltrimethyl ammonium bromide on the concentration of aliphatic alcohols at 25° C; Bt-OH: ■ 0.2 M, ● 0.5 M, and ▲ 0.8M, Pr-OH: ● 0.5 M, ■ 1 M, ■ 1.5 M, and ○ 2 M Et-OH: □ 1 M, ○ 3 M, △ 2 M, and ▽ 4 M, Me-OH: □ 1 M, ○ 2 M, △ 3 M, and □ 4 M

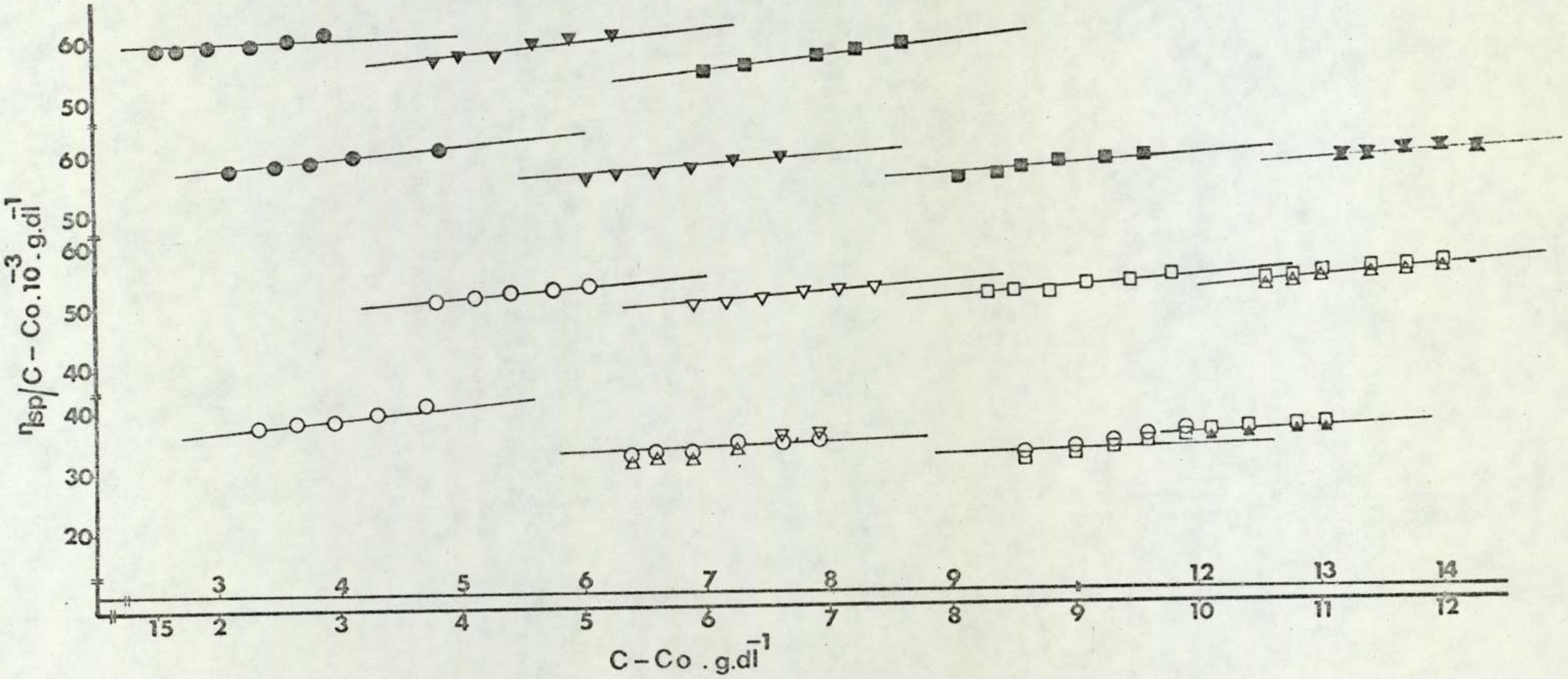


Fig. II.10.A Dependence of the reduced viscosity of dodecyltrimethyl ammonium bromide on the concentration of aliphatic alcohols at 25° C; Bt-OH: ● 0.2 M, ▼ 0.5 M, and ■ 0.8 M, Pr-OH: ● 0.5 M, ▼ 1 M, ■ 1.5 M, and ⧗ 4 M, Et-OH: ○ 1 M, △ 1.5 M, □ 2 M, and ⊠ 2.5 M, Me-OH: ○ 1 M, ⊗ 2 M, ⊟ 3 M, and ⊠ 4 M

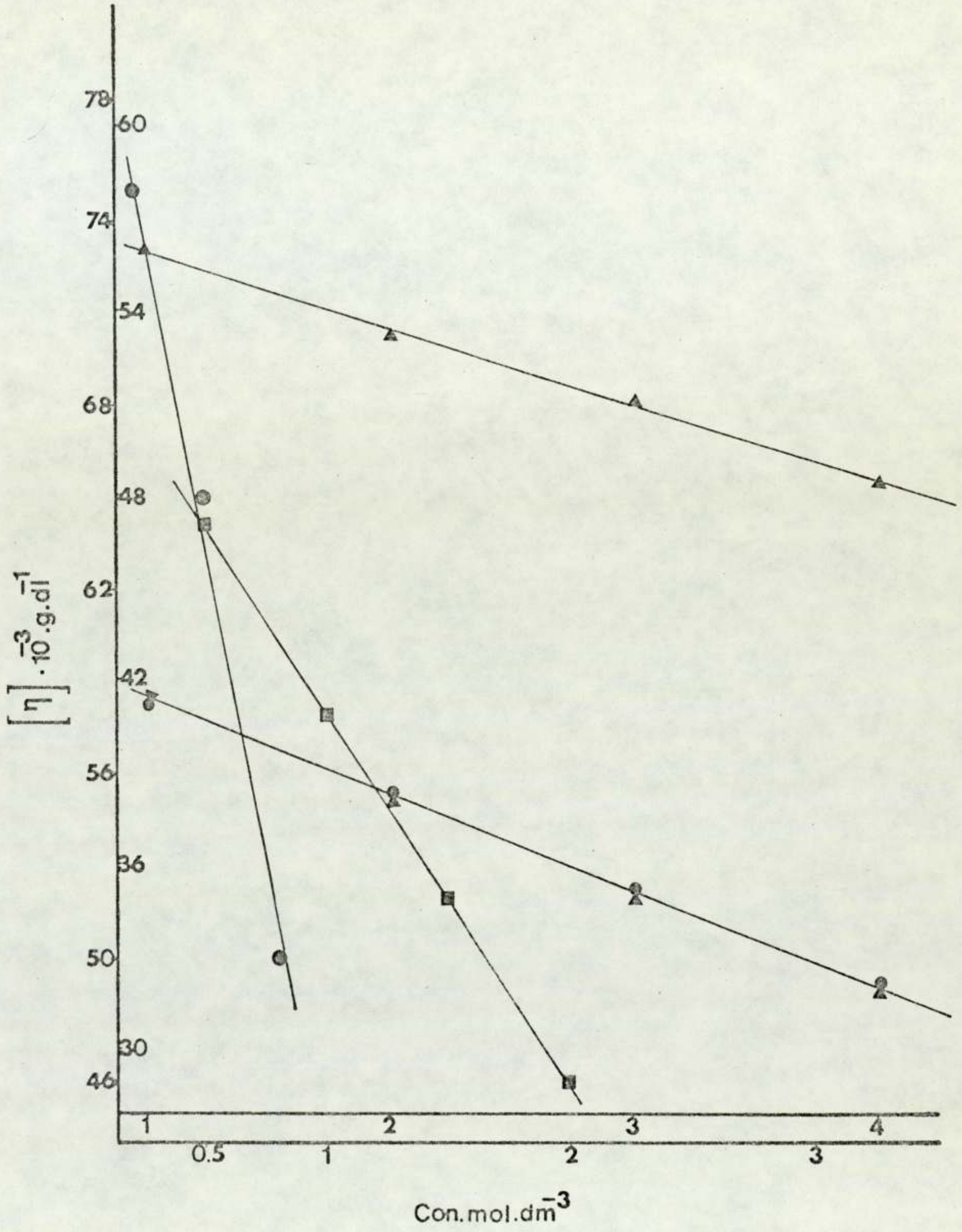


Fig. II.11 Dependence of the intrinsic viscosity of Co of the decyltrimethyl ammonium bromide on organic additives in water at 25° C; ⚲ Me-OH, ▲ Et-OH, ■ Pr-OH, and ● Bt-OH

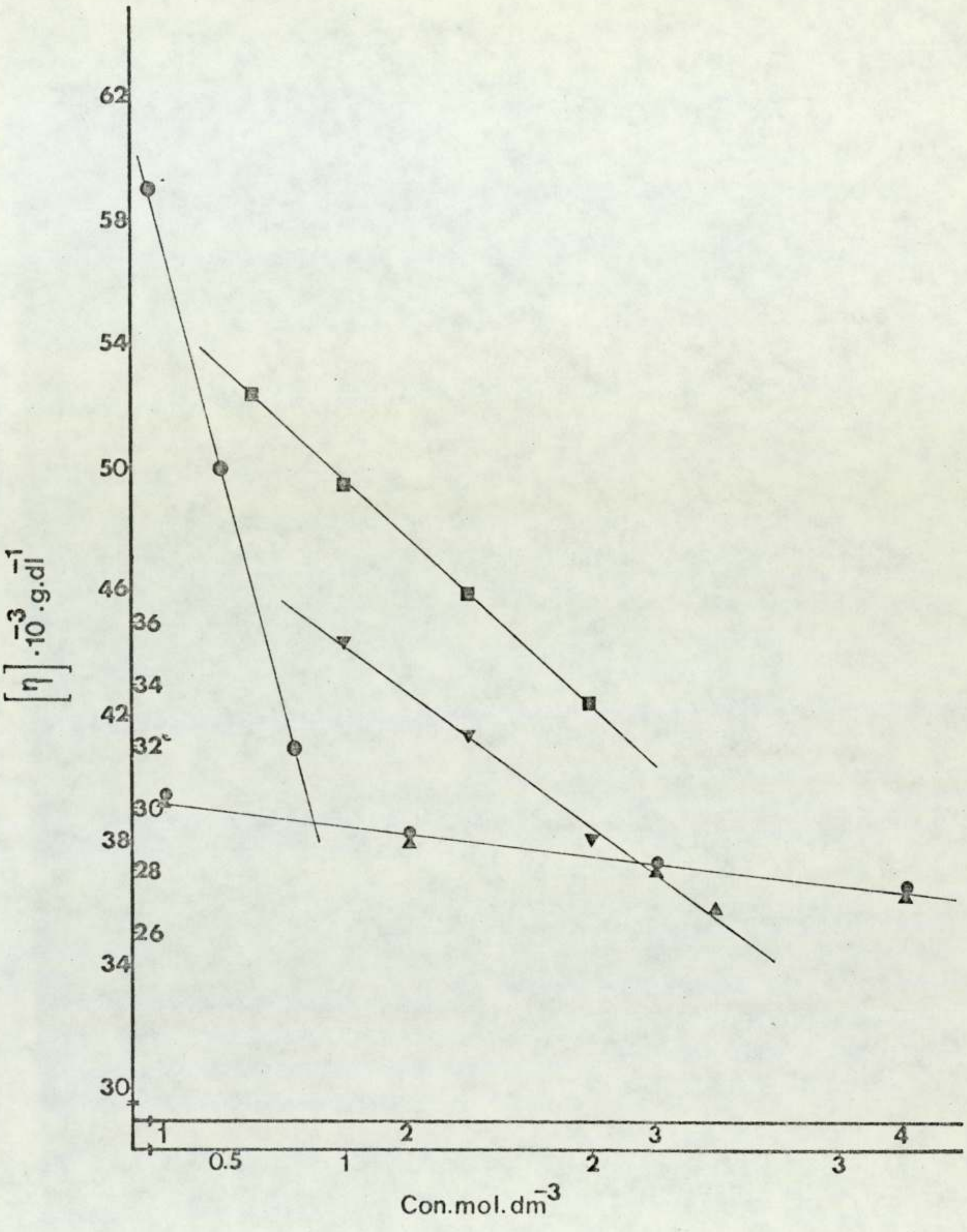


Fig. II.11.A Dependence of the intrinsic viscosity of Co of the dodecyltrimethyl ammonium bromide on organic additives in water at 25° C; ⚲ Me-OH, ▲ Et-OH, ■ Pr-OH, and ● Bt-OH

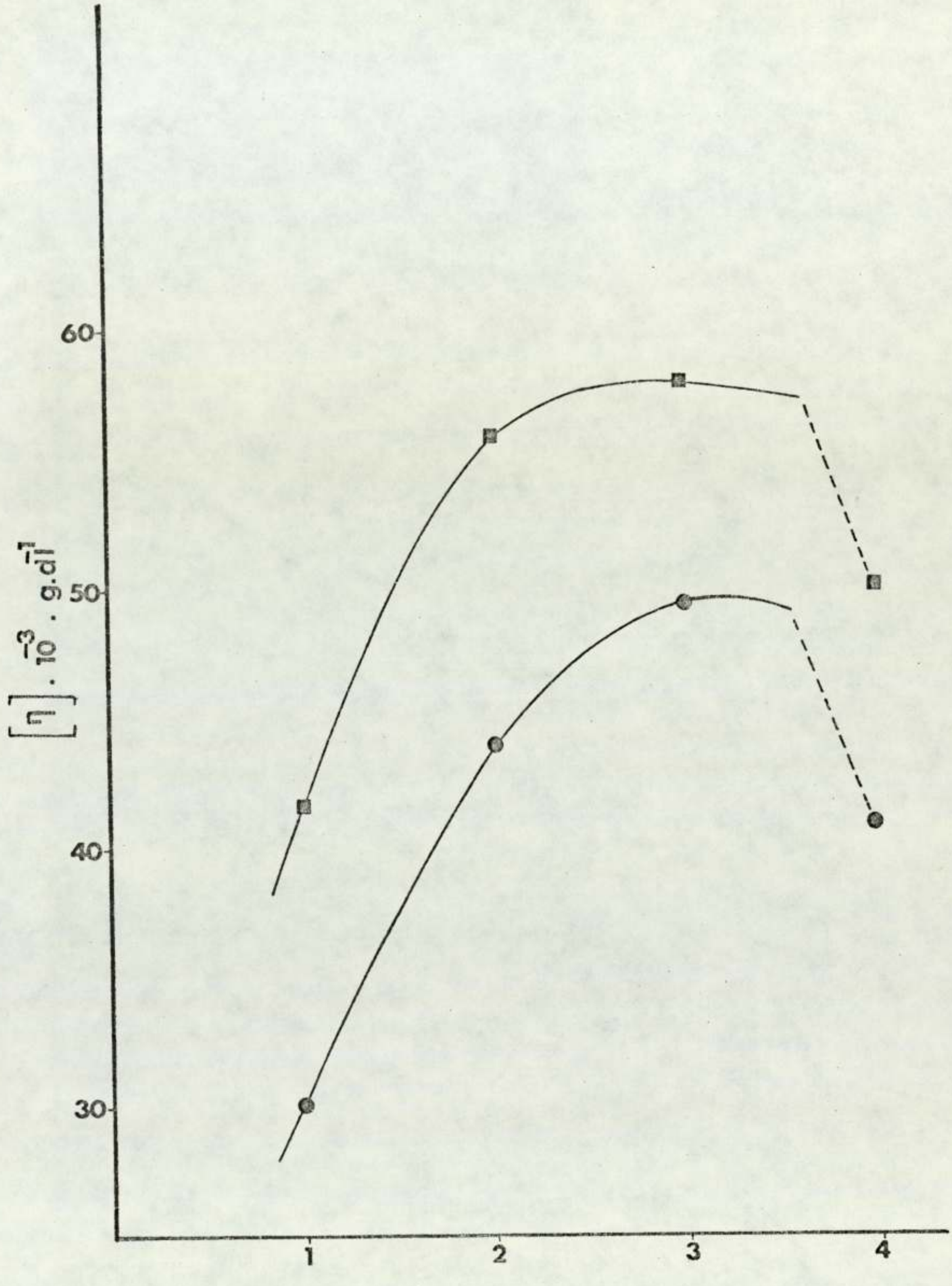


Fig. II.12 Intrinsic viscosities of the Co of C_{10} and C_{12} containing IM various aliphatic alcohols in water as function of the hydrocarbon chain length;

VISCOSITY AND SURFACE TENSION DATA FOR THE SOLUTIONS

OF ALKLAMMONIUM BROMIDES IN WATER AT 25° C

TABLE II.I.1

Vicosity									Surface Tension		
C $mol.dm^{-3}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$\frac{\eta-1}{C-C_o}$ $g.dl^{-1}$	$[\eta]$ $10^{-2} g.dl^{-1}$	$\frac{\frac{1}{\eta_{sp}}}{C}$	C $mol.dm^{-3}$	C_o $mol.dm^{-3}$	γ $dyne.cm^{-1}$	C_o $mol.dm^{-3}$
C_{10}											
1×10^{-1}	1.00020	0.9630	1.0761	0.0761	0.0775	6.0	36.84	6.5×10^{-2}	1×10^{-1}	39.95	6.0×10^{-5}
9×10^{-2}	0.99910	0.9401	1.0505	0.0505	0.0720		37.00		9×10^{-2}	39.91	
7×10^{-2}	0.99861	0.9468	1.0580	0.0580	0.414		33.78		8×10^{-2}	39.75	
6×10^{-2}	0.99831	0.9391	1.0494	0.0494			34.03		7×10^{-2}	39.73	
5×10^{-2}	0.99810	0.9310	1.0403	0.0403			34.74		6.5×10^{-2}	39.78	
4×10^{-2}	0.99791	0.9232	1.0316	0.0316			35.50		5×10^{-2}	41.32	
3×10^{-2}	0.99771	0.9157	1.0233	0.0233			36.09		4×10^{-2}	43.10	
2×10^{-2}	0.99753	0.9085	1.0152	0.0152			36.84		3×10^{-2}	45.82	
1×10^{-2}	0.99741	0.8974	1.0027	0.0027					2.5×10^{-2}	47.60	
C_{12}											
6×10^{-2}	0.99841	0.9789	1.0938	0.0938	0.0704	6.9	19.71	1.68×10^{-2}	6×10^{-2}	40.10	1.9×10^{-2}
5×10^{-2}	0.99823	0.9593	1.0711	0.0711	0.0699		21.43		5×10^{-2}	40.20	
4×10^{-2}	0.99805	0.9410	1.0505	0.0505	0.0707		24.44		4×10^{-2}	40.32	
3×10^{-2}	0.99788	0.9307	1.0399	0.0399	0.0981		23.14		3×10^{-2}	40.35	
2×10^{-2}	0.99774	0.9167	1.0244	0.0244			25.31		2.5×10^{-2}	40.20	
1.7×10^{-2}	0.99771	0.9117	1.0188	0.0188			27.28		2×10^{-2}	40.30	
1.4×10^{-2}	0.99768	0.9077	1.0144	0.0144			30.11		1.4×10^{-2}	44.00	
1×10^{-2}	0.99761	0.9024	1.0081	0.0081			38.146		1.9×10^{-2}	48.32	

TABLE II.I.1.A

7 x 10^{-3}	0.99757	0.9990	1.0046	0.0046	-	-	-	-	6 x 10^{-3}	52.10	-
4 x 10^{-3}	0.99753	0.8981	1.0035	0.0035					5 x 10^{-3}	56.00	
C_{14}											
6 x 10^{-2}	0.99852	1.0389	1.1609	0.1609	0.0849	8.2	12.59	3.7x10^{-3}	8 x 10^{-3}	39.87	3.4x10^{-3}
5 x 10^{-2}	0.99835	1.0173	1.1257	0.1257	0.0810		13.38		7 x 10^{-3}	39.90	
4 x 10^{-2}	0.99812	0.9876	1.1036	0.1036	0.0840		13.00		6 x 10^{-3}	39.90	
3 x 10^{-2}	0.99790	0.9601	1.0728	0.0728	0.0820		13.85		5 x 10^{-3}	39.35	
2 x 10^{-2}	0.99771	0.9283	1.0374	0.0374			17.06		4 x 10^{-3}	39.93	
1 x 10^{-2}	0.99750	0.9113	1.0183	0.0183			18.33		3.5x 10^{-3}	39.95	
7 x 10^{-3}	0.99746	0.9122	1.0190	0.0190			18.99		3 x 10^{-3}	40.45	
4 x 10^{-3}	0.99740	0.9010	1.0067	0.0067			20.17		2 x 10^{-3}	43.90	
2.5x 10^{-3}	0.99737	0.8982	1.0037	0.0037			22.59		1 x 10^{-3}	49.00	
1 x 10^{-3}	0.99731	0.8976	1.003	0.003					5 x 10^{-4}	54.25	
C_{16}											
6 x 10^{-2}	0.99861	1.0959	1.2246	0.2246	0.104	9.6	9.73	8 x10^{-4}	3 x 10^{-3}	40.0	8.8x10^{-4}
5 x 10^{-2}	0.99841	1.0613	1.1859	0.1859	0.103		9.81		2.5x 10^{-3}	39.97	
4 x 10^{-2}	0.99819	1.0179	1.1375	0.1375	0.096		10.59		2 x 10^{-3}	39.95	
3 x 10^{-2}	0.99798	0.9903	1.1069	0.1069	0.1004		10.22		1.5x 10^{-3}	40.0	
2 x 10^{-2}	0.99776	0.9468	1.0581	0.0581	0.828		12.56		1 x 10^{-3}	40.0	
1 x 10^{-2}	0.99754	0.9189	1.0269	0.0269			13.54		8 x 10^{-4}	40.72	
7 x 10^{-3}	0.99748	0.9112	1.0183	0.0183			13.97		6 x 10^{-4}	42.71	
4 x 10^{-3}	0.99742	0.9042	1.0103	0.0103			14.15		3.5x 10^{-4}	46.90	
2 x 10^{-2}	0.99740	0.8994	1.0051	0.0051			14.42		2.3x 10^{-4}	49.62	
7 x 10^{-3}	0.99737	0.8964	1.0017	0.0017			14.67		1.5x 10^{-4}	52.45	
4 x 10^{-4}	0.99737	0.8954	1.0006	0.0006			22.85				

HYDRO DYNAMIC DATA FOR THE SOLUTIONS OF DECYL TRIMETHYL AMMONIUM BROMIDE CONTAINING ALIPHATIC ALCOHOLS AT 25° C

TABLE II.I.2

C $mol.dm^{-3}$	da $q.ml^{-1}$	η cp	η_r	η_{sp}	$C-C_o$ $g.dl^{-1}$	$\frac{\eta-1}{C-C_o}$ $g.dl^{-1}$	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ $g.dl^{-1}$	C_o $mol.dm^{-3}$
1M Me-OH									
0.1	0.99521	1.0872	1.2148	0.2148	4.247	0.0505	27.95	0.0415	$6.24x10^{-2}$
0.08	0.9947	1.0623	1.1871	0.1871	3.6964	0.0506	29.11		
0.07	0.9945	1.0522	1.1758	0.1758	3.4961	0.0503	29.38		
0.065	0.99439	1.0456	1.1684	0.1684	3.2759	0.051	29.84		
0.06	0.99421	1.0427	1.1652	0.1652			29.57		
0.05	0.99392	1.0326	1.1538	0.1538			29.92		
0.04	0.99365	1.0228	1.1429	0.1429			30.25		
0.03	0.99321	1.0130	1.1320	0.1320			30.64		
0.02	0.99306	1.0097	1.1283	0.1283			29.34		
2M									
0.1	0.99071	1.1822	1.3210	0.3210	7.561	0.0425	28.68	0.0380	$5.88x10^{-2}$
0.08	0.99012	1.1592	1.2953	0.2953	7.004	0.0421	29.28		
0.07	0.98985	1.1482	1.2830	0.2830	6.7201	0.0421	29.56		
0.06	0.98921	1.1383	1.2720	0.2720	6.4398	0.0422	29.73		
0.05	0.98861	1.1272	1.2595	0.2595			30.08		
0.04	0.98842	1.1164	1.2475	0.2475			30.41		
0.03	0.98812	1.1051	1.2349	0.2349			30.85		
0.02	0.98781	1.0926	1.2210	0.2210			31.54		
3M									
0.1	0.98490	1.2621	1.4103	0.4103	10.485	0.0391	30.25	0.035	$6.9x10^{-2}$
0.08	0.98420	1.2398	1.3854	0.3854	9.9244	0.0388	30.75		
0.07	0.98401	1.2301	1.3744	0.3744	9.6441	0.0388	30.90		
0.06	0.9837	1.2192	1.3623	0.3623	9.3638	0.0387	31.16		
0.05	0.98341	1.2089	1.3510	0.3510			31.38		
0.04	0.98352	1.20	1.3410	0.3410			31.48		
0.03	0.98120	1.1881	1.3276	0.3276			31.90		
0.02	0.98089	1.1816	1.3206	0.3206			31.74		

TABLE II.I.2.A

C $mol.dm^{-3}$	da $g.dl^{-1}$	η cp	η_r	η_{sp}	$C-C_o$ $g.dl^{-1}$	$\frac{\eta-1}{C-C_o}$ $g.dl^{-1}$	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ $g.dl^{-1}$	Co $mol.dm^{-3}$
4M									
0.1	0.98041	1.3462	1.5043	0.5043	13.419	0.0375	30.96		
0.08	0.97981	1.3241	1.4795	0.4795	12.858	0.0372	31.39		
0.07	0.97952	1.3140	1.4683	0.4683			31.55		
0.065	0.97931	1.3080	1.4616	0.4616			31.70		
0.06	0.97920	1.3074	1.4610	0.4610			31.66	0.032	7.85×10^{-2}
0.05	0.97891	1.2939	1.4458	0.4458			31.88		
0.04	0.97852	1.2843	1.4352	0.4352			32.03		
0.03	0.97620	1.2722	1.4216	0.4216			32.38		
0.02	0.9778	1.2653	1.4139	0.4139			32.31		
1 M, Et-OH									
0.1	0.99212	1.1776	1.3159	0.3159	5.690	0.0555	23.45		
0.08	0.99161	1.1543	1.2898	0.2898	5.1294	0.0565	23.63		
0.07	0.99140	1.14241	1.2765	0.267	4.849	0.0570	23.75		
0.06	0.99112	1.1298	1.2625	0.2625			23.95		
0.05	0.99081	1.1173	1.2485	0.2485			24.17	0.056	6.14×10^{-2}
0.04	0.99061	1.1070	1.2370	0.2370			24.16		
0.03	0.99021	1.0952	1.2239	0.2239			24.33		
0.02	0.99002	1.0859	1.2134	0.2134			24.20		
2M									
0.1	0.98482	1.4003	1.5647	0.5647	10.387	0.0543	21.27		
0.08	0.98425	1.3712	1.5322	0.5322	9.826	0.0541	21.52		
0.07	0.98411	1.3583	1.5179	0.5179	9.546	0.0542	21.57		
0.06	0.98371	1.3457	1.5037	0.5037	9.265	0.0543	21.62		
0.05	0.98340	1.3346	1.4914	0.4914			21.60	0.053	5.82×10^{-2}
0.04	0.98320	1.3207	1.4758	0.4758			21.72		
0.03	0.98291	1.3083	1.4619	0.4619			21.76		
0.02	0.9827	1.2993	1.4518	0.4518			21.63		

TABLE II.I.2.B

C mol.dm^{-3}	da g.ml^{-1}	η cp	η_r	η_{sp}	$C-C_o$ g.dl^{-1}	$\frac{\eta-1}{C-C_o}$ g.dl^{-1}	$\frac{\frac{1}{\eta}}{c}$	$[\eta]$ g.dl^{-1}	C_o mol.dm^{-3}
3M									
0.1	0.97841	1.6444	1.8375	0.8375	15.074	0.0555	19.84	0.0510	5.53x10^{-2}
0.08	0.97782	1.6161	1.8059	0.8059	14.513	0.0545	19.93		
0.07	0.97752	1.6028	1.79106	0.79106	14.23	0.0541	19.95		
0.06	0.97731	1.5901	1.7769	0.7769			19.95		
0.05	0.97692	1.5775	1.7628	0.7628			19.95		
0.04	0.97661	1.5646	1.7484	0.7484			19.96		
0.03	0.97632	1.5551	1.7378	0.7378			19.87		
0.02	0.97601	1.5547	1.7372	0.7372			19.51		
4M									
0.01	0.97192	1.8837	2.1043	1.1043	19.479	0.056	19.22	0.0484	6.25x10^{-2}
0.08	0.97131	1.8619	2.0806	1.0806	18.922	0.0574	19.12		
0.07	0.97102	1.8511	2.0685	1.0685	18.638	0.0570	19.083		
0.06	0.97071	1.8370	2.0527	1.0527			19.12		
0.05	0.97042	1.7923	2.0028	1.0028			19.77		
0.04	0.97021	1.7791	1.9881	0.9881			19.79		
0.03	0.96981	1.7681	1.9757	0.9757			19.74		
0.02	0.96962	1.7558	1.9621	0.9621			19.76		
0.5M.PrOH									
0.1	0.99531	1.1296	1.2623	0.2623	4.168	0.0629	22.14	0.064	5.85x10^{-2}
0.08	0.99502	1.1072	1.2373	0.2373	3.607	0.0657	22.117		
0.07	0.99471	1.0924	1.2207	0.2207	3.327	0.066	22.51		
0.06	0.99442	1.0799	1.2067	0.2067	3.046	0.067	22.66		
0.05	0.99403	1.0724	1.1984	0.1984			22.2		
0.04	0.99372	1.0630	1.1878	0.1878			21.96		
0.03	0.99343	1.0572	1.1813	0.1813			21.20		
0.02	0.99312	1.0464	1.1694	0.1694			21.05		

TABLE II.I.2.C

C mol.dm^{-3}	da g.ml^{-1}	η cp	η_r	η_{sp}	$C-C_0$ g.dl^{-1}	$\frac{\eta-1}{C-C_0}$ g.dl^{-1}	$\frac{\frac{1}{\eta_{sp}}}{C}$	$\left[\eta\right]$ g.dl^{-1}	C_0 mol.dm^{-3}
1 M									
0.1	0.9904	1.4389	1.4423	0.4423	7.313	0.0604	19.92		
0.08	0.99031	1.269	1.4180	0.4180	6.752	0.0619	19.74		
0.07	0.99021	1.2552	1.4026	0.4026	6.472	0.062	19.79		
0.06	0.9901	1.2396	1.3852	0.3852	6.1918	0.062	19.96		
0.055	0.990	1.2352	1.3803	0.3803	6.0516	0.062	19.85	0.058	5.35×10^{-2}
0.050	0.9891	1.2251	1.3690	0.3690			20.08		
0.04	0.98899	1.2086	1.3506	0.3506			20.34		
0.03	0.98819	1.1980	1.3387	0.3387			20.22		
0.02	0.9881	1.1879	1.3274	0.3274			20.08		
1.5 M									
0.1	0.98571	1.4707	1.6434	0.6434	10.468	0.0614	18.36		
0.08	0.98551	1.4338	1.6022	0.6022	9.897	0.0608	18.67		
0.07	0.9854	1.4178	1.5843	0.5843	9.617	0.0607	18.76		
0.06	0.98531	1.4064	1.5716	0.5716	9.336	0.0612	18.80		
0.055	0.98526	1.3903	1.5536	0.5536			19.05	0.052	4.82×10^{-2}
0.05	0.98521	1.3766	1.5383	0.5383			19.34		
0.04	0.98512	1.3658	1.5262	0.5262			19.24		
0.03	0.98502	1.3535	1.5125	0.5125			19.22		
0.02	0.98401	1.3371	1.4942	0.4942			19.35		
2 M									
0.1	0.9813	1.6482	1.8417	0.8417	13.713	0.0614	17.60		
0.08	0.98112	1.6091	1.7981	0.7981	13.153	0.0606	17.86		
0.07	0.98101	1.5894	1.7761	0.7761	12.872	0.0603	18.02		
0.06	0.98093	1.5823	1.7686	0.7686	12.592	0.061	17.83		
0.055	0.98041	1.5696	1.7539	0.7539	12.452	0.0605	17.98	0.046	3.96×10^{-2}
0.05	0.97991	1.5612	1.7445	0.7445			18.02		
0.04	0.97941	1.5514	1.7337	0.7337			17.91		
0.03	0.97862	1.5356	1.7159	0.7159			17.96		
0.02	0.97783	1.5227	1.7015	0.7015			17.93		
0.01	0.97701	1.5172	1.6953	0.6953			17.68		

TABLE II.I.2.D

C mol.dm^{-3}	da g.ml^{-1}	η cp	η_r	η_{sp}	$C-C_o$ g.dl^{-1}	$\frac{\eta-1}{C-C_o}$ g.dl^{-1}	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ g.dl	C_o mol.dm^{-3}
0.2 M,Bt-OH									
0.1	0.9973	1.0644	1.1894	0.1894	2.625	0.0721	22.62		
0.08	0.99711	1.0402	1.1623	0.1623	2.064	0.0786	22.94		
0.07	0.99701	1.0265	1.1470	0.1470	1.784	0.0824	23.42		
0.06	0.99692	1.0173	1.1368	0.1368	1.5038	0.091	23.12		
0.05	0.98681	1.0092	1.1277	0.1277			22.57	0.075	$5.9\text{x}10^{-2}$
0.04	0.9967	1.0001	1.1175	0.1175			22.14		
0.03	0.99661	0.9907	1.1071	0.1071			21.69		
0.02	0.9965	0.9813	1.0965	0.0965			21.16		
0.01	0.9964	0.9711	1.0851				20.71		
0.5M									
0.1	0.9939	1.1902	1.3300	0.330	5.109	0.064	19.72		
0.08	0.9937	1.1620	1.2981	0.2981	4.548	0.065	19.95		
0.07	0.99362	1.1488	1.2838	0.2838	4.268	0.066	19.97		
0.06	0.9935	1.1354	1.2687	0.2687	3.987	0.067	20.05		
0.05	0.99339	1.1226	1.2544	0.2544			20.07	0.065	$5.\ \text{x}10^{-2}$
0.04	0.9933	1.1108	1.2412	0.2412			20.01		
0.03	0.9932	1.1004	1.2296	0.2296			19.79		
0.02	0.9931	1.0893	1.2172	0.2172			19.64		
0.8 M									
0.1	0.9903	1.2957	1.4479	0.4479	7.6626	0.0584	19.49		
0.08	0.98981	1.2642	1.4126	0.4126	7.102	0.057	19.80		
0.07	0.9897	1.2493	1.3960	0.3960	6.822	0.058	19.92		
0.06	0.98961	1.2341	1.3791	0.3791	6.541	0.0579	20.07		
0.05	0.9895	1.2104	1.3526	0.3526	6.261	0.0563	20.78	0.050	$3.8\text{x}10^{-2}$
0.04	0.98941	1.1991	1.3401	0.3401	6.081	0.0559	21.03		
0.03	0.9893	1.1877	1.3272	0.3272			20.68		
0.02	0.98922	1.1836	1.3226	0.3226			20.115		
0.01	0.98910	1.1764	1.3145	0.3145			19.72		

HYDRO DYNAMIC DATA FOR THE SOLUTIONS OF DODECYL TRIMETHYL AMMONIUM BROMIDE CONTAINING ALIPHATIC ALCOHOLS AT 25°C

TABLE II.I.3

C mol.dm^{-3}	da g.ml^{-1}	η cp	η_r	η_{sp}	C - C$_o$ g.dl^{-1}	$\frac{\eta-1}{C-C_o}$ g.dl^{-1}	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ g.dl^{-1}	C$_o$ mol.dm^{-3}
1 M Me-OH									
0.06	0.99261	1.0667	1.1920	0.1920	4.644	0.0413	26.33		
0.05	0.99221	1.0475	1.1705	0.1705	4.296	0.0397	27.82		
0.04	0.99181	1.0320	1.1532	0.1532	3.986	0.0384	28.95		
0.03	0.99142	1.0215	1.1415	0.1415	3.678	0.0384	29.16		
0.02	0.99102	1.0061	1.1243	0.1243	3.371	0.0368	30.73	0.0302	1.44×10^{-2}
0.018	0.99074	1.0029	1.1207	0.1207	3.309	0.0364	31.13		
0.016	0.99034	0.9977	1.1144	0.1144			32.16		
0.014	0.99012	0.9955	1.1125	0.1125			32.31		
0.012	0.98982	0.9905	1.1068	0.1068			33.44		
0.01	0.98953	0.9847	1.1004				34.97		
2 M									
0.06	0.98791	1.1459	1.2839	0.2839	7.888	0.0359	29.086		
0.05	0.98763	1.1318	1.2647	0.2647	7.580	0.0349	30.023		
0.04	0.9874	1.1122	1.2428	0.2428	7.27	0.0334	31.45		
0.03	0.98717	1.1014	1.2308	0.2308	6.963	0.0331	31.76		
0.02	0.98694	1.081	1.2077	0.2077	6.654	0.0312	33.82	0.0292	1.2×10^{-2}
0.018	0.98690	1.088	1.2164	0.2164	6.593	0.032	32.17		
0.016	0.98682	1.0797	1.2065	0.2065	6.5314	0.031	33.42		
0.014	0.98676	1.0771	1.2036	0.2036	6.469	0.0314	33.59		
0.01	0.98664	1.0723	1.1983	0.1983			33.88		
3 M									
0.06	0.98215	1.2375	1.3828	0.3828	10.9324	0.0350	29.93		
0.05	0.98182	1.2163	1.3592	0.3592	10.624	0.0338	31.05		
0.04	0.98159	1.1977	1.3384	0.3384	10.314	0.0328	32.048		
0.03	0.98135	1.1829	1.3218	0.3218	10.007	0.0322	32.74		
0.02	0.98112	1.1670	1.3041	0.3041	9.698	0.0313	33.64	0.0282	1.72×10^{-2}
0.018	0.98106	1.1622	1.2988	0.2988	9.637	0.0310	34.02		
0.014	0.98101	1.1604	1.2966	0.2966			33.85		
0.01	0.98085	1.1567	1.2925	0.2925			33.907		
0.007	0.98079	1.1536	1.2891	0.2891			33.93		
0.004	0.98073	1.1505	1.2856	0.2856			34.08		

TABLE II.I.3.A

C $mol.dm^{-3}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$C-C_o$ $g.dl^{-1}$	$\frac{\eta-1}{C-C_o}$ $g.dl^{-1}$	$\frac{1}{\eta_{sp}/C}$	$[\eta]$ $g.dl^{-1}$	C_o $mol.dm^{-3}$
4 M									
0.06	0.9767	1.3642	1.5244	0.5244	14.026	0.0373	27.96	0.0275	2.08×10^{-2}
0.05	0.9765	1.3440	1.5018	0.5018	13.718	0.0365	28.61		
0.04	0.9763	1.3246	1.4802	0.4802	13.408	0.0358	29.25		
0.03	0.9760	1.3031	1.4561	0.4561	13.101	0.0348	30.13		
0.02	0.97582	1.2814	1.4318	0.4318			31.10		
0.018	0.97576	1.2837	1.4344	0.4344			30.77		
0.014	0.97564	1.2787	1.4289	0.4289			30.88		
0.01	0.97561	1.2753	1.4251	0.4251			30.94		
0.007	0.97542	1.2725	1.4219	0.4219			30.88		
0.004	0.9755	1.2687	1.4177	0.4177			30.97		
1M,Et-OH									
0.06	0.99032	1.1854	1.3246	0.3246	6.057	0.0535	19.89	0.044	1.29×10^{-2}
0.05	0.99002	1.1695	1.3068	0.3968	5.749	0.0533	20.04		
0.04	0.9899	1.1511	1.2863	0.2863	5.439	0.0526	20.39		
0.03	0.98988	1.1310	1.2637	0.2637	5.132	0.0514	20.97		
0.02	0.98951	1.1157	1.2468	0.2468	4.824	0.0512	21.16		
0.018	0.98942	1.1103	1.2406	0.2406	4.762	0.0512	21.45		
0.014	0.98927	1.1051	1.2348	0.2348			21.43		
0.01	0.98910	1.1001	1.2293	0.2293			21.43		
0.007	0.98889	1.0930	1.2213	0.2213			21.78		
1.5 M									
0.06	0.98671	1.2974	1.4498	0.4498	8.4005	0.0535	19.47	0.0415	1.16×10^{-2}
0.05	0.98652	1.2773	1.4272	0.4273	8.0925	0.0528	19.78		
0.04	0.98563	1.2627	1.4110	0.4110	7.783	0.0528	19.81		
0.03	0.98558	1.2376	1.3830	0.3830	7.475	0.0512	20.45		
0.02	0.98548	1.2193	1.3630	0.3630	7.167	0.0505	20.76		
0.018	0.98542	1.2176	1.3606	0.3606	7.105	0.0513	20.70		
0.014	0.98537	1.2056	1.3472	0.3472	6.982	0.0502	21.14		
0.01	0.98531	1.2016	1.3428	0.3428			21.06		
0.007	0.98525	1.1978	1.3385	0.3385			21.05		
0.004	0.98520	1.1945	1.3348	0.3348			21.00		

TABLE II.I.3.B

C mol.dm^{-3}	da g.ml^{-1}	η cp	η_r	η_{sp}	C−C$_o$ g.dl^{-1}	$\frac{\eta-1}{C-C_o}$ g.dl^{-1}	$\frac{\frac{1}{\eta_{sp}}}{C}$	$[\eta]$ g.dl^{-1}	C mol.dm^{-3}
2 M									
0.06	0.98272	1.4177	1.5842	0.5843	10.764	0.0543	18.94		
0.05	0.98260	1.3939	1.5576	0.5576	10.456	0.0533	19.28		
0.04	0.98251	1.3763	1.5379	0.5379	10.146	0.0530	19.42		
0.03	0.98239	1.3466	1.5047	0.5047	9.838	0.0513	20.08		
0.02	0.98228	1.3414	1.4990	0.4990	9.5306	0.0523	19.70		
0.018	0.98224	1.3392	1.4964	0.4964	9.469	0.0524	19.67	0.038	9.73x10^{-3}
0.014	0.9822	1.3315	1.4879	0.4879	9.3457	0.0522	19.76		
0.01	0.98219	1.3257	1.4814	0.4814			19.79		
0.007	0.98215	1.3246	1.4802	0.4802			19.63		
0.004	0.98211	1.323	1.4789	0.4789			19.49		
2.5 M									
0.06	0.9793	1.5504	1.7325	0.7325	13.0179	0.0562	18.25		
0.05	0.97912	1.5227	1.70163	0.70163	12.7095	0.0551	18.62		
0.04	0.9790	1.50263	1.67911	0.67911	12.399	0.0547	18.77		
0.03	0.97891	1.4811	1.6551	0.6551	12.0920	0.0542	18.99		
0.02	0.97882	1.4577	1.6289	0.6289	11.784	0.0533	19.29		
0.018	0.9788	1.4537	1.6245	0.6245	11.722	0.0532	19.33	0.0358	1.13x10^{-2}
0.014	0.97876	1.4478	1.6178	0.6178	11.599	0.0533	19.34		
0.012	0.97872	1.4460	1.6158	0.6158			19.30		
0.01	0.97871	1.4423	1.6116	0.6116			19.33		
0.007	0.97860	1.4399	1.609	0.609			19.26		
0.004	0.97851	1.4337	1.6021	0.6021			19.33		
0.5 MPr-OH									
0.06	0.99351	1.1402	1.2741	0.2741	4.485	0.061	17.71		
0.05	0.9934	1.1208	1.2524	0.2524	4.177	0.060	18.01		
0.04	0.99332	1.1001	1.2292	0.2292	3.867	0.059	18.48		
0.03	0.99316	1.0825	1.2096	0.2096	3.559	0.058	18.74		
0.02	0.99312	1.0662	1.1946	0.1946	3.252	0.058	18.91		
0.018	0.99309	1.0614	1.1861	0.1861	3.182	0.058	19.10	0.0524	1.2x10^{-2}
0.014	0.99302	1.0561	1.1801	0.1801			19.07		
0.012	0.9930	1.0528	1.1764	0.1764			19.12		
0.01	0.99271	1.04929	1.1725	0.1725			19.21		
0.007	0.99252	1.04820	1.1713	0.1713			18.79		
0.004	0.99231	1.0440	1.1671	0.1671			18.72		

TABLE II.I.3.C

C $mol.dm^{-3}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$C-C_o$ $g.dl^{-1}$	$\frac{\eta-1}{C-C_o}$ $g.dl^{-1}$	$\frac{\frac{1}{\eta_{sp}}}{C}$	$\left[\eta\right]$ $g.dl^{-1}$	Co $mol.dm^{-3}$
1M									
0.06	0.98890	1.2991	1.4517	0.4517	7.564	0.0597	17.41		
0.05	0.98887	1.2776	1.4276	0.4276	7.252	0.0589	17.65		
0.04	0.98874	1.2569	1.4045	0.4045	6.932	0.0583'	17.87		
0.03	0.98861	1.2366	1.3819	0.3819	6.6349	0.0575	18.15		
0.02	0.9885	1.2178	1.3608	0.3608	6.326	0.0570	18.36		
0.018	0.98847	1.2107	1.3529	0.3529	6.265	0.0563	18.59	0.0495	9.7×10^{-3}
0.014	0.98844	1.1977	1.3384	0.3384	6.142	0.0551	19.04		
0.012	0.98841	1.1973	1.3379	0.3379			18.87		
0.01	0.98837	1.1969	1.3374	0.3374			18.72		
0.007	0.98814	1.1948	1.3352	0.3352			18.57		
0.004	0.98811	1.1934	1.3336	0.3336			18.38		
1.5M									
0.06	0.9845	1.4576	1.6288	0.6288	10.585	0.0594	17.27		
0.052	0.9843	1.4372	1.6059	0.6059	10.348	0.0585	17.57		
0.04	0.9842	1.4105	1.5761	0.5761	9.967	0.0578	17.78		
0.03	0.98417	1.3884	1.5515	0.5515	9.659	0.0571	18.02		
0.022	0.98412	1.3675	1.5281	0.5281	9.416	0.056	18.36		
0.018	0.9841	1.3534	1.5124	0.5124	9.291	0.0555	18.67	0.046	9.1×10^{-3}
0.014	0.98406	1.3491	1.5075	0.5075	9.166	0.0557	18.61		
0.012	0.98402	1.3479	1.5063	0.5063	9.1051	0.0556	18.53		
0.01	0.98399	1.3465	1.5047	0.5047			18.47		
0.007	0.98396	1.3452	1.5032	0.5032			18.34		
0.004	0.98392	1.3443	1.5021	0.5021			18.19		
2M									
0.06	0.9800	1.6262	1.8171	0.8171	13.651	0.0598	16.97		
0.05	0.97984	1.6008	1.7889	0.7889	13.342	0.0591	17.19		
0.04	0.97978	1.5841	1.7702	0.7702	13.032	0.0591	17.21		
0.03	0.97963	1.5615	1.7449	0.7449	12.725	0.0585	17.37		
0.02	0.97948	1.5472	1.7289	0.7289	12.410	0.0587	17.33		
0.018	0.97945	1.5305	1.7103	0.7103	12.355	0.0576	17.70	0.0425	7.1×10^{-3}
0.014	0.979411	1.5239	1.7028	0.7028	12.231	0.0574	17.71		
0.012	0.97937	1.5202	1.6988	0.6988			17.72		
0.01	0.97934	1.5193	1.6977	0.6977			17.66		
0.007	0.97931	1.5182	1.6965	0.6965			17.56		
0.004	0.97927	1.5137	1.6915	0.6915			17.56		

TABLE II.I.3.D.

C mol.dm^{-3}	da g.ml^{-1}	η cp	η_r	η_{sp}	$C - C_o$ g.dl^{-1}	$\frac{\eta - 1}{C - C_o}$ g.dl^{-1}	$\frac{1/\eta_{sp}}{C}$	$[\eta]$ g.dl^{-1}	C_o mol.dm^{-3}
0.2M,Bt-OH									
0.06	0.9959	1.0553	1.1792	0.1792	2.9155	0.0614	18.59	0.059	1.4×10^{-2}
0.05	0.99581	1.0363	1.1580	0.1580	2.6071	0.0606	19.14		
0.04	0.99572	1.0177	1.1372	0.1372	2.2988	0.0597	19.78		
0.03	0.9956	1.0010	1.1184	0.1184	1.9910	0.0595	20.33		
0.02	0.9955	0.9845	1.1002	0.1002	1.682	0.0595	20.94		
0.017	0.995471	0.9790	1.0879	0.0879	1.5885	0.0592	21.34		
0.014	0.99544	0.9735	1.0879	0.0879			21.59		
0.01	0.99541	0.9691	1.0829	0.0829			21.58		
0.007	0.99537	0.9645	1.0778	0.0778			21.80		
0.5M									
0.06	0.9926	1.1791	1.3175	0.3175	5.247	0.0605	17.49	0.050	1.0×10^{-2}
0.05	0.99249	1.1601	1.2963	0.2963	4.939	0.060	17.70		
0.04	0.99239	1.1405	1.2744	0.2744	4.6311	0.059	18.00		
0.03	0.99232	1.1190	1.2504	0.2504	4.322	0.057	18.49		
0.02	0.99220	1.1005	1.2297	0.2297	4.014	0.057	18.68		
0.017	0.99217	1.0953	1.2239	0.2239	3.922	0.057	18.88		
0.014	0.99214	1.0953	1.2239	0.2239	3.814	0.056	19.18		
0.01	0.992110	1.0792	1.2059	0.2059			19.48		
0.007	0.99207	1.070	1.1956	0.1956			20.04		
0.004	0.99204	1.0576	1.1818	0.1818			21.06		
0.001	0.99201	1.0538	1.1776	0.1776			21.04		
0.8M									
0.06	0.9892	1.2933	1.4452	0.4452	7.579	0.0587	17.47	0.041	6.5×10^{-3}
0.05	0.98912	1.2718	1.4211	0.4211	7.271	0.0579	17.74		
0.04	0.9890	1.2547	1.4021	0.4021	6.963	0.0577	17.81		
0.02	0.98881	1.2098	1.3518	0.3518	6.346	0.0554	18.60		
0.017	0.98877	1.2040	1.3454	0.3454	6.253	0.0551	18.68		
0.014	0.98874	1.1989	1.3397	0.3397	6.246	0.0544	18.97		
0.01	0.98871	1.1897	1.3294	0.3294	6.037	0.0545	18.93		
0.007	0.98867	1.1807	1.3194	0.3194	5.945	0.0537	19.23		
0.004	0.98867	1.1769	1.3151	0.3151			19.20		
0.001	0.98861	1.1722	1.3098	0.3098			19.24		

HYDRODYNAMIC DATA FOR THE MICELLES OF ALKYLTRIMETHYL
AMMONIUM BROMIDES AT 25° C

TABLE II.I.4

S.A.A	Vh	Va	$Wg.g^{-1}$	$\overline{\upsilon}$	Light Scattering		Viscosity	K
	$ml.10^{-19}$	$ml.10^{-19}$		$ml.g^{-1}$	Incorrect $R^{O}.A^{o}$	Correc. $R^{C}.A^{o}$	$R^{V}.A^{o}$	
C_{10}	0.4025	0.158	1.458	0.94542	16	18	21	
C_{12}	0.705	0.2360	1.841	0.92445	18	20	25	2.5
C_{14}	1.232	0.352	2.348	0.93783	20	22	30	
C_{16}	1.990	0.479	2.923	0.92465	23	24	36	

MICELLAR DIMENSIONS OF THE DODECYLTRIMETHYL AMMONIUM BROMIDE IN WATER CONTAINING ALIPHATIC ALCOHOLS

TABLE II.I.5

C $mol.dm^{-3}$	K	A_R	A_a A°	A_b A°
Et-OH				
1 M	4.7	4.1	70	17
2 M	3.9	3.3	56	17
Pr-OH				
0.5 M	5.4	4.7	70	15
1.0 M	5.1	4.4	62	14
1.5 M	4.7	4.1	53	13
Bt-OH				
0.5 M	5.1	4.4	57	13
1.0 M	4.6	3.9	43	11

CHAPTER III - The effects of additives on B-coefficients of Alkylammonium bromides in aqueous solutions

III-Ia - Theory of viscosity of the electrolyte solutions.

In electrolyte solutions the presence of coulomb forces between the ions effect the viscosity of the medium. The change in viscosity of the dispersion medium has been successfuly examined by Falkenhagen et al.(188,189,190). According to his theory, a part of stress in an ionic solution is produced by the deformation of the ionic atmosphere. According to the Debye-Hückel(191) theory each ion in the solution, is surrounded by an atmosphere of ions of opposite sign, at an average distance of $1/\kappa$.

If we assume that we have such a situation in the unperturbed solution, then the distribution will possess a spherical symmetry. Due to the velocity gradient in the solution, the atmosphere of an ion is deformed from a spherical to an ellipsoidal form. As a result of this process, the electrostatic forces and thermal motion tend to restore the atmospheres to their original form. The magnitude of the deformation of the ionic atmosphere, could be given by an expression(188) such as,

$$\frac{a_i}{\kappa^2 kT} \frac{\partial v_x}{\partial y} \qquad \text{III-1}$$

and the forces between two ions of charge e at distance $1/\kappa$ is $e^2\kappa^2/D$, and the total transfer of forces act between the ion and its atmosphere is $1/\kappa$ times the quantity of the $e^2\kappa^2/D$ or $e^2\kappa D$.

Substituting this quantity into expression (III-1) and considering the displacement of the ionic atmosphere, we get the following expression,

$$\frac{e^2 a_i}{\kappa D kT} \frac{\partial \nu_x}{\partial y} \qquad \text{III-2}$$

which is the order of the magnitude of the stress transferred between the ion and its atmosphere.

By substitution of $\kappa = \left[\frac{4\pi\epsilon^2}{DkT} \sum_{i=1}^{s} n_i z_i^2 \right]$ into expression

III- 2 the electrostatic contribution to the stress is obtained

$$S_a \sim \kappa a_i \frac{\partial v_x}{\partial y} \qquad \text{III-3}$$

when $\frac{1}{a_i} = \omega_1 = \omega_2 = \ldots \omega_s$ this becomes,

$$S_a = \frac{1}{480\pi} a_i \kappa \frac{\partial v_x}{\partial y} \qquad \text{III-4}$$

The stress between the solvent molecules is given by the equation

$$S_b = \eta_0 \frac{\partial v_x}{\partial y} \qquad \text{III-5}$$

Hence the contribution of the ionic atmosphere to the viscosity is,

$$\eta_1 = \frac{a_i \kappa}{480\pi} \qquad \text{III-6}$$

This Falkenhagen's result, was later confirmed experimentally by Jones-Dole(192) for the dilute solutions.

III-Ib - The B-coefficients of ionic solutions.

Due to the long range nature of coulombic interactions, the properties of ionic solutions are influenced by interionic effects. These properties can be examined by the Debye-Hückel limiting law, by assuming that the ions do not approach each other so closely. Otherwise owing to their hydration envelopes, they interfere with each other introducing an extra term into the activity coefficient(80).

At higher concentrations, it has been observed that the behaviour of the ionic solutions deviate from simple concentration dependence. The properties of aqueous electrolyte solutions are highly specific to the individual ions concerned. In the case of viscosity, Jones-Dole have developed(192) a relationship between concentration dependence, and the viscosity of dilute electrolyte solution, which is given by the equation

$$\eta/\eta_o = 1 + A\sqrt{C} + BC \qquad \text{III-7}$$

Falkenhagen et al.(188,189,190) showed that the square root term is due to the long range interionic forces, and that the coefficient A can be calculated from the Debye-Hückel(191) limiting law. Since, in general $A/B \leqslant 1$, the square root term could be neglected at concentrations above 0.002M, when the equation takes the form(193)

$$\eta/\eta_o = 1 + BC \qquad 0.002M < C < \sim 0.1M \qquad \text{III-8}$$

The B coefficient which is a specific property of the solute, can be derived in terms of the individual contributions of the solute constituent ions. Hence

$$B = {}_{z+}^{B-} + {}_{z-}^{B+} \qquad \text{III-9}$$

The viscosity B coefficients can be either positive or negative. If we consider the B value as a measure of the ion-solvent interactions, then we can introduce the following effects, which influence the B value of the electrolyte solution(194),

1) The interaction of solvent molecules with the ion which causes an increase in viscosity.
2) The effect of the field ion in producing long-range order of solvent molecules, which also causes an increase in viscosity.
3) The destruction of water molecules due to structure breaking effect of the ion, which causes a decrease in viscosity.
4) Steric effects.

In the case of suspensions, Einstein introduced(126,127) an equation for the relative viscosity of the dilute suspension of the rigid spheres which is

$$\eta/\eta = 1 + 2.5\phi$$

Tuan-Fuoss(195) and Moulik(196) have examined the relationship between the Einstein and Jones-Dole equations. As a result of this investigation, they have postulated an expression such as,

$$\phi = c\ V \qquad \text{III-10}$$

then the B coefficient could be related to the molar volume of the solute by,

$$B = 2.5\ V \qquad \text{III-11}$$

If we consider concentrated electrolyte solutions, then the relative viscosity can be represented by a polynomial of the form(193)

$$\eta/\eta_0 = 1 + 2.5\phi + k_1\phi^2 + k_2\phi^3 \qquad \text{II-12}$$

Vand(197) has concluded that the second and higher order terms, which were added to the Einstein equation, is due to the particle interactions of various types. The investigation of the viscosity of the concentrated eletrolyte solutions has been extended by Thomas(198). He introduced a second degree equation, which could be defined by an expression,

$$\eta/\eta_0 = 1 + 2.5\phi + 10.05\phi^2 \qquad \text{III-13}$$

This expression is valid for highly concentrated suspensions. If we substitute the expression $\phi = c\ Ve$ into the equation (III-13) we obtain(193)

$$\eta/\eta_0 = 1 + 2.5\ c\ Ve + 10.05\ c^2\ Ve^2 \qquad \text{III-14}$$

This equation may be rearranged to solve for Ve, which is the effective rigid molar volume of the salt,

$$Ve = \frac{-2.5\ c + \sqrt{(2.5c)^2 - 4(10.05c^2)(1-\eta/\eta_0)}}{2(10.05)c^2} \qquad \text{III-15}$$

Cox-Wolfenden(199) examined the individual B coefficients of the ions of lithium iodate, in terms of the temperature coefficient of mobility of the ions. They calculated the B coefficients of several ions, considering the ionic volumes which are inversely proportional to the cube of the ionic mobilities. The negative values of B coefficients have been interpreted, by means of the depolymerization of the solvent by the ions. In aqueous solution of electrolyte, the ionic radius is altered by the change in nature of the number of neighbour molecules by the ion considered.

Kaminsky(194) studied the B_{ion} values of KCl at different temperatures, by examining the ionic mobilities of K^+ and Cl^- ions. He has found that the difference is less than 3%. As a result of this fact, he concluded that at every temperature B_{K^+} is equal to B_{Cl^-}. These values are very close to the B_{ion} values of KCl derived by Cox-Wolfenden(199).

On the other hand he observed that the B_{ion} values for NH_4^+ are very close to zero. The reason has been attributed to the structure of the ion which does not influence the structure of the solvent.

However in the case of the alkali metals, alkaline earths and halogens, at wide temperature range, the B_{ion} values decrease as the crystal ionic radii increase. But the temperature coefficient of B_{ion} values increases as the crystal ionic radius increases. He discussed also the negative values of B coefficients, in terms of the structure breaking influence of the ions on the solvent structure.

III-Ic - Cosphere effects.

Born(200) first considered the effect of static dielectric on the ionic mobilities, and put forward the suggestion that the solvent dipoles in the cosphere of ion could be orientated by the motion of the ion. These orientated dipoles relax at finite time to their random orientations.

This observation has been examined and in semi-empirical form presented by Fuoss(201). Later Boyd(202) extended this approach. Fernandez-Prini-Atkinson(203) suggested that the dielectric constant of the cosphere of an ion could be altered due to the high charge density of the small ion. They were able to obtain a constant, which accounts for the mobilities of the ions in a number of aprotic solvents.

There has been an indication that the viscosity of the cosphere of an ion, is also influenced by the ionic charge. This effect on the viscosity would affect the mobilities. In this case the dielectric saturation effect appears as a second-order correction.

Endom et al.(204) observed that the larger metal ions decrease the amount of long range order in the cosphere in aqueous solutions. Giese(205) et al. showed that water molecules have greater rotational and translational freedom in the vicinity of the metal ions than in bulk water. In the Frank-Wen(c) treatment, the cosphere contains two regions. The region 'A' which is adjacent to the ion surface contains water molecules and the other region B which is further away from the centre of the ion. In this region A it is believed that the tetrahedrally bonded water molecules are disrupted by the ionic charges. It is further assumed that the region A is bigger than that of region B for the ions of high charge density, whereas the ions of low charge density have the reverse situation.

This approach has been employed by Kay-Evans(206) to examine the ionic transport phenomenon and the cospheres of the large univalent ions in aprotic solvents. When the ion is sufficiently large, the solvent molecules in the cosphere, could be orientated into favourable positions by neighbouring molecules. This behaviour arises from ions (i.e. tetraalkylammonium), which contain an inert surface.

As a result of this fact one can postulate that a cosphere of this type of ions contain greater degrees of hydrogen bonding than the bulk water does. It has also been observed that these ions increase the viscosity of water.

Another view of the structural cosphere effect has been introduced$^{(101)}$ from conductance data for D_2O solutions. The higher viscosity of D_2O solution over that of H_2O at 25°C, has been attributed to their hydrogens bonding characteristics. They have further showed that the structure breakers have higher mobility in D_2O than in H_2O, which is the reverse for the structure makers.

III-Id - Information from Experimental Data.

The viscosities of aqueous solutions of alkyltrimethyl ammonium bromides, and the solutions containing additives have been measured, as mentioned in Chapter II.The Jones-Dole equation$^{(192)}$ (III- 7) has been used to analize the hydrodynamic data of the electrolyte solutions.

In order to evaluate A and B coefficients equation (III- 7) can be written as

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} \qquad \text{III-16}$$

The plots of $\frac{n_r - 1}{\sqrt{c}}$ versus $\sqrt{c}$ are shown in Figs.III.1, III.2,III.3,III.4. The A intercept obtained is very small (0,009) in the aqueous solutions studied (Fig.III.1). The plot of equation (III-16) was found to be linear with $\sqrt{c}$ for C_{10}. But in the case of higher chain lengths, it is observed that the linear relationship with $\sqrt{c}$ is up to 0,15M, then it increases nonlinearly as the concentration increases. (Fig.III.1, Table III.I.1).

Frank-Evans$^{(4)}$ postulated that the presence of apolar solute increases water structure surrounding the solute. In the light of this approach, Krishnan-Friedman$^{(91)}$ and other investigators$^{(100,106,107)}$ have observed that the long apolar groups govern the interactions of the ions with water structure.

They showed that the apolar solution effects were large, for the structural contribution to the thermal properties of the solutions. As a result of these observations, they concluded that the apolar side of the ion behaves as structure maker in the solution.

Due to the apolar group of the ion, the viscosity of water increases by increasing the ice-like structure (structure maker). The calculated positive B coefficients (0.78 and 1.52 for C_{10} and C_{14} respectively) indicate that the alkylchain length of the ions tend to order the solvent structure, and increase the viscosity of the solution(207). The positive B coefficients of the hydrated ions appear to be proportional to the effective radius of Frank's(6) A region, in which the water is highly ordered. On the other hand the ions might also have small B regions. But the effect of this region is negligibly small.

It is apparent that the structure breaking effect decreases with the increase in radius of the ion(194). This can be explained in terms of the low charge density of the large ions. However, the increase in the ice-like structure, is proportional to the size of the nonpolar region(207).

When the surface charge is low, the electrostatic ion-solvent interactions do not affect the hydrogen bonded structure of the solvent(208). The order producing ions with positive B coefficients increase the energy and entropy of the activation for viscous flow, which increases with the increase in the chain length of ion. This is due to the increase in ice like structure around the apolar group(140,209).

The division of the B coefficients into individual ionic values is a kind of arbitrary process, because it is rather difficult to evaluate the corresponding transport numbers of the individual ions. The B_{ion} values of K^+ and C^- have been computed by Cox-Wolfenden(199), Kaminsky(194) and Gurney(69). The obtained ionic values were in good agreement with each other.

In order to obtain individual B_{ion} coefficients of the alkylammonium bromides, Kaminsky's procedure has been considered and his data was used for Br^- ion (-0.042, Table III.I.1).

Relatively small ions(194), multivalent ions, such as Li^+, Na^+, H_3O^+, Ca^{2+}, Mg^{2+} increase the viscosity of water. They polarize, immobilize and electrostrict nearest-neighbour water molecules(131). They are said to have net structure-making effects. Large mono valent ions have a net structure-breaking(131) (entropy increasing effect). Thus ions, such as Cl^-, Br^-, I^-, NO_3^-, Cs^-, K^+ increase the fluidity of water. The water molecules which are not in the vicinity of these ions become more mobile than those in pure water. As the temperature of water is increased, the net structure breaking influence of ions like Cl^-, Br^- and I^- decreases as the number of hydrogen bonded water molecules decreases.

Consequently the existence of negative viscosity B coefficients of the ions arises from the structure breaking effect. In view of the Frank-Wen(6) model, the negative B coefficients indicate that for large ions, because of the weak electric field, the B-region encroaches upon the A-region. The order destroying ions possess negative activation energies.

The cosphere of the positive ion causes a local increase in the viscosity, while cospheres of negative ions cause a decrease in the viscosity(69). If a cancellation occurs than the B coefficient will be near to zero. When the B coefficient is negative, it can be postulated that one of the ions is diminishing the viscosity.

On the addition of aliphatic alcohols to the aqueous solution of decyltrimethyl ammonium bromide, it is observed that the viscosity B coefficient becomes negative, as the concentration of alcohol increases. (0,641, 0,529 and -0,870 for C_{10} containing 0.4M, 1M and 2M CH_3OH respectively Fig.III.2, Table III.I.1,A). On the other hand, the decreasing effect of the alcohol increases linearly as the chain length increases (Fig.III.5). The observed negative values of the viscosity B coefficients can be discussed in terms of the effect of alcohols on the solvent structure and the possible interactions.

It is generally considered(91,97,210) that the apolar region of the alcohol molecule behaves as an apolar solute, which affects the solvent structure. The addition of alcohol to water causes at first an increase in the solvent structure(at low concentration structure maker). As the alcohol content is progressively increased, the structure is destroyed by the alcohol molecules, consequently the networks around the apolar groups are influenced by the apolar sides of the alcohol molecules, and the binding of alcohol molecule to the alkyl group of the ion might occur. Due to the high concentration of alcohol in the solution, polymeric hydrogen bonding mechanism takes place. These interactions alter the physico-chemical environment of the alkyl group and bromide ion in the solution.

Cox-Wolfenden(199) stated that the negative viscosity B coefficient is due to the depolymerization of thewater structure.

Gurney(69) explained that if a solute at room temperature causes the local loosening of the water structure, then the viscosity B coefficient is negative.

In this work it is reasonable to assume that the negative values of B coefficients arise from the destruction of networks around the apolar region by alcohol molecules. The alkyl group associated with alcohol molecule may behave as a structure breaker. As a result of this fact the negative B coefficient will increase as the particular alcohol concentration increases.

III.Ie - Conclusions.

The viscosity B coefficients of alkylammonium bromides in aqueous solutions are all positive. The B coefficient increases as the chain length increases. The increment of B is due to the long apolar group , which promotes the hydrogen bonded water structure.

The electrostatic ion-solvent interactions do not affect the hydrophobic interactions, due to the low surface charge of the apolar group. The energy and entropy of the activation for viscous flow, increase with increasing chain length. On the other hand, the Br^- ion behaves as a structure breaker and introduces the negative B coefficient.

The addition of alcohol to the system, affects the positive viscosity B coefficient of the ion. It becomes negative as the concentration of alcohol increases. This behaviour of the B coefficient is due to the effect of alcohol molecules on the solvent structure, the networks around the nonpolar groups, and the structure breaker effects of the alkyl and Br^- ions is a positive explanation of the negative B coefficients.

VISCOSITY B COEFFICIENTS FOR THE ALKYLTRIMETHL AMMONIUM BROMIDES

IN WATER AND CONTAINING ALIPHATIC ALCOHOLS AT 25° C

TABLE III.I.1

C mol. dm^{-3}	$\sqrt{C}$	$\frac{[\eta_r - 1]}{\sqrt{C}}$	B	Ionic B Coefficient	
				$R-\overset{\vert}{\underset{\vert}{N}}-{}^{+}$	Br^{-}
C_{10}					-0.042
0.1	0.3162	0.241	0.78	0.822	
0.08	0.2830	0.239			
0.07	0.2645	0.220			
0.06	0.2449	0.202			
0.05	0.2236	0.180			
0.04	0.20	0.158			
C_{12}					
0.06	0.2449	0.383	0.95	0.992	
0.05	0.2236	0.317			
0.04	0.20	0.253			
0.03	0.1732	0.231			
0.02	0.1414	0.172			
0.017	0.1304	0.144			
0.014	0.1183	0.121			
0.004	0.0632	0.055			
C_{14}					
0.05	0.2236	0.561	1.52	1.562	
0.04	0.20	0.461			
0.03	0.1732	0.378			
0.02	0.1414	0.265			
0.01	0.10	0.184			
0.004	0.0632	0.106			
0.0025	0.05	0.074			
C_{16}					
0.05	0.2236	0.831	2.5	2.542	
0.04	0.20	0.687			
0.03	0.1732	0.617			
0.02	0.1414	0.411			
0.01	0.10	0.269			
0.007	0.0836	0.219			
0.004	0.0632	0.162			

TABLE III.I.1.A

C mol.dm^{-3}	$\sqrt{C}$	$\frac{[\eta_r - 1]}{\sqrt{C}}$	A	B
C_{10}; 0.4 M, Me-OH				
0.1	0.3160	0.482	0.2675	0.641
0.08	0.2828	0.455		
0.07	0.2646	0.447		
0.06	0.2449	0.433		
0.05	0.2236	0.450		
0.04	0.20	0.432		
1M				
0.1	0.3160	0.680	0.505	0.529
0.08	0.2828	0.663		
0.07	0.2646	0.665		
0.065	0.2549	0.660		
0.06	0.2449	0.674		
0.05	0.2236	0.687		
0.04	0.20	0.715		
0.03	0.1732	0.763		
0.02				
2M				
0.1	0.316	1.016	-	-0.870
0.08	0.2828	1.047		
0.07	0.2646	1.070		
0.06	0.2449	1.110		
0.04	0.20	1.230		
0.03	0.1732	1.350		
0.02				
1 M, Et-OH				
0.1	0.316	0.999	-	-0.936
0.08	0.2828	1.027		
0.07	0.2646	1.047		
0.06	0.2449	1.071		
0.05	0.2236	1.109		
0.04	0.20	1.180		
2M				
0.1	0.316	1.787	-	-0.303
0.08	0.2828	1.880		
0.07	0.2646	1.960		
0.06	0.2449	2.050		
0.05	0.2236	2.190		

TABLE III.I.1.B

C mol. dm^{-3}	$\sqrt{C}$	$\frac{[\eta_r - 1]}{\sqrt{C}}$	A	B
0.5 M, Pr-OH				
0.1	0.316	0.829	-	-0.257
0.08	0.2828	0.841		
0.07	0.2646	0.835		
0.06	0.2449	0.844		
0.05	0.2236	0.886		
0.04	0.20	0.939		
1 M				
0.1	0.316	1.399	-	-2.3
0.08	0.2828	1.482		
0.07	0.2646	1.520		
0.06	0.2449	1.570		
0.05	0.2236	1.640		
0.2 M, Bt-OH				
0.1	0.316	0.599	0.415	0.540
0.08	2.2828	0.575		
0.07	0.2646	0.556		
0.06	0.2449	0.558		
0.05	0.2236	0.570		
0.04	0.20	0.587		
0.5 M				
0.1	0.316	1.044	-	-0.681
0.08	0.2828	1.056		
0.07	0.2646	1.076		
0.06	0.2449	1.096		
0.05	0.2236	1.135		
0.04	0.20	1.120		
0.8 M				
0.1	0.316	1.417	-	-1.72
0.08	0.2828	1.463		
0.07	0.2646	1.50		
0.06	0.2449	1.547		
0.05	0.2236	1.574		
0.04	0.20	1.70		

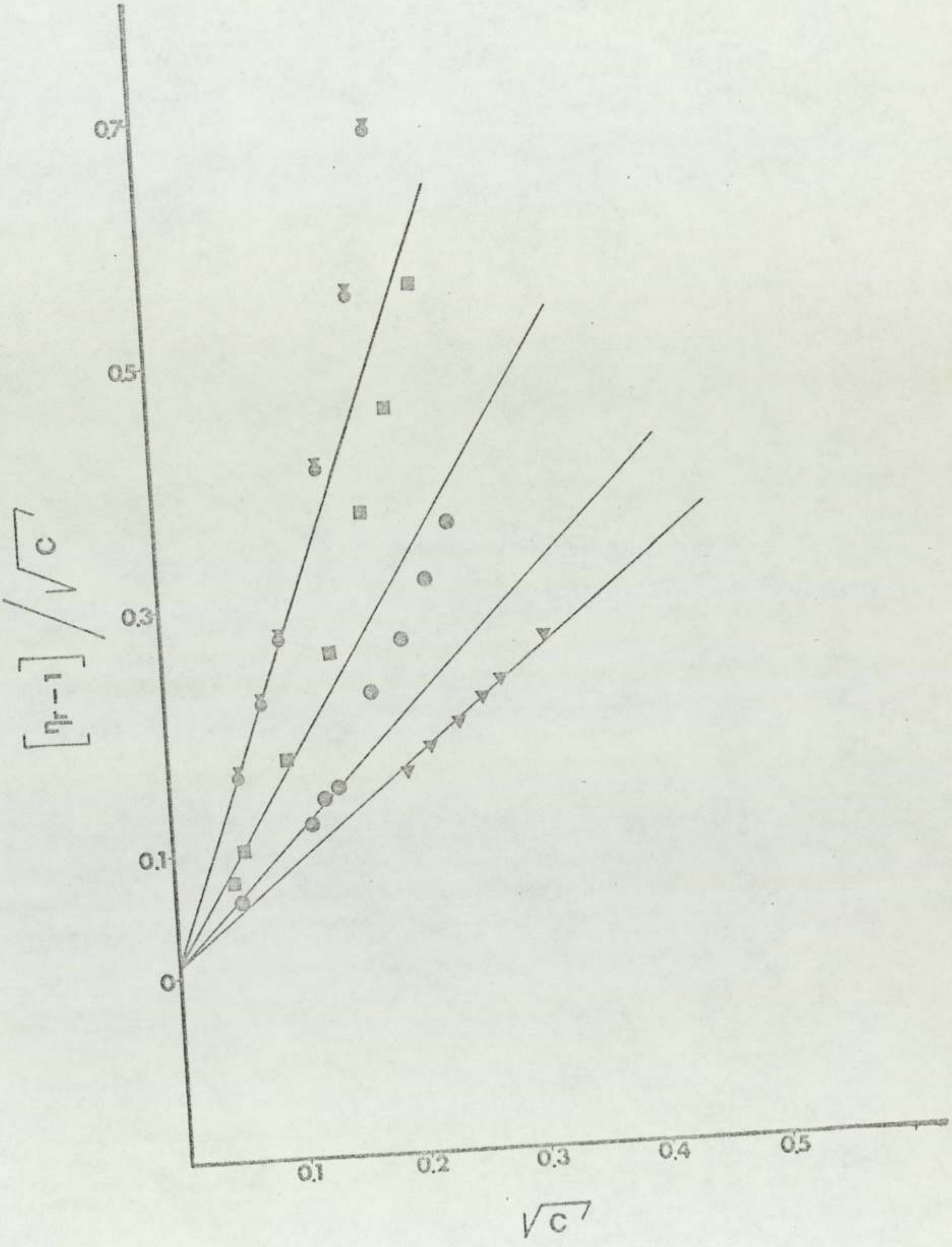


Fig.III.I Plots of $[\eta_r - 1]/\sqrt{C}$ versus $\sqrt{C}$ for the alkyl-ammonium bromides in water at 25° C; ▲ C_{10}, ● C_{12} ■ C_{14}, and ⧗ C_{16}

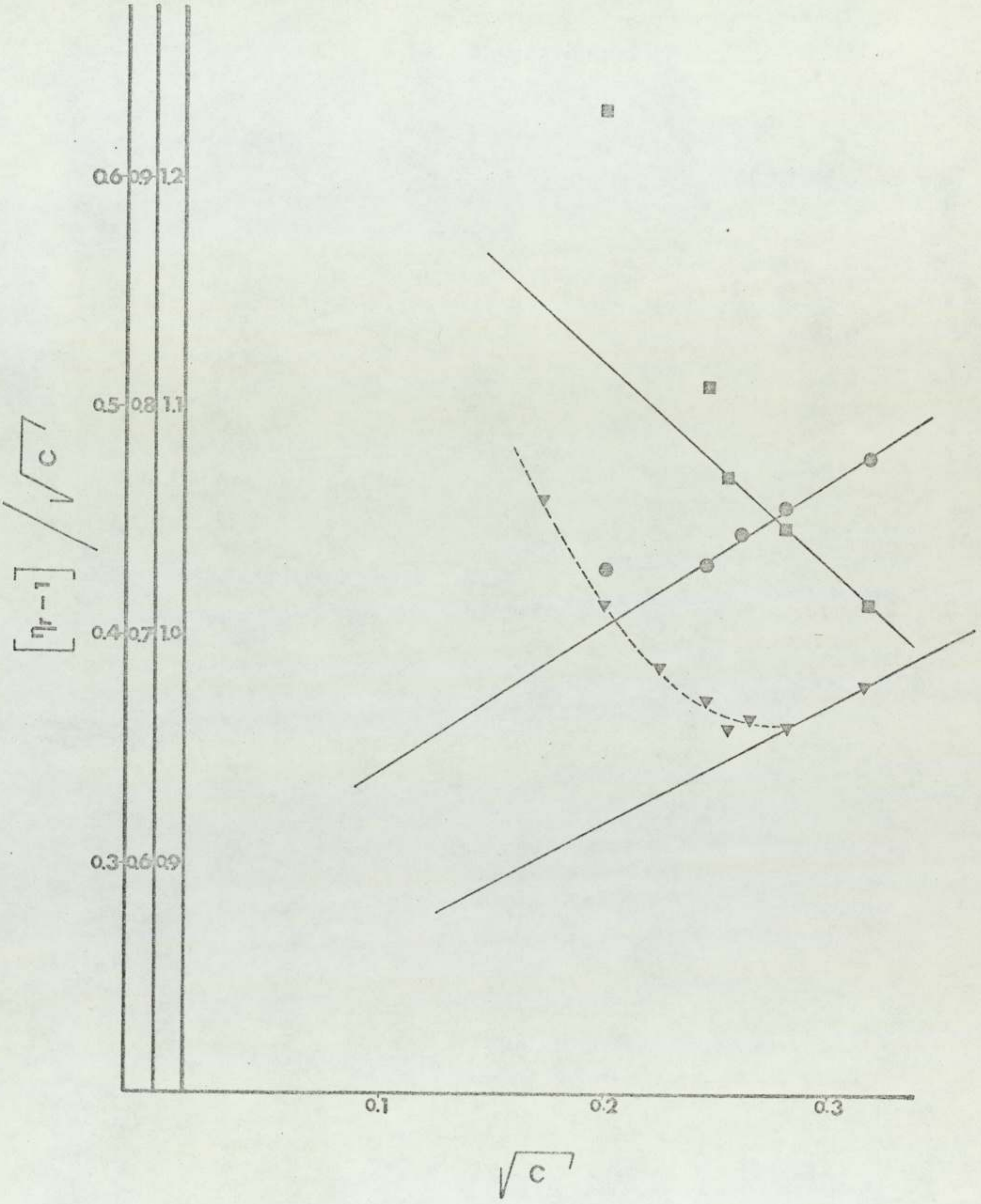


Fig.III.2 Plot of $[\eta - 1]/\sqrt{C}$ versus $\sqrt{C}$ for the [illegible] decyl trimethyl ammonium bromide containing various concentration of the methanol in water at 25° C; Me-OH: ● 0.4 M, ▲ 1 M, and ■ 2 M

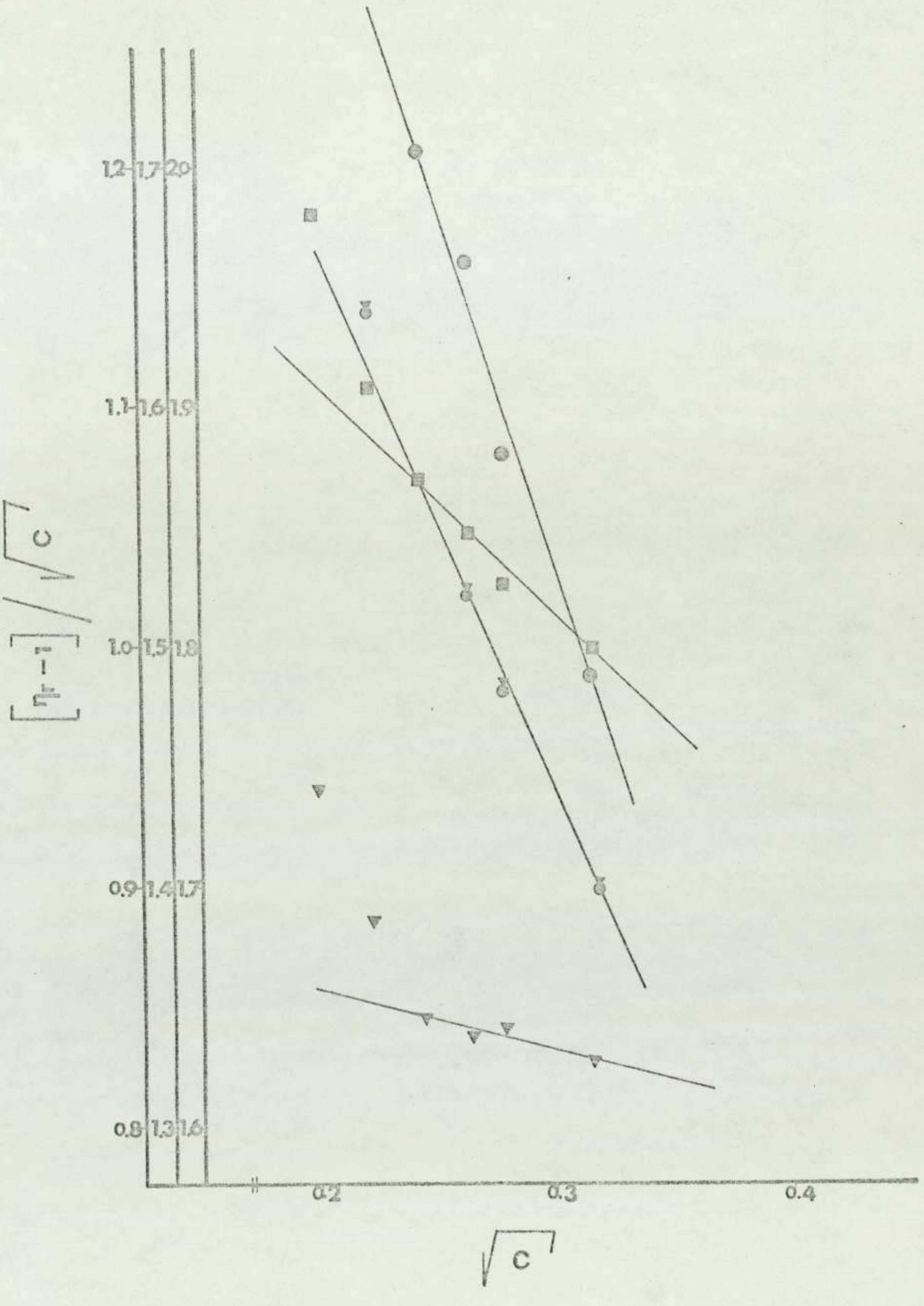


Fig.III.3 Plot of $[\eta - 1]/\sqrt{C}$ versus $\sqrt{C}$ for the decyl trimethyl ammonium bromide containing various concentration of the aliphatic alcohols in water at 25° C; Et-OH: ● 1 M, ■ 2 M; Pr-OH: ▲0.5 M, ▽ 1 M

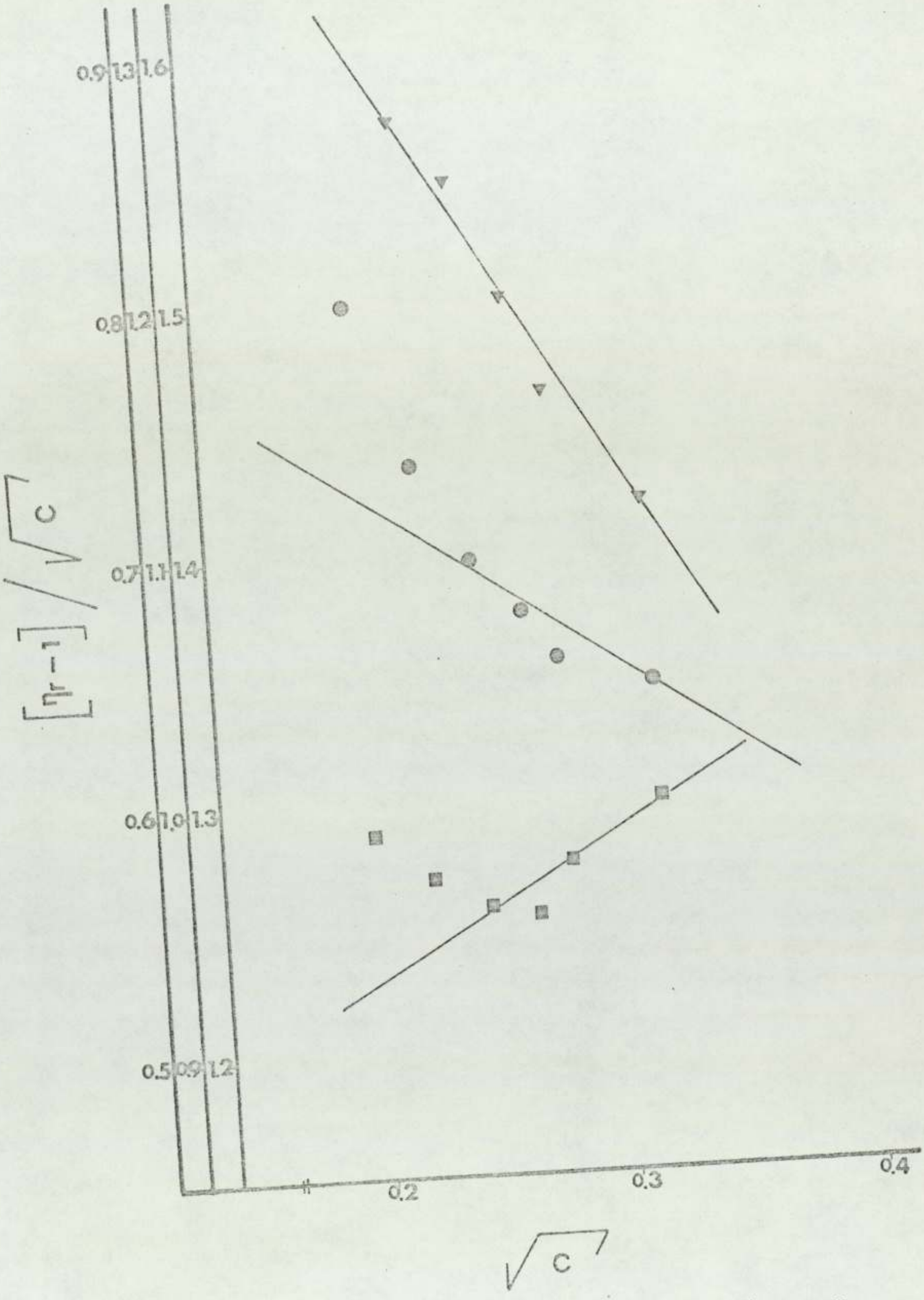


Fig. III.4 Plot of $[\eta - 1] / \sqrt{C}$ versus $\sqrt{C}$ for the decyltrimethyl ammonium bromide containing various concentration of the butanol in water at 25° C; Bt-OH: ■ 0.2 M, ● 0.5M, and ▲ 0.8 M

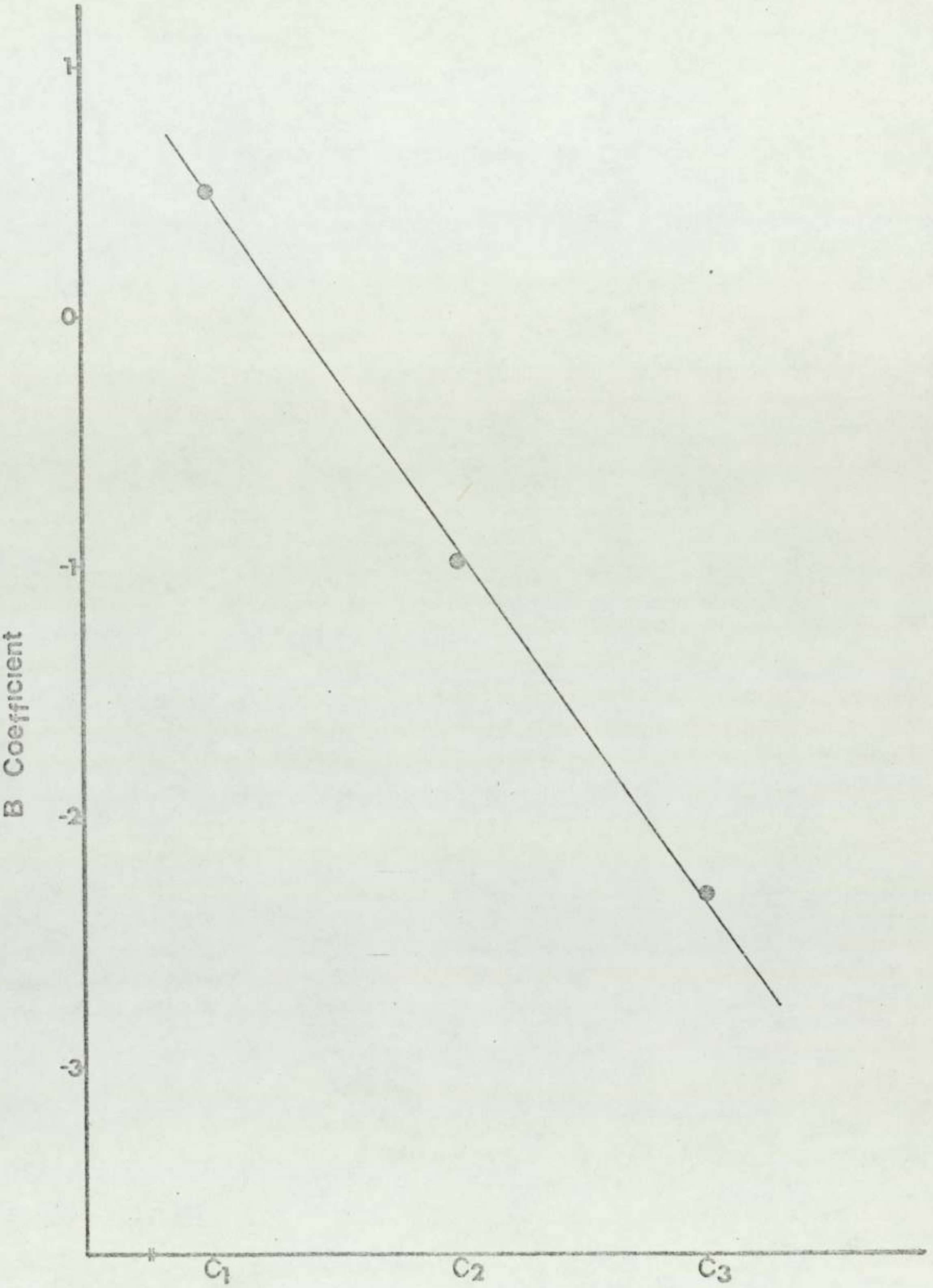


Fig.III.5 Dependence of B coefficient of C_{10} containing I M aliphatic alcohols in water on the hydrocarbon chain length of the alcohol

CHAPTER IV - Partial Molal Volume properties of Alkyl ammonium Bromides.

IV.Ia - The partial molar volumes of solutions.

Certain characteristics common to all partial molal quantities can be considered, in order to obtain any extensive property of a given solution. It is assumed for the present that the temperature and pressure are constant(88,141).

Consider Y as an extensive property of a given solution such as volume, heat capacity, or internal energy which is a function of temperature, pressure and the amounts of the several constituents(88). So Y depends only on $n_1, n_2 \ldots$ However we can define the partial molal values by the equations,

$$\overline{Y}_1 = \left(\frac{\partial Y}{\partial n_1}\right)_{p,T,n_1,n_3 \ldots} \qquad \overline{Y}_2 = \left(\frac{\partial Y}{\partial n_2}\right)_{p,T,n,n_3 \ldots} \qquad \text{IV-1}$$

which takes the form for general partial differentiation,

$$dY = \left(\frac{\partial Y}{\partial n_1}\right)_{p,T,n_2,n_3 \ldots} dn_1 + \left(\frac{\partial Y}{\partial n_2}\right)_{p,T,n_1,n_3} dn_2 + \ldots \qquad \text{IV-2}$$

or $dY = \overline{Y}_1 dn_1 + \overline{Y}_2 dn_2 + \ldots$ IV-3

It is apparent that $\overline{Y}_1$ and $\overline{Y}_2$ depend on the total amount of each constituent, and the composition. In view of this expression, we can integrate equation (IV-3) in terms of keeping $n_1, n_2 \ldots$ in constant proportions and we obtain

$$\begin{aligned} dY &= (\overline{Y}_1 x_1 + \overline{Y}_2 x_2 + \ldots)dn \\ Y &= (\overline{Y} x_1 + \overline{Y}_2 x_2 + \ldots)n \qquad \text{IV-4} \\ Y &= n_1 \overline{Y}_1 + \overline{Y}_2 n_2 + \ldots \end{aligned}$$

Since this equation is entirely general, it can be differentiated with respect to any change of composition, then the equation takes the form

$$dY = n\, d\overline{Y}_1 + \overline{Y}_1 dn_1 + n_2 d\overline{Y}_2 + \overline{Y}_2 dn_2 \qquad \text{IV-5}$$

and substitution of equation (IV-3) into equation (IV-5) gives

$$n_1 d\overline{Y}_1 + n_2 d\overline{Y}_2 + \dots = 0 \qquad \text{IV-6}$$

These equations (IV-4 and IV-6) can be called the partial molal equations(88). If we consider the number of moles of one constituent say n_1, as the main variable in terms of the constancy of p and T, then we can rewrite equation (IV-6) with respect to n_1 and n_2

$$n_1 \left(\frac{\partial \overline{Y}_1}{\partial n_1}\right)_{p,T} + n_2 \left(\frac{\partial \overline{Y}_2}{\partial n_1}\right)_{p,T} + \dots = 0 \qquad \text{IV-7}$$

when n_1 moles of component 1 are mixed with n_2 moles of component 2, the total volume of the solution V is

$$V = n_1 \left(\frac{\partial V}{\partial n}\right)_{n_2,T,p} + n_2 \left(\frac{\partial V}{\partial n_2}\right)_{n,T,p} \qquad \text{IV-8}$$

where $\left(\frac{\partial V}{\partial n_1}\right)_{n_2,T,p} = \overline{V}_1$ and $\left(\frac{\partial V}{\partial n_2}\right)_{n,T,p} = \overline{V}_2$ are the partial molal volumes of components 1 and 2 respectively.(88) The total volume of the solution is an extensive property of the system. The differential molar volumes or partial molar volumes are usually dependent on concentration.

IV.Ib - The Volumetric Properties of Solutions.

Partial molal volume properties of the dilute solutions of mixed solutes are fruitful sources of information on solute-solvent interactions. Friedman-Scheraga(211) showed that the negative excess limiting partial molal volume, for a series of aliphatic alcohols increases with temperature and molecular size. They attempted to correlate their results, in terms of the Nemethy-Scheraga(7) theory considering that the polar and nonpolar sides of the molecule produce additive volume effects.

Franks-Smith(212) introduced a large negative value of $\overline{V}_1^{op}$ for butanols, and that has been attributed to solvent-structure stabilization. On the other hand, Nakanishi(213) showed that the negative value of $\overline{V}_1^{op}$ depends not only on the molar volume of the solute, but also on the polar and nonpolar groups in the solute molecule.

A further approach has been demonstrated by Franks et al.(214) in view of the effect of polar and nonpolar groups on the volume properties of the system. They conclude that the molar volume of the pure solute cannot give reliable indication of solute size, since similar size of cyclic ethers have different molar volumes. The plots of $\overline{V}_2(x_2)$ of many mixed solutes indicate that long-range interaction between the solute molecules does not exist(80). It is reasonable to assume that it is transmitted specifically by the solvent.

The minimum point of the $\overline{V}_2(x_2)$ curves, can be considered as a point at which reinforcement of solvent sheaths are replaced by the interference between solvent sheaths, as the solvent is no longer sufficient to support the structuring ability of the solute molecule.

It is difficult to interpret volume effects at higher concentrations, due to solute-solute, solute-solvent and solvent-solvent interactions. It has been shown(213) that the slope of partial molal volume-mol fraction curve, depends on the ratio of polar and nonpolar groups in the solute molecule.

As the proportion of polar groups increases, the negative slope of the curve decreases. In the case of hydrophilic solutes, the slope of the curve $\partial\bar{V}_2/\partial x_2$ is near to zero(80).

As a result of this fact Franks suggested(80) that the effect of solute on water structure at long range decreases, as the apolar nature of the solute decreases.

As the nonpolar group of alcohol molecule increases, $\partial\bar{V}_2/\partial x_2$ becomes more negative, and the minimum on the curve moves to a lower x_2. This is due to the structure promoting effect of the alcohol molecule at low concentration. Wada-Umeda(215) examined the volumetric behaviour of the alcohols, certain amines, and cyclic ethers, and showed that the temperature of maximum density of water for lower alcohols, ketones and ethers is positive. This observation indicates that these solutes increase the structure of water molecules.

However, a structure making solute at low concentrate exhibits a negative $\partial\bar{V}_2/\partial T$, whereas a structure breaking solute shows a positive $\partial\bar{V}_2/\partial T$. Usually all solutes behave as structure breakers at sufficiently high concentrations.

IV.Ic - The nature of partial molal volume of micelles of alkylammonium bromides.

In order to study volumetrically the solute solvent interactions in aqueous solutions of alkylammonium bromides, it is necessary to derive partial molal volumes from the measurements carried out at finite concentrations. The apparent molal volume of the solute ϕ(211,216), can be related to the densities by the equation

$$\phi = \frac{M}{p_1} - \frac{1000(p_1 - p_1 H_2O)}{m p_1 \; p_1 H_2O} \qquad \text{IV-9}$$

The partial molal volume $\bar{V}_1$ can be related to ϕ by an equation

$$\bar{V}_1 = \phi + m \left[\frac{\partial \phi}{\partial m} \right]_{T,p,n_0} \qquad \text{IV-10}$$

If ϕ is plotted against m, and extrapolation of the obtained curve to zero concentration, the intercept gives $\bar{V}_0$ at infinite concentration. The measurement of densities of the solutions has been described in Chapter IIand the same density data (TablesII.I.1, II.I.1.A, II.I.3,A,B,C,D) has been employed for the determination of partial molal volumes of the alkylammonium bromides in aqueous solutions.

The partial molal volumes at different concentrations, have been derived by using equations (IV- 9 and IV-10). In order to obtain the partial molal volume of micellar species, the $\bar{V}$ value has been plotted against concentration ($C-C_0$), and the extrapolation of the curve to C = 0 gives the intercept, which is the $\bar{V}_1$ value of the micelle (Fig.IV.2).

The observed $\bar{V}_1$ value of the micelles for C_{10}, and C_{12} is 265, and 285 ml/mole respectively (Table IV.I.1). The $\bar{V}_1$ value for C_{10} is very close to the value (262 ml/mole), given by Corkill et al.(217) for the respective alkylammonium salt.

However the $\bar{V}_1$ values for higher chain lengths are lower than given by Corkill et al(217) (295 ml/mole for C_{12}). On the other hand, the partial molal volume below C_0, has been derived by using equation (IV- 9) amd plotting ϕ value against concentration C. The extrapolation of the obtained curve to C = 0, gives the partial molal volume $\bar{V}_0$ below the C_0 (Fig.IV.1).

These results follow a similar pattern, the $\bar{V}_0$ value for C_{10} and C_{12} (258.2 and 278.05 ml/mole respectively) are also different from the respective values (255 and 287 ml/mole) given by Corkill et al.(217). (Table IV.I.1). As can be seen in Fig.IV.3 the partial molal volume of alkylammonium bromides in aqueous solution, in both cases increases as the chain length increases. The observed volume change in $\overline{V}_1$ per $-CH_2-$ group is 17 ml/mole ($\overline{V}^o_{1A}$), which agrees well with the values given (17.4 ml/mole) by Corkill et al$^{(217)}$ for alkylammonium bromides, and Huggins$^{(218)}$ (16.7 ml/mole per $-CH_2-$) for n-alkanes at chain lengths C_8-C_{14}.

On the other hand, the volume change per $-CH_2-$ group below C_0 is 15.45 ml/mole ($\overline{V}^o_{1B}$), which is slightly different from Corkhill's$^{(217)}$ value (16.1 ml/mole). Gurney$^{(69)}$ introduced the idea that the partial molal volumes of electrolytes, could be examined in terms of unsolvated ionic radius. In his approach, it is assumed that the hydration sheath around the ion is compressed by electrostatic forces.

However the volume change which occurs in hydrocarbon water systems has been examined by Nemethy-Scheraga$^{(5)}$ in terms of hydrophobic interactions. In view of this treatment, they consider that the pertubation of water molecules by the apolar group of an alkyl chain, causes a volume change.

It is apparent that the partial molar volume of a solution species, does not depend on the environment. It describes solvent-solute interactions. Micelle formation is accompanied by an increase in $\overline{V}_1$, which is due to the elimination of hydrocarbon water contact. The formation of micelles involves the transfer of hydrocarbon from an aqueous to a non-polar region with an increase in volume$^{(219)}$. The observed volume change $\Delta\overline{V}_1$ at the C_0 for C_{10}, and C_{12} is 6.8 ml/mole and 7.1 ml/mole respectively, (Table VI.I.1). These results are very close to the values given by Corkhill et al$^{(217)}$(6.9 and 8.5 ml/mole).

The alkyl chain length of surfactants studied possess a high hydrocarbon water interfacial energy$^{(220)}$, and this tends to reduce surface area. When complete reduction in interfacial energy is reached, the chain is more free to expand. As a result of this process, the partial molal volume $\overline{V}_1$ increases(221).

The volumetric change which occurs during the micellization process, has been discussed by Benjamin (219), in terms of hydrophobic interactions. According to his view, one can consider the volume change as due to the decreased hydration of the head group, and possible electrostriction effects. If this view is correct, one could consider the head group, and adjacent alkyl chain to remain unchanged during the micellization process.

The micelles have a high charge density due to their head groups, which are adsorbed in the Stern layer(155). The changing environment of the head group, can be expected to give a small contribution to $\overline{V}_1$. The $\Delta\overline{V}_1$ has been plotted as a function of chain length(217,219) (Fig.IV.3), and as can be seen, with extrapolation of the curve, the $\Delta\overline{V}_1$ becomes zero for the lower chain lengths of 3-5 carbon atoms. This has been attributed to the negative contribution of head group to $\overline{V}_1$, or to the methylene group adjacent to the hydrophilic head, which is assumed to give a small contribution to $\overline{V}_1$.

It is generally accepted that, due to strong electrical interactions, counterions are adsorbed in the Stern layer, and are bound to the surfaces of the micelles(155). The electrostatic interactions between the charges on the micelles, covalent bonding, charge transfer and desolvation influence $\overline{V}_1$ and $\Delta\overline{V}_1$ (222).

Since the micelle includes the firmly attached counter-ions, and firmly attached water molecules(155,222), the observed partial molal volumes of the micelles are not true $\overline{V}_1$'s of the micelles(222). They include partial molal volumes of bound counter-ions and water molecules, which locate in the Stern layer around the kinetic micelle.

The effect of aliphatic alcohols on the volumetric properties of the micelles has also been examined. The addition of alcohol to the aqueous solutions of surfactant, changes the solvent-solute interactions in the system. The three component system consisting of an aqueous phase containing surfactant ions, additive molecules (alcohol), and a mixed micellar phase, composed of alkylamonium bromide ions (and counter ions + water + alcohol) has been treated as a two-phase system(223). The $\bar{V}_2$ value of alkylammonium bromide at different concentration of 25°C, has been calculated from density data using the following equation(223),

$$\bar{V}_2 = \frac{M}{p_1} - \frac{(n_oM_o + nM + n_2M_2}{p_1^2} \left[\frac{\partial p_1}{\partial n_1}\right]_{p,T,n_o,n_2} \qquad \text{IV-11}$$

The same density data has been employed, (Tables II.I.3.A,B,C,D) in order to obtain the slope of the density-concentration curve, for dodecylammonium bromide containing alcohol molecule. (FigsIV.4,IV.4.A).

The $\bar{V}^o_2$ value of micelles has been derived by plotting $\bar{V}_2$ value against $C-C_o$, and extrapolation of the curve to $C = 0$, gives the $\bar{V}^o_2$ value of the mixed micelles. (FigsI V.5.,IV.5.A).

When one mole CH_3OH is added to the aqueous solution of alkylammonium bromide, the $\bar{V}^o_2$ value of micelles increases (285.90 ml/mole for C_{12}). The increase in $\bar{V}^o_2$, increases as the concentration of alcohol increases (Fig.IV.6). In the higher concentration studied (4M.CH_3OH), the $\bar{V}^o_2$ value is 310.04 ml/mole (Table IV.I.2).

On the other hand, the observation indicates that the $\bar{V}^o_2$ value increases as the chain length of alcohol increases. As can be seen in Fig.IV.6, the $\bar{V}^o_2$ value of the micelles of dodecyltrimethyammonium bromide containing 1M, and 2M alcohol from methanol to n-propanol increases. However on addition to 2M alcohol to the system, $\bar{V}^o_2$ decreases when n-propanol is added.

The addition of alcohol molecules to aqueous solution of alkylammonium bromides, as has been discussed in Chapter II.h2 causes a change in structure of solvent molecules, and solute solvent interactions. The aliphatic alcohols are usually structure promoting at low concentration(91,210). This behaviour tends to the opposite direction as the concentration increases.

Consequently this nature of the alcohol molecule affects the kinetic properties of micelles(155). The transfer of an alcohol molecule from a nonpolar environment to the aqueous region causes an increase in $\overline{V}_1$ of the alcohol molecule(211). Since the alcohol molecule behaves as a hydrocarbon due to its apolar group(91,97,210), it is reasonable to assume that the $\overline{V}^o_2$ value increases, when the molecule is transferred from an aqueous region to a nonpolar environment. The alcohols penetrate into the kinetic micelle through the Gouy-Chapman-Stern electrical double layer around the micelle(155). The volume change due to the penetration process of alcohol molecules into the micelle, contributes to the increase in $\overline{V}^o_2$ of the micelle, as can be seen in Table IV.I.2 the difference between $\overline{V}_1$ and $\overline{V}^o_2$ is 0.8 ml/mole for 1M CH_3OH. In the higher concentration (4M CH_3OH) $\Delta\overline{V}_2$ is 24.94 ml/mole.

It is apparent that the partial molal volume of the micelle increases with addition of alcohol molecules the increment $\Delta\overline{V}_2$ indicates that $\overline{V}^o_2$ is altered by the increase in alcohol concentration. (Fig.IV.7. Tables IV.I.2, A,B).

Since the decrease in volume for an homologous series of paraffins and alcohols during fusion is of the order of 10-20%, the higher $\overline{V}$ values below C_0 and at the C_0 compared to crystal molar volumes $\overline{V}_c$ of alkylammonium bromides are consistent with a partial melting process(224) (Table IV.I.1).

IV.Id - Conclusions.

The volumetric properties of alkylammonium bromides below the C.M.C and at the critical micelle concentration show that the partial molal volume of the surfactant, in both cases increases with increasing the chain length. This observation indicates that the micelle formation is accompanied by an increase in volume. This is due to the transfer of alkylammonium ions, from an aqueous environment to a nonpolar region, in terms of the limitation of interfacial energy with water molecules. The decrease in contact with polar molecules causes an increase in the partial molal volume of the micelles.

The addition of aliphatic alcohol to the system also contributes volume change, and an increase in the partial molal volume of the micelles. The influence of the alcohols to the volumetric properties of the micelles, can be discussed in terms of hydrophobic interactions, since they behave as hydrocarbons in aqueous solutions. The volume change in partial molal volume of the micelles, per $-CH_2-$ group of alcohol increases with increasing chain length. They penetrate into the interior of micelle and contribute positive partial molal volume increase, as the concentration of alcohol increases. The increment decreases at higher concentration due to the saturation effect on the interior of the kinetic micelle.

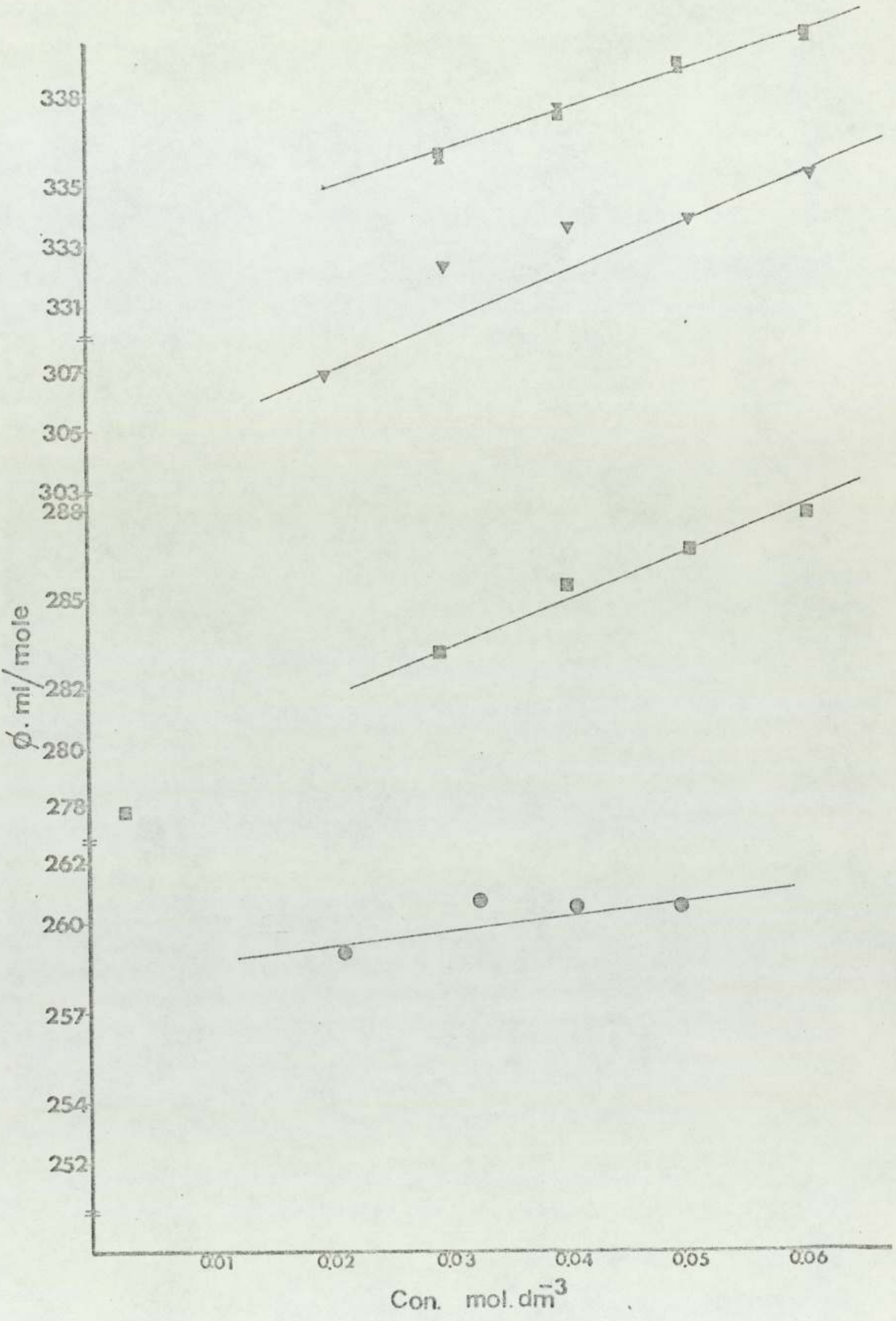


Fig.IV.I The concentration dependence of the apparent molal volumes of alkyltrimethyl ammonium bromides at 25° C; ● C_{10}, ■ C_{12}, ▼ C_{14}, and ▨ C_{16}

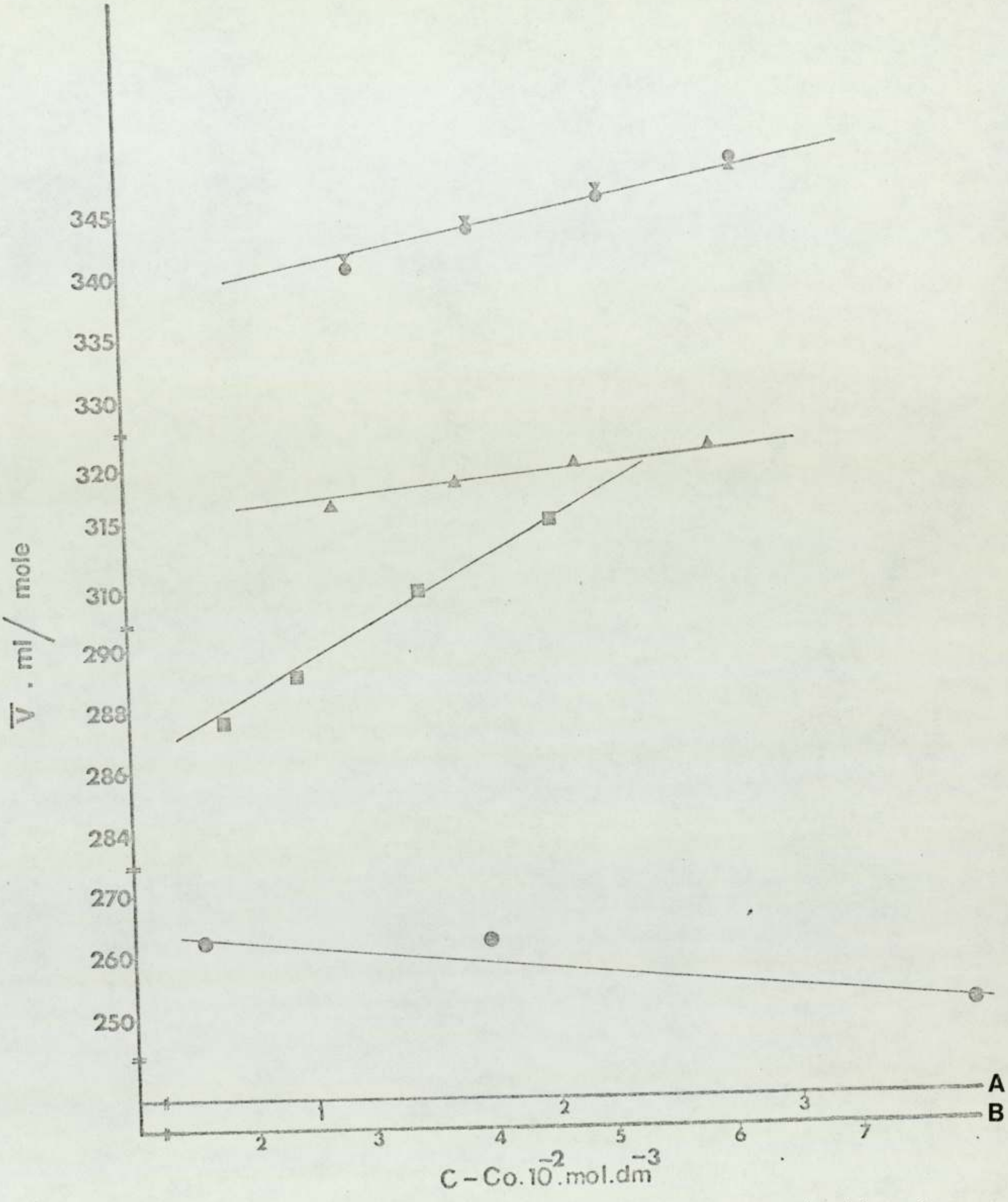


Fig.IV.2 The partial molal volumes versus concentration for the alkyltrimethyl ammonium bromides above the C.M.C at 25° C; ● C_{10}, ■ C_{12}, ▲ C_{14}, and ⧗ C_{16}; **A** C_{10}, **B** C_{12}, C_{14}, C_{16}

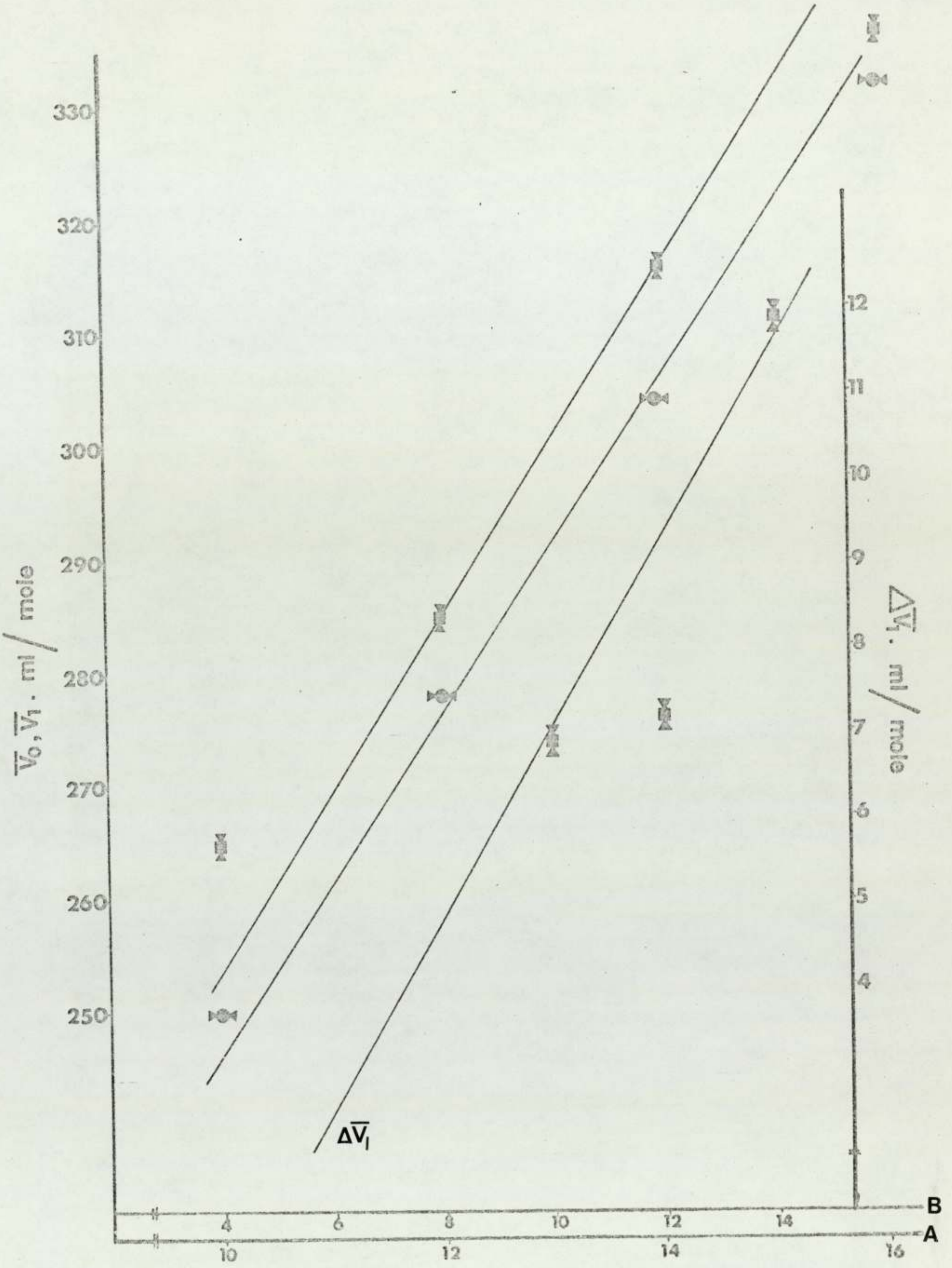


Fig.IV.3 **A,** The partial molal volumes of the alkyltrimethyl ammonium bromides below the Co, and above the Co, as a function of the hydrocarbon chain length; ● below the Co, ⧗ above the Co. **B,** The behaviour of $\Delta\overline{V}_1$ as a function of the main alkyl chain length.

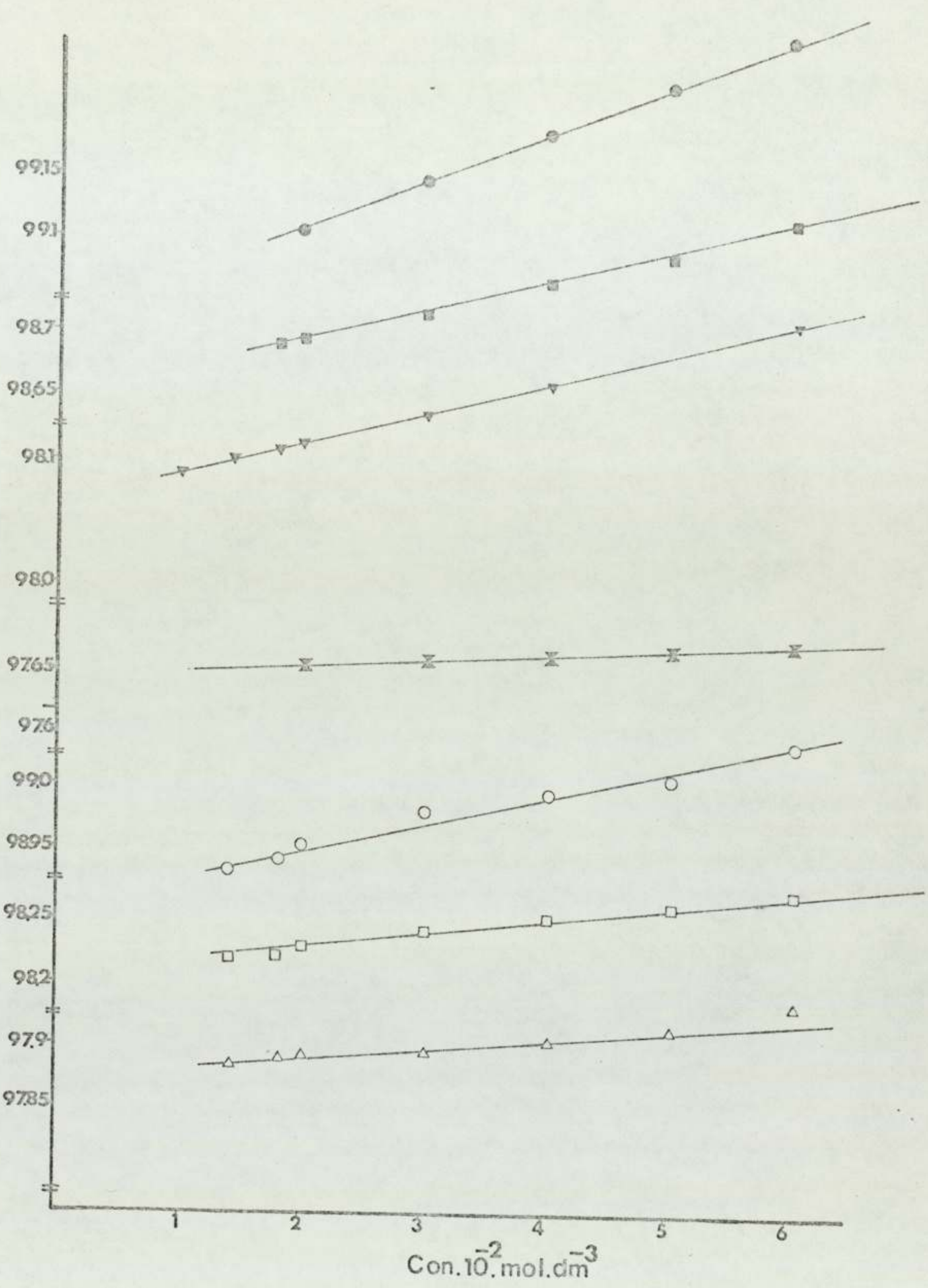


Fig. IV.4 Variation of the density of dodecyltrimethyl ammonium bromide with the various concentration of methanol and ethanol in water at 25° C; Me-OH: ● 1M, ■ 2M, ▲ 3M, and ⧗ 4M; Et-OH: ○ 1M, □ 2M, and △ 2.5M

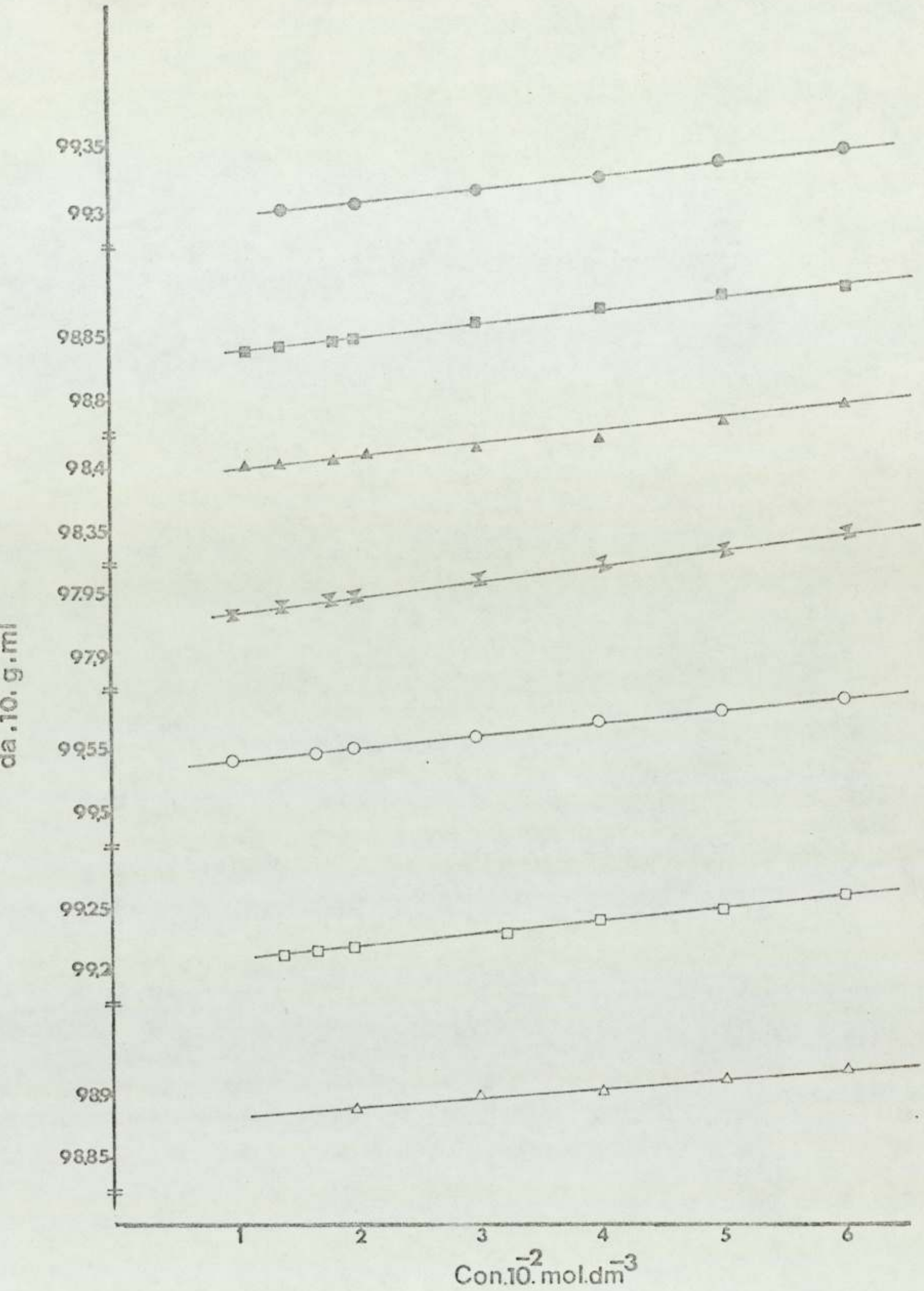


Fig.IV.4.A Variation of the density of dodecyltrimethyl ammonium bromide with the various concentration of propanol and butanol in water at 25° C; Pr–OH: ● 0.5 M, ■ 1 M, ▲ 1.5 M and ⧗ 2 M: Bt–OH: ○ 0.2 M, □ 0.5 M, and △ 0.8 M

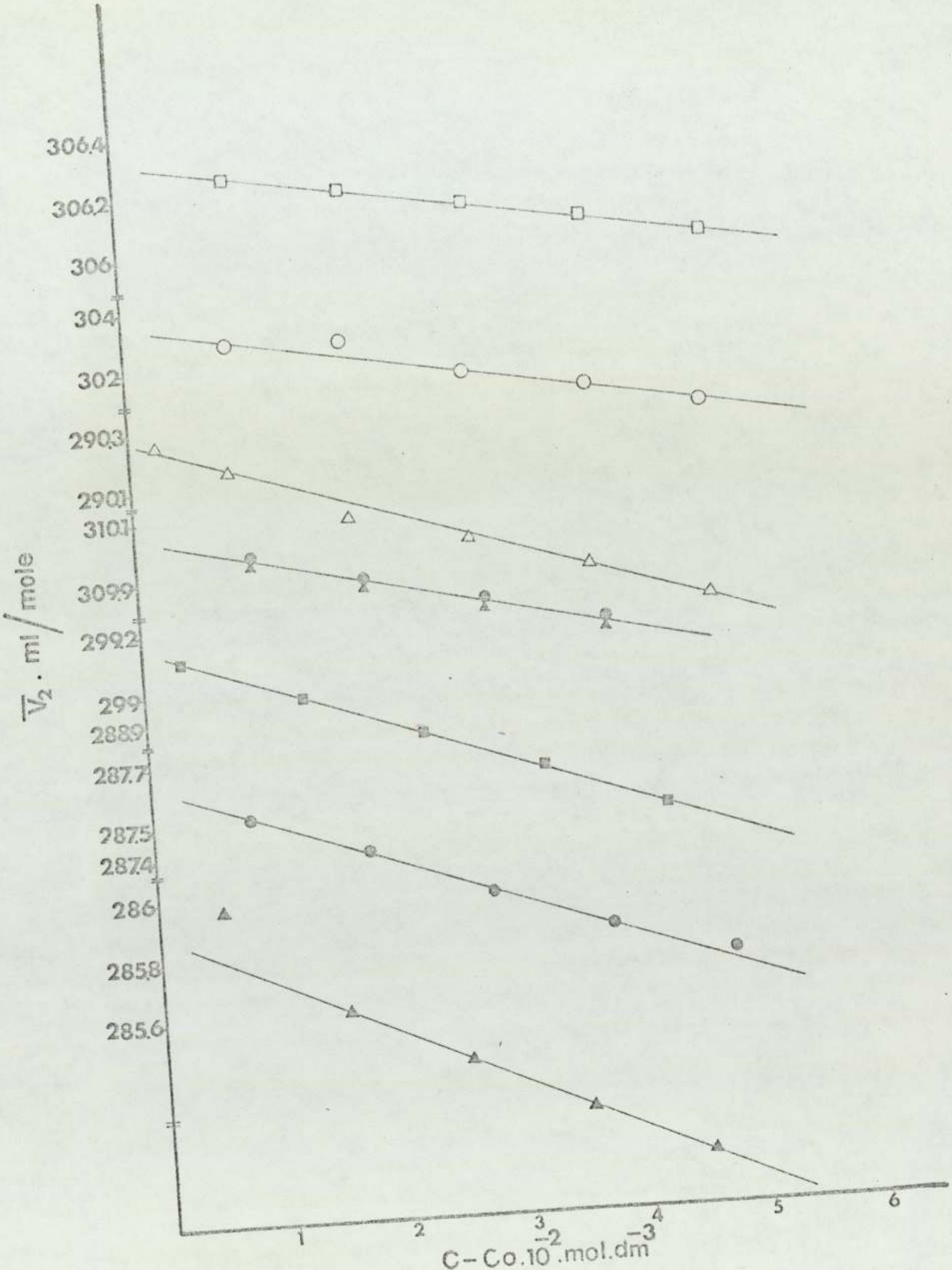


Fig. IV.5 The various methanol and ethanol concentration dependence of the partial molal volume of the dodecyltrimethyl ammonium bromide in water at 25° C; Me-OH: ▲ 1M, ● 2M, ■ 3M, and ●▲ 4M ; Et-OH: △ 1M, ○ 2M, and □ 2.5M

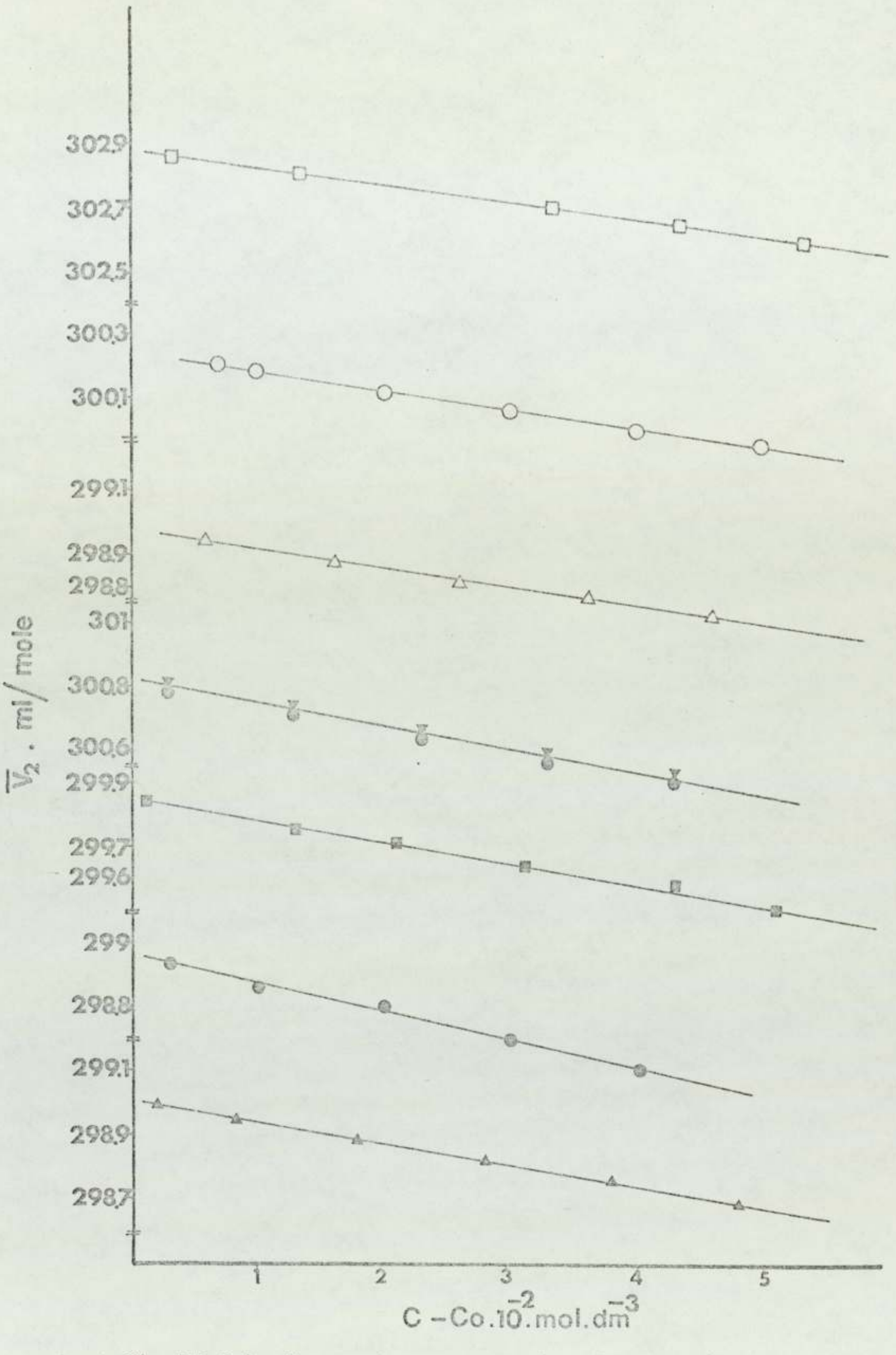


Fig. IV.5.A The various propanol and butanol concentration dependence of the partial molal volume of the dodecyltrimethyl ammonium bromide in water at 25° C; Pr–OH: ▲ 0.5 M, ● 1 M, ▣ 1.5 M, and ◈ 2 M; Bt–OH: △ 0.2 M, ○ 0.5 M, and □ 0.8 M

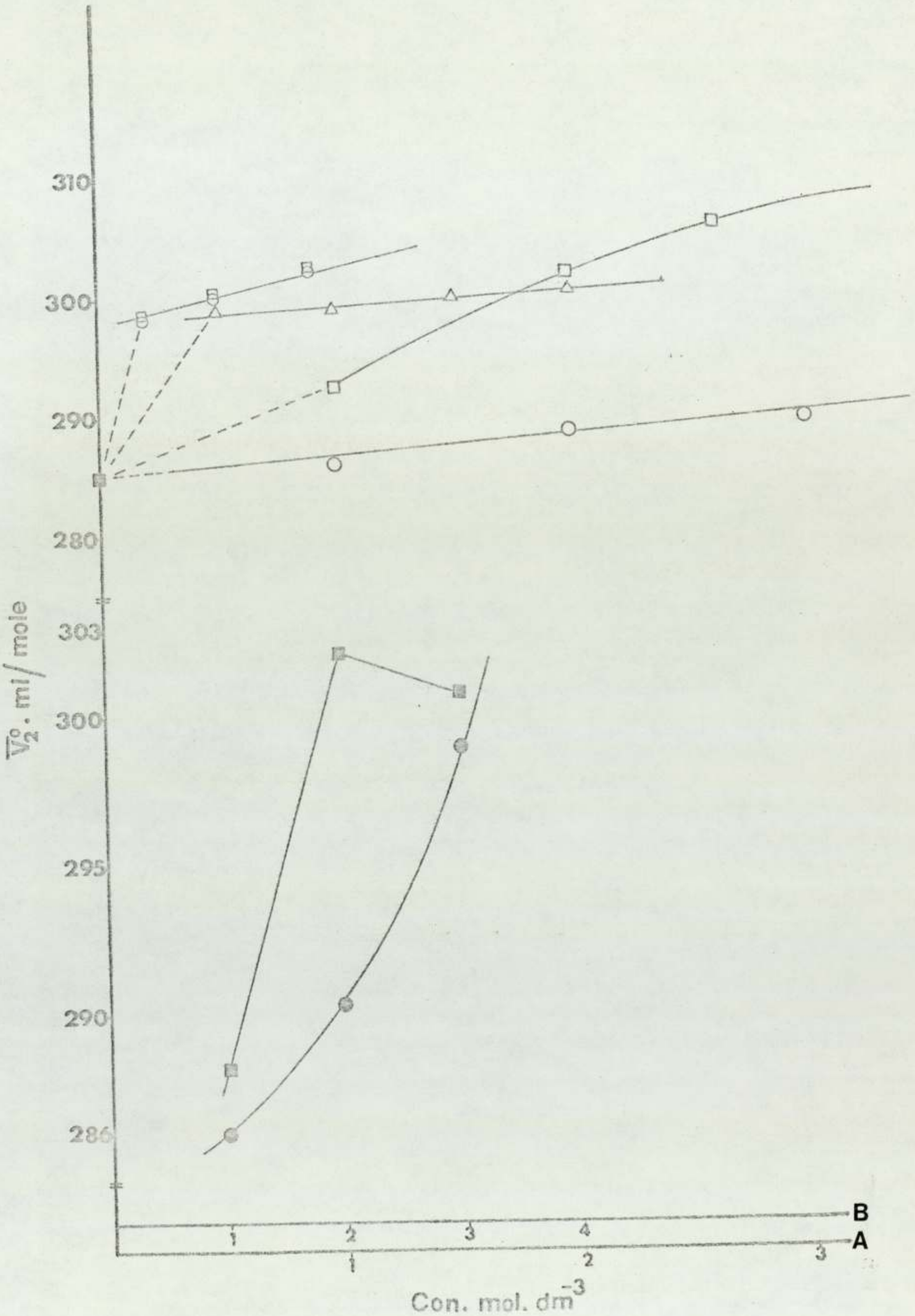


Fig.IV.6 **A,** The partial molal volume of dodecyltrimethyl ammonium bromide at Co, as a function of the concentration of aliphatic alcohols; **B,** Dependence of the partial molal volume of Co on the alkyl chain length at 25° C; **A** ○ Me-OH, □ Et-O, △ Pr-OH ⊟ Bt-OH; **B** ● **IM** , ■ **2M** Alcohols

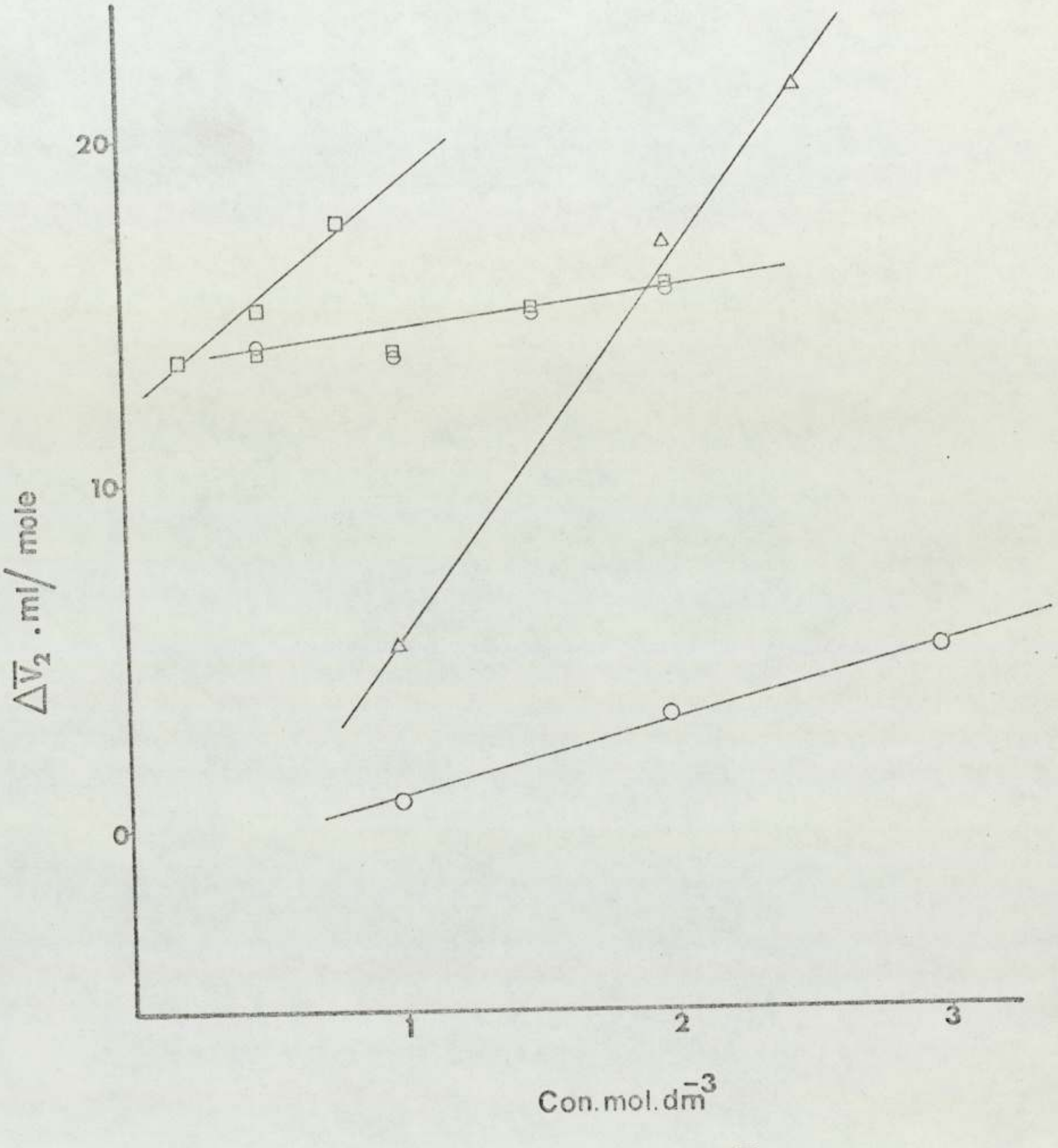


Fig.IV.7 The relationship between the $\Delta\overline{V}_2$ and the concentration and alkyl chain length of the aliphatic alcohols; □ Bt-OH, ⊜ Pr-OH, △ Et-OH, and ○ Me-OH

PARTIAL MOLAL VOLUMES OF ALKYL AMMONIUM BROMIDES

IN WATER AT 25° C

TABLE IV.I.1

C mol.dm^{-3}	$\varnothing$ ml.mole^{-1}	$\overline{V}$ ml.mole^{-1}	$\overline{V}_o$ ml.mole^{-1}	$\overline{V}_1$ ml.mole^{-1}	$\overline{V}^o_{1A}$ ml.	$\overline{V}^o_{1B}$ mole^{-1}	$\Delta\overline{V}_1$ ml.mole^{-1}	$\overline{V}_c$ ml.mole^{-1}	D_s g.ml^{-1}
C_{10}									
0.1	250.06	255.25	258.20	265.00	17	15.45	6.8	254.9	1.0996
0.08	258.32	262.5							
0.07	259.68	262.64							
0.06	265.27								
0.05	260.75								
0.04	260.71								
0.03	260.96								
0.02	258.90								
0.01	249.50								
C_{12}									
0.06	287.66	294.10	278.05	285.10			7.1	276.40	1.1155
0.05	286.59	291.90							
0.04	285.43	289.60							
0.03	283.03	286.22							
0.02	277.25	279.36							
C_{14}									
0.06	313.64	323.45	303.6	315.50			11.9	297.34	1.1314
0.05	312.3	320.44							
0.04	311.8	318.29							
0.03	310.66	315.52							
0.02	306.83								
C_{16}									
0.06	340.14	348.06	332.20	337			4.8	319.06	1.1423
0.05	339.24	345.82							
0.04	338.19	343.43							
0.03	336.09	340.20							

PARTIAL MOLAL VOLUME OF DODECYL TRIMETHLY AMMONIUM BROMIDE IN WATER CONTAINING ALIPHATIC ALCOHOLS AT 25°C

TABLE IV.I.2

C mol.dm^{-3}	$\overline{V}_2$ ml.mole^{-1}	$\overline{V}_2^o$ ml.mole^{-1}	S_{pv} ml.g^{-1}	$\Delta\overline{V}_2$ ml.mole^{-1}	$\left[\frac{\partial d}{\partial n}\right]_{p,t,n_o,n}$
1 M, Me-OH					
0.06	285.10	285.90	0.92704	0.8	0.0240
0.05	285.27				
0.04	285.45				
0.03	285.62				
0.02	285.98				
0.018	285.90				
2M					
0.06	287.02	288.33	0.93492	3.23	0.0227
0.05	287.13				
0.04	287.25				
0.03	287.40				
0.02	287.53				
0.016	287.58				
3M					
0.06	288.57	289.15	0.93758	4.05	0.0220
0.05	288.73				
0.04	288.85				
0.03	288.99				
0.02	289.12				
4M					
0.06	309.71	310.04	1.00531	24.94	0.005
0.05	309.78				
0.04	309.86				
0.03	309.97				
1M, Et-OH					
0.06	289.69	290.26	0.94118	5.16	0.02
0.05	289.83				
0.04	289.91				
0.03	289.99				
0.02	290.16				
0.014	290.26				
2M					
0.06	301.83	302.15	0.97973	17.05	0.0104
0.05	301.90				
0.04	301.95				
0.03	302.03				
0.02	302.09				
0.01	302.15				

TABLE IV.I.2.A

C $mol.dm^{-3}$	$\overline{V}_2$ $ml.mole^{-1}$	$\overline{V}_2^o$ $ml.mole^{-1}$	S_{pv} $ml.g^{-1}$	$\Delta\overline{V}_2$ $ml.mole^{-1}$	$\left[\frac{\partial d}{\partial n}\right]_{p,t,n_o,n}$
		2.5M			
0.06	306.01	306.32	0.99325	21.22	0.0075
0.05	306.09				
0.04	306.15				
0.03	306.22				
0.02	306.26				
0.01	306.32				
		0.5M, Pr-OH			
0.06	298.69	299.0	0.96984	14	0.011
0.05	298.76				
0.04	298.82				
0.03	298.90				
0.02	298.99				
0.014	299.03				
		1M			
0.06	298.89	298.96	0.96939	13.86	0.012
0.05	298.60				
0.04	298.70				
0.03	298.80				
0.02	298.86				
0.01	298.94				
		1.5M			
0.06	299.5	299.86	0.97231	14.76	0.012
0.05	299.58				
0.04	299.65				
0.03	299.71				
0.02	299.75				
0.01	299.85				
		2M			
0.06	300.2	300.83	0.97545	15.73	0.012
0.05	300.52				
0.04	300.58				
0.03	300.66				
0.02	300.74				
0.01	300.82				

TABLE IV.I.2.B

C $mol.dm^{-3}$	$\overline{V}_2$ $ml.mole^{-1}$	$\overline{V}_2^o$ $ml.mole^{-1}$	S_{pv} $ml.g^{-1}$	$\Delta\overline{V}_2$ $ml.mole^{-1}$	$\left[\frac{\partial d}{\partial n}\right]_{p,t,n_o,n_2}$
0.2M, Bt-OH					
0.06	298.70	298.98	0.96945	13.88	0.0105
0.05	298.76				
0.04	298.81				
0.03	298.88				
0.02	298.94				
0.017	298.96				
0.5M					
0.06	299.95	300.20	0.97341	15.10	0.01
0.05	300.02				
0.04	300.08				
0.03	300.13				
0.02	300.19				
0.017	300.21				
0.8M					
0.06	302.59	302.88	0.98210	17.78	0.0083
0.05	302.64				
0.04	302.71				
0.02	302.82				
0.01	302.87				

CHAPTER V - The Effects of Various Additives on Conductance properties of micelles.

V.Ia - Conductivity of Electrolytes.

The conductivity or resistivity arises as a proportionality coefficient, in the relation between the resistance of a conductor R, its length L and cross-section S.

$$\frac{1}{R} = \frac{1}{Q}\ \frac{S}{L} = x\ \frac{S}{L} \qquad \text{V-1}$$

The electrolytic conductivity can be defined in terms of mobility, concentration, and charge of the ions(225).

$$x = \sum \frac{z_i^2\ F^2}{RT}\ D_i c_i = \sum \left| z_i \right|\ F c_i\ U_i \qquad \text{V-2}$$

The above expression, if the solution contains a single strong electrolyte, can be related to a unit equivalent concentration by the equation

$$x = \frac{F c_{eq}}{1000}\ (U_+ + U_-) \qquad \text{V-3}$$

which is known as the equivalent conductivity. Its limiting value at infinite dilution is a constant for a given solution. The equation (V-2) can be rewritten in terms of the dissociation constant.

$$x = \alpha\ \frac{F c_{eq}}{1000} \left[U_+ + U_- \right] \qquad \text{V-4}$$

then the equivalent conductivity takes the form,

$$\Lambda = \frac{1000\ x}{c_{eq}} = F \left[U_+ + U_- \right] \qquad \text{V-5}$$

It is usually represented in Ω^{-1} cm^2 per 1 gram equivalent. In the case of strong and weak electrolytes, the equivalent conductivity at limiting dilution can be defined as(188,225)

$$\Lambda^{\circ} = F \left| U_{+}^{\circ} + U_{-}^{\circ} \right| = \lambda_{+}^{\circ} + \lambda_{-}^{\circ} \qquad \text{V-6}$$

This equation is valid in both cases, when the dissociation constant is equal to 1. According to Kohlrausch's law, which describes independent ionic conductivities for a solution containing S_1 ionic species equation (V-6) takes the form

$$\Lambda = \sum_{i=1}^{S_1} \lambda_i^{\circ} \qquad \text{V-7}$$

On the other hand, at low concentrations, the specific conductivity is directly proportional to concentration, while at higher concentration, it increases due to decrease in equivalent conductivity.

Kohlrausch has shown that the equivalent conductivity can be defined by the relation

$$\Lambda = \Lambda^{\circ} - k\sqrt{c} \qquad \text{V-8}$$

However, the limiting law which has been discussed by Onsager for a uni-univalent electrolyte, can be given by the equation(68,188,225)

$$\Lambda = \Lambda^{\circ} - \left[B_1\Lambda^{\circ} + B_2\right]\sqrt{\alpha c} \qquad \text{V-9}$$

It is apparent that equation (V-9) is identical with the Kohlrausch relation, where B_1 and B_2 are experimental constants. In view of expression (V-9), the Onsager limiting law for weak electrolytes has the form(68,188,225)

$$\Lambda = \alpha\left[\Lambda^{\circ} - \left[B_1\Lambda^{\circ} + B_2\right]\sqrt{\alpha c}\right] \qquad \text{V-10}$$

The ratio of equivalent conductivities to the limiting equivalent conductivity at a given and infinite dilution, is known as the conductivity coefficient[225]

$$\frac{\Lambda}{\Lambda^{\circ}} = q \qquad \text{V-11}$$

This ratio can be rewritten at a given concentration, in terms of the dissociation constant of the electrolyte

$$\frac{\Lambda}{\Lambda^{\circ}} = \alpha q \qquad \text{V-12}$$

V.Ib - The effect of aromatic alcohols and ureas on the micellar properties of alkylammonium bromides.

V.Ib1 - Aromatic alcohols.

The solute-solute and solvent solute interactions in aqueous solutions of alkylammonium bromides, has been examined by the addition of various concentration of aromatic solutes to the systems, at 25°C by using the conductivity method.

The observation indicates that the addition of 0.01M phenol to the aqueous system of C_{14} and C_{16} changes the micellar properties of surfactants.

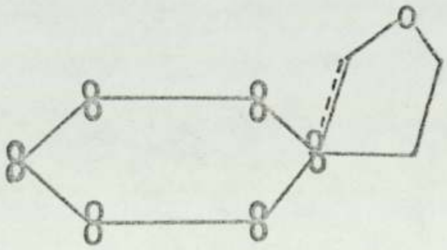
On the addition of 0.01M phenol to the system, as can be seen in Figs.V.1,V.2 and tables V.I.1,V.I.2, the C_0 has increased from 3.7×10^{-3} mol.dm^{-3} and 1.08 mol dm^{-3} to 3.82×10^{-3} mol.dm^{-3} and 1.26×10^{-3} mol dm^{-3} for C_{14} and C_{16} respectively.When 0.02M phenol is added to the system, C_0 has decreased. A similar effect has been observed in both systems. The decrement in C_0 is 0.35×10^{-3} mol dm^{-3} and 0.14 mol dm^{-3} respectively. It is apparent that the effect of phenol on the micelles is not the same magnitude.

In view of this observation, one can postulate that the interactions between phenol and water clusters around the nonpolar group of the surfactant ion, and water molecules[5] decrease the structural order of water molecules more effectively in the aqueous solution of C_{14} than that of C_{16}. The penetration of phenol molecules into the core of the micelle, increases the molecular weight of the micelle, which has been observed in non-ionic surfactant aqueous system. The degree of penetration depends on the interaction between the benzene ring, and hydrocarbon chain length of the surfactant, and adsorption of the aromatic solutes in the Stern layer.

It is known(158) that hydrophobic interactions between nonpolar groups in the micellar core, restricts the penetration of additive molecules. On the other hand -OH groups in the Stern layer(155) associate with the hydrated polar head groups counter-ions and water molecules in terms of hydrophobic interactions.

The decreasing static dielectric constant of the Stern layer influences the dipole orientation of the counter ions, and adsorbed phenol and water molecules. The decrement in charge density of micelles due to the described effects, consequently the magnitude of the decrement in free energy, presumably influences more effectively the micelles of C_{14} than those of C_{16}.

It has been shown(226) that intramolecular hydrogen bonding occurs between the hydroxyl group, and π electrons at the 1-position of the aromatic nucleus of phenethyl alcohol in 0.5% CCl_4 such as



Brown-Brady have postulated(227) that an electrophilic atom, or group could be attracted by the electron cloud at the position of greatest density. According to their view the electron density is low near the centre of the ring, and high above and below the ring of carbon atoms.

Due to this fact, an electrophilic atom can move readily around the electron cloud. The formation of a covalent bond with one of carbon atom of the ring, in terms of π-electron clouds association, increases the electrophilic nature of the reagent.

The penetration and distortion of the π-electron cloud, involves the formation of complexes in the polar medium. Dewar has interpreted(228) that the positive ion is able to move over the π-electron layer of the aromatic molecule, due to electron deficiency of the cation, which interacts with the π electrons of aromatic molecule. Because of this fact the displacement of a hydrogen by cationic attack, induces the positive ion to take its place.

On the addition of an aromatic alcohol to the aqueous system, the dielectric constant of the solution decreases. Since the phenolic hydroxyl group is a stronger proton donor(229) than the aliphatic alcohol -OH group, it associates with water molecules in terms of hydrogen bonding. However, because of having a nonpolar side and polar group, aromatic alcohols influence the surfactant ion in the solution, an association occurs by means of interaction of the aromatic molecule with the nonpolar side of the monomer, due to the cationic effect of Br^- ion, on the π-electron cloud of aromatic molecule(228). The structural order of water molecules, and water networks is effectively influenced by this association(5). The structure breaking effect of the aromatic molecule increases with increasing concentration.

On the other hand, aromatic alcohols associate also with nonpolar groups of the surfactant ions, with their hydrophobic sides, in terms of hydrophobic hydration(5) (hydrophobic interaction). Owing to the hydrophilic nature of the medium, intramolecular hydrogen bonding can occur between the aromatic nucleus, and hydroxyl group(226).

This might have additional effect on the solution properties.

The effect of cations on the π-electron cloud of the aromatic molecule, and ionized Br^- ion in water, cause the hydrophobic association between aromatic alcohol, hydrocarbon chain, surfactant and water molecules.

It is apparent that these effects in the bulk solution, influence the micellar properties of the systems. As can be seen in Fig.V.3, and Table V.I.1. On the addition of 0.01M phenol to the aqueous solution of C_{14} and C_{16} the specific conductance (0.284 m ohm^{-1} cm^{-1}) of the micellar solution is lower than that of the aqueous solution (0.293m ohm^{-1} cm^{-1}). The conductance and specific conductance of the micelles, have been calculated from the recorded graph, in terms of the equations (V-15, V-16).

The equivalent conductance of micelles has been calculated by using equation (V-5). The decrement in specific conductance, decreases with the increasing concentration of phenol. However, the addition of 0.01M benzyl alcohol increases the specific conductance of the micelles (0.305 m ohm^{-1} cm^{-1}) (similar in C_{16}), then decreases with increasing concentration (Figs.V.3,V.4).

The increase in specific conductance on the addition of 0.01M aromatic alcohol to the system is presumably due to the structure maker character of the aromatic alcohol at low concentration. As is seen in Figs.V.3,V.4, the higher specific conductance is observed, when the hydrophobic surface of molecule is increased (0.305m ohm^{-1} cm^{-1} and 0.298m ohm^{-1} cm^{-1} for 0.01M benzyl alcohol and 0.01M DL-1-phenylethanol in aqueous solution of C_{14} respectively). The C_0 increases slightly as the $-CH_2$ group increases, on the alcohol side of the molecule (Fig.V.5). The reason could be attributed to the cooperative effect of the $-CH_2-OH$ group in low concentration in the aqueous solution. In the presence of phenyl-propanol, the specific conductance of the micelles falls between phenol and DL-1-phenylethanol. In both systems

(Fig.V.3,V.4). The equivalent conductance of the micelles except in the case of phenyl-propanol, decreases up to the certain concentration (0.04M in phenol = 73.00 cm^2 ohm^{-1} mol^{-1}, 0.06M in benzyl alcohol = 71.00 cm^2 ohm^{-1} mol^{-1}), then it increases as the concentration increases (Fig.V.6 and Table V.I.1).

In the case of phenyl-propanol the equivalent conductance increases nonlinearly with the increase in concentration (Fig.V.6). However the situation with C_{16} is different. The equivalent conductance increases with increasing alcohol concentration, but not with so great a magnitude (Fig.V.7 and Table V.I.2).

The factors involved for the conductance properties of the mixed micelles is not clearly known. But one can postulate that ion-pair formation(230), due to the low dielectric constant of solution, the anion size, the degree of dissociation of surfactant ion, the formation of ionic complex, and the effect of aromatic alcohol on the charge density of the micelles(158), influences the conductance properties of the micelles.

An increase in C_0 has been also observed up to a certain concentration, followed by a decrease in C_0 with the increasing concentration, for the addition of benzyl alcohol, and the other higher aromatic alcohols to the aqueous system of alkylammonium bromides.

The maximum increase in C_0 for all aromatic alcohols used, occurs on the addition of 0.01M alcohol to the system. On the addition of 0.02M alcohol to the aqueous solution of C_{14}, the observed C_0 except phenol, is higher than C_0 of the aqueous solution of C_{14} (3.79 × 10^{-3} mol.cm^{-3} for benzyl alcohol, and 3.79 × 10^{-3} mol.dm^{-3} for phenyl-propanol, Table V.I.1).

In the case of C_{16}, except with phenol, the C_0 increases also with the addition of 0.02M aromatic alcohol to the system (1.18 × 10^{-3} mol.dm^{-3} for benzyl alcohol, and 1.31 × 10^{-3} mol.dm^{-3}

for phenyl-ethanol Table V.I.2).

However in both cationic systems, the addition of 0.04M of any alcohol to the system, decreases the C_0 (Figs.V.1,V.2 and Tables V.I.1, V.I.2) the decrement in C_0 increases with the increasing concentration.

In the light of this observation, it is reasonable to assume the following reasons as possible driving force, to change the micellar properties of alkylammonium bromides, on the addition of aromatic alcohols.

It has been shown(231) that there is no high-field shift, in the low concentration of surfactant solution containing 2% phenol. When the concentration of surfactant is increased above 8%,a high chemical shift has been observed. The reason has been attributed to the effect of phenol, on the structure of water molecules.

The higher concentration of surfactant removes the phenol molecules from the aqueous region to the micellar pseudophase(231). It has been observed that the solubility of alcohols gradually decreases after 0.04M concentration. The decrement in solubility increases, as the chain length of the alcohol group increases. On the addition of 0.01M phenol to the aqueous system of C_{14} and C_{16}, the alcohol molecule penetrates into the micellar core, through the Gouy-Chapman-Stern electrical double layer around the micelle(155).

This process is favoured due to the described features of the structure of aromatic alcohols. They behave as structure makers at low concentration. Presumably the adsorption of aromatic solutes at low concentration, does not effectively influence the properties of the Stern layer. When the concentration of solute is increased, the effect of solute molecule on water structure, and water networks around the nonpolar groups increases. This increment breaks the cooperative effect of water molecules(5).

On the other hand, the aromatic molecule is forced by the penetration of the cation into the π-electron cloud, to associate with an anion(227,228). This association takes place with the formation of an ionic complex(227,228). The migration of an unassociated alcohol molecule, from the bulk solution to the electrical double layer of micelle, influences the micellar structure through the Stern layer, micellar core interface(155).

The molecular size of the aromatic solute also plays a unique role in solubilization. The solubility of alcohol in the interior of the micelle is influenced by hydrophobic interactions between aromatic ring and hydrophobic chain length in the micellar core. A saturation effect could occur due to the restriction in the penetration process.

However the increase in concentration, increases the effect aromatic solutes have on the electrokinetic properties of the Stern layer. Due to adsorption of aromatic alcohol in the Stern layer, the repulsion energy of the hydrated polar head group increases. The aromatic solute interacts with adsorbed counter ions, and bound water molecules, in terms of hydrophobic interactions and electrostatic forces. The charge transfer process causes reduction in the charge density of the micelle(158), consequently there is a decrease in C_o. It is believed also that the thermodynamic properties of the micelle would substantiate the above observations.

It is known that the increase in hydrophobicity affects the surface charge of the micelle, and decreases the charge density(158). The decrement in C_o with the increasing concentration of aromatic alcohol, can be attributed to the described effects of the aromatic molecules.

V.Iba - Ureas and Urethane.

The mechanism of the action of urea on water structure and solute solvent interactions has not been discussed quantitatively. The addition of urea to an aqueous solution, causes a change in the structural order of water molecules and disordered water(232). It has been postulated that the urea can only mix into disordered water regions, by reason of geometry. This process lowers the chemical potential of unbonded water, and melts some clusters in order to re-establish the equilibrium.

Mukerjee et al.(233) have shown that urea at higher concentrations reduces the cooperative structure of water, due to its ability to increase the dielectric constant, and surface tension of water. According to this view urea affects the entropy change on micellization, rather than enthalpy change, in terms of the weakening of hydrophobic bonding.

It has also been shown(155) that the urea decreases the repulsive forces between the ionic heads of the monomers, and at 25°C breaks up the micelles. The hydrophobic character of urea is increased with increasing the hydrophobic surface, which is believed to increase the order of demicellizing effectiveness and weakening of the hydrophobic bonding(179).

Jones has also postulated(234) that the breaking down of water structure, due to the presence of urea in aqueous solution, decreases the cooperative nature of the water molecules.

A similar conclusion such as urea reduces the strength of hydrophobic bonding, has been introduced by Schick(235). Wetlaufer et al.(236) have suggested that the increase in solubility of hydrocarbons in aqueous solution, is due to the solvation of the hydrocarbon by water in the presence of urea, or to the urea molecules which have also taken an active part in the solvation of hydrocarbon. On the other hand, it has been shown(237) that hydrogen bonding contributes denaturating effectiveness of DNA, due to hydrogen bonding between urea and DNA. Herskovits et al.(238) have concluded that hydrophobic forces contribute to the stability of native DNA(238).

The other approach is(239) that the aqueous urea solutions are able to accommodate nonpolar amino acid sides better than water can. The stabilization of the polar side chain of asparagine, has been interpreted in terms of urea contribution to the stability.

A different view indicates that the effect of alkyl urea, or the increased hydrophobic surface of substituted urea, decreases the denaturating effectiveness(240). However it is known that urea in aqueous solution, takes an active part in the cooperative effect of water molecules (formation of clusters). Due to this fact, urea contributes to the open structure by the same mechanism as water molecule(241).

Since the hydrogen bonded solutes or groups such as (OH. NH_2 or NH_3) do not effectively alter water structure, it has been discussed that urea participates in cluster formation in aqueous solution. Further evidence shows that urea is extremely soluble in water, and its partial molal heat capacity at infinite dilution is very close to that of the solid. It is known that urea in the solid state is hydrogen bonded(241). In the light of this observation, it has been concluded that urea must be hydrogen bonded in water.

Beside these facts, the B coefficient of urea in water also supports the idea that urea behaves as a structure maker rather than breaker.

It has been observed that the addition of ureas to an aqueous solution of alkyl ammonium bromides, influenced the micellar properties. As can be seen in Fig.V.8, the C_o increases with increasing concentration of additive. On the addition of 1M urea to the aqueous solution of C_{14} C_o is increased up to $4.72 \cdot 10^{-3}$ mol.dm^{-3}.

When 0.5M urethane, ethylurea or dimethylurea is added to the system (C_{14}), the C_0 has markedly increased, compared with the urea (4.8×10^{-3} mol.dm^{-3}, 5.2×10^{-3} mol.dm^{-3} and 5.22×10^{-3} mol.dm^{-3} respectively. Table V.I.3.)

The effect of urethane on C_0 is more pronounced compared with urea and ethylurea. On the addition of 2M solute to the aqueous system of C_{14},C_0 is increased (7.86×10^{-3} mol.dm^{-3}, 5.38×10^{-3} mol.dm^{-3} and 7.6×10^{-3} mol.dm^{-3} for urethane, urea and ethylurea respectively), it would be assumed that the observed higher specific conductance, and marked increase in C_0 for urethane, arises from the mutual orientation of the urethane in aqueous solution. It has a more effective polar side than ureas, which associate strongly with water molecules by means of hydrophobic bonding. This polar group increases the structure forming character of the molecule, because of its tendency for hydrogen bonding(116).

Urethane differs only from ethylurea, by having one more "O" atom instead of 'N' atom. It is apparent that the structure promoting effect of the molecule arises from the replacement of the N atome by 'O', which gives a polar character to the group, or molecule. In view of this fact the higher specific conductance of C_0 can be attributed to the cooperative nature of the molecule. However the power of raising C_0 for dimethylurea is higher compared with the other ureas and urethane (Fig.V.8, Table V.I.3).

The addition of the same solutes to the aqueous solution of C_{16} showed results of a similar pattern (Fig.V.8, Table V.I.4). The increase in C_0 for the systems studied, could be interpreted in terms of the cooperative nature of the ureas and urethane in aqueous solution.

Urea has great ability to participate in hydrogen bonding with water molecules, in terms of having three potential bonding centres(233,241), and it also affects the polarity of water. Since it participates in cluster formation, it is expected that the hydrocarbon solutes would also dissolve in aqueous urea solutions.

On the other hand urea forms clathrates in the solid state. This association might take place in aqueous urea solution(241). The cooperative effect of urea increases the solubility of the hydrocarbons in water urea solution, and increases the dielectric constant of water(179,233). This evidence supports the idea that urea actively participates in the formation of mixed clusters in aqueous urea solutions(241).

The increase in C_0 with the addition of various ureas, could be attributed to those described effects. However the equivalent conductance of C_0 in both systems, decreases as the hydrophobic surface of the molecule increases (Fig.V.9). The C_0 increases also as the concentration of solute increases (Tabs.V.I.3, V.I.4). On the addition of 1M urea to the aqueous solution of C_{14}, the observed equivalent conductance of C_0 is high compared with the ureas and urethane (77.542 $cm^2\ ohm^{-1}\ mol^{-1}$, 73.333 $cm^2\ ohm^{-1}\ mol^{-1}$ and 59.0 $cm^2 ohm^{-1}\ mol^{-1}$ for urea, urethane and ethylurea respectively) (Table V.I.3).

As is seen in Fig.V.9, on the addition of any solute, at any concentration, the obtained equivalent conductance of C_{14} is lower than in aqueous solution. This confirms also that they behave as structure promoting in aqueous solution.

In the aqueous solution of C_{16}, the equivalent conductance of C_0 is higher, compared with C_0 in aqueous solution, when 0.5M urea is added (80.34 $cm^2\ ohm^{-1}\ mol^{-1}$ and 73.61 $cm^2\ ohm^{-1}\ mol^{-1}$ in urea and H_2O respectively. Fig.V.9). Similar behaviour has been observed on the addition of 0.5M ethylurea. The reason for the increase in equivalent conductance at C_o is not known.

The decrement in equivalent conductance at C_o indicates that the hydrophobic behaviour of the molecules increases with increasing hydrophobicity. The participation in mixed cluster formation increases the solubility of the hydrocarbon molecule. Hydrophobic association of ureas with water molecules, the effect of hydrocarbon chain length and the increment in dielectric constant induce the formation of suitable cavities to accommodate hydrocarbons or hydrophobic groups, which is easier than in pure water, due to the formation of large cavities.

This process might also cause an increase in specific conductance, due to the increase in cooperative character of the medium(241). In this work, it is assumed that ureas and urethane increase the structural order of water molecules, in terms of hydrophobic bonding, taking an active part in mixed cluster formation around nonpolar moeities(241). Herskovits(242) concluded that the hydrophobic influence of the solute on water molecules contributes to the viscosity increment of aqueous solutions. He found that the B coefficient of ureas increases with increasing hydrophobic surface (0.035, 0.155 and 0.265 for urea, ethylurea and 1.3 dimethylurea respectively). If water molecules hydrogen bonded to urea do not participate in hydrogen bonding with neighbouring molecules, this should reflect in the B coefficient of the solute, in terms of the Dole-Jones(192) relationship. It has been shown that structure breaker ions have negative B coefficients, because of their disturbing effect on water structure(69,194). In view of this fact one can say that ureas and urethane do not behave as structure breaker in aqueous solution.

V.Ic - Experimental Procedure

V.Ic₁ - Materials

V.Ic₁A- Aromatic alcohols

Benzyl alcohol, DL-1-phenylethanol were BDH L.R.material. 3-phenylpropyl alcohol was obtained from Pfaltz and Bauer Inc. as L.R. grade and phenol was Fisons A.R. material.

V.I.c₁B- Ureas and Urethane.

Urea (BDH A.R. grade), N-ethylurea (Koch-light pure grade), and dimethylurea (Sigma L.R. material) were recrystallized(179) several times from hot ethanol, and dried under vacuum. Potassium-chloride (BDH L.R.grade) was dried in a vacuum oven at approximately 80 to 100°C, before using for redetermination ofthe conductivity cell constant. Water used for preparation of dilute solutions was double distilled water ($\Delta w < 1 \times 10^{-6}$ ohm^{-1} cm^{-1}).

The preparative procedures for surface active agents used in this work have been described in Chapter II.

V.Ic₂ - Measurement and Instrumentation.

The conductivities of aqueous alkylammonium bromides solutions and containing aromatic alcohols and ureas were measured using a continuous infusion technique(243).

V.Ic₂A - Setting and Calibration.

The conductivity bridge (Wayne Kerr Universal Bridge B.642) was trimmed, and calibrated according to the instrument(244) manual. The chart recorder which was connected to the bridge was also checked, to obtain accurate chart speed and linearity, and that was adjusted to the bridge reading in order to get zero reading.

The zero conductivity reading was considered as the base line, and any increase in conductivity due to conductance of electrolyte in solution was recorded by corresponding pen movement.

The automatic motorized infusion apparatus (unita continuous infusion apparatus, B.Braun Melsungen) used consists of a calibrated glass barrel, and a steel plunger fitted with a rubber gasket. The accuracy of the volume infused from the syringe was checked by two methods(243) and was found to be 20 ml.

a) The volume infused into the calibrated volumetric flask of suitable volume at time (t), was in good agreement with the volume corresponding to the time given by manufacturer.

b) In the second method, the double distilled water, of a known volume, was titrated by the KCl solution of a known concentration, by using the calibrated conductivity bridge, chart recorded and checked conductivity cell. The increase in conductance, corresponding to the rate of KCl added, was recorded with the chart recorder of known speed. The obtained specific conductivity of KCl by this experiment, for a known concentration was compared with the corresponding values given in literature $K = 0.012856\ ohm^{-1}\ cm^{-1}$ and $0.0014087\ ohm^{-1}\ cm^{-1}$ at 25°C for 10^{-1} molar and 10^{-2} molar KCl respectively(68). The value of specific conductance of 0.1 M. KCl derived ($0.012875\ ohm^{-1}\ cm^{-1}$) is in good agreement with the above value.

The concentration of the solution can be obtained by the equation.

$$C_t = \frac{V_t}{V_i' + V_t} C_a \qquad \text{V-13}$$

The volume infused by the syringe at time (t) can be calculated from the following equation

$$V_t = \frac{\Delta D \times \Delta F}{C_{sp}} \qquad \text{V-14}$$

At any instant of the titration, the specific conductivity can be obtained from the following relationship.

$$\Lambda_{sp} = (\Lambda_i + \Lambda_t)pt \ k_{cell} \qquad V\text{-}15$$

where

$$pt = \frac{V_i' + V_t}{V_i} \qquad V\text{-}16$$

at time (t).

V.Ic2B - Determination of the Co of Alkylammonium bromides in water and mixed solutions.

In order to obtain a sharper end point where the conductivity slope changes, and minimize the dilution effect, the higher concentration of surfactant solution was employed, as the concentration of titrant. Before using the bridge the described procedure for calibration was applied to the bridge, then set to the conductivity of the doubled distilled water (Λw (1×10^{-6} ohm^{-1} cm^{-1}).

Following this procedure, the double distilled water of known volume (50 ml) was pipetted into a thermostated cleaned and dried beaker, then the dip-type conductivity cell (Philips) of known cell constant (which was redetermined by using standard KCl solutions (k_{cell} = 1.42), and the bridge was set for the determining of Co's of surfactants. A standard solution of 0.1 mol dm^{-3} of C_{14} was placed in 20 ml syringe, so that no air bubbles would be injected from the syringe into the titration beaker. The syringe was then mounted onto the unita infusion apparatus, with its tip submerged in the solution in the titration beaker. The rate of flow and the chart recorder was set to the position (Rate 8 = 66.1/60 ml/min.) and (50 secs/cm. = 0.833 min/cm) respectively. After the equilibrium of distilled water with temperature 25°C, setting the sensitivity of bridge to the position (2), the chart recorder was started at a speed mentioned above, then the motor was driven to infuse the aqueous solution of C_{14} into the titration beaker. The addition of the titrant was continued well above the Co, in order to obtain the slope of the conductivity at the below and above C_o.

Studies of the effect of aromatic alcohols and ureas on the C_o of alkylammonium bromides were carried out in a similar manner. The standard solutions of various additives in different concentration were titrated, instead of 50 ml double distilled water, with the surfactant solution containing the respective additive of known concentration. In the case of C_{16} the concentration of titrant used was 0.02M.

The C_o of alkylammonium bromides was determined from the recorded conductivity graph, by obtaining the point of critical conductivity change on the graph, and calculating the corresponding concentration C_o by using equations (V-13 and V-14). The obtained C_o values of alkylammonium bromides were 3.7×10^{-3} mol.dm^{-3}, and 1.08×10^{-3} mol.dm^{-3} for C_{14} and C_{16} respectively.

V.Id - Conclusions.

The effect of aromatic alcohols, ureas and urethane on micellar properties of alkylammonium bromides in aqueous solution, has been examined by a conductivity method. It has been observed that all aromatic alcohols, increase the C_0 of the systems examined, when 0.01M additive is added to the aqueous solution, then it decreases as the concentration increases. The reason for this has been discussed in terms of hydrophobic interactions, structure maker effects of the aromatic molecules at low concentration, and the influence of alcohols on the electrical double layer properties of micelles.

The addition of ureas and urethane has markedly changed the micellar properties of studied systems. The C_0 is increased as the concentration of urea or urethane increases,the mechanism of action of these solutes on micellar properties has also been examined by means of hydrophobic association of these molecules. The increase in specific conductance with the addition of additive, has been attributed to the cooperative effect of the solute on water structure. It is further assumed that ureas and urethane behave as structure promoters, and take active part in the formation of mixed icebergs in the aqueous solution in terms of hydrophobic interactions.

The conductance properties also support the idea that these solutes behave as structure promoters, in terms of active participation in hydrophobic interactions, and in formation of water networks around the nonpolar groups.

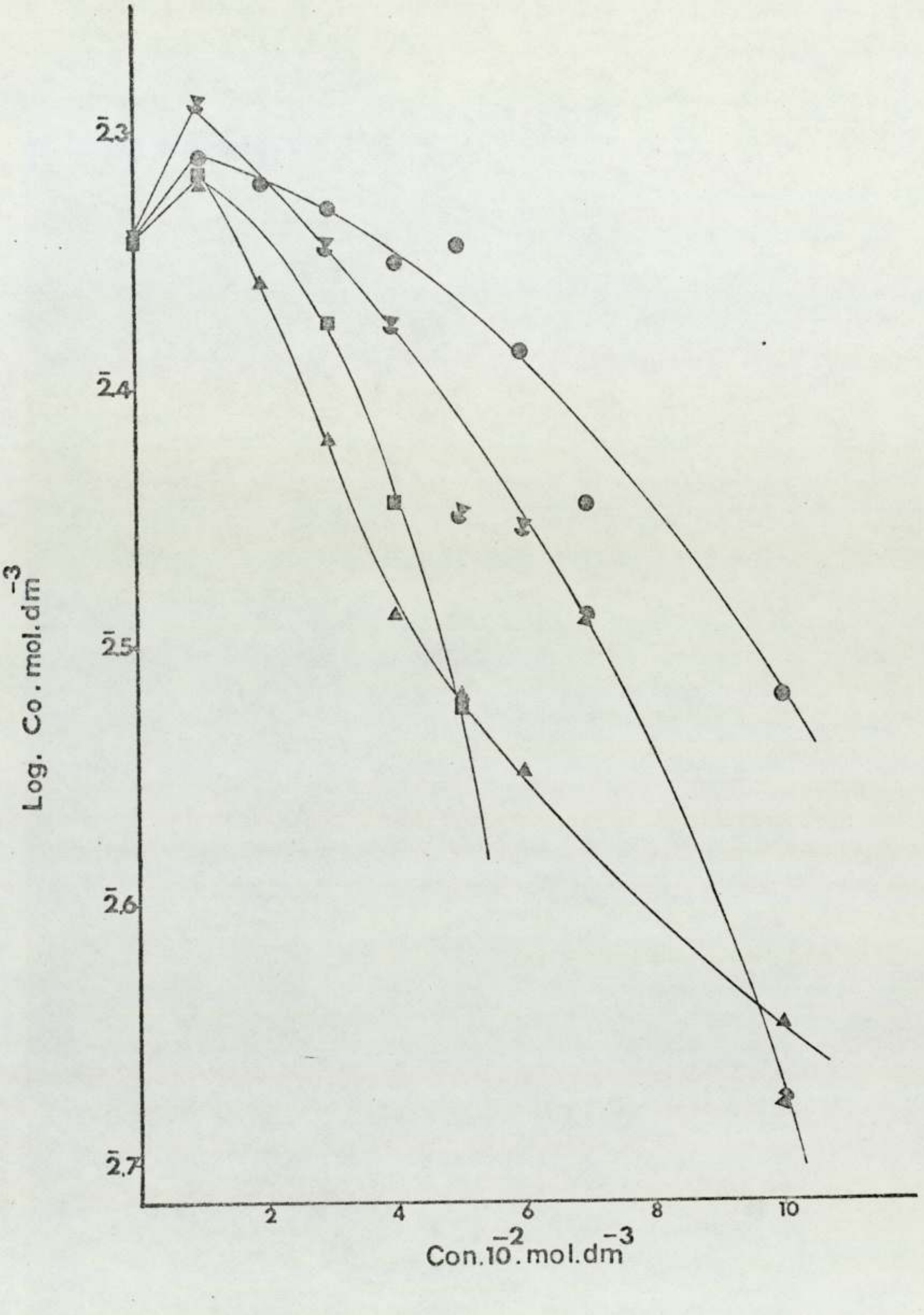


Fig.V.I Dependence of log Co of the tetradecyl trimethyl ammonium bromide on the various concentration of the aromatic alcohols in water at 25° C; ▲ Phenol, ● Benzylalcohol, ⧗ Phenylethanol, and ■ Phenylpropanol

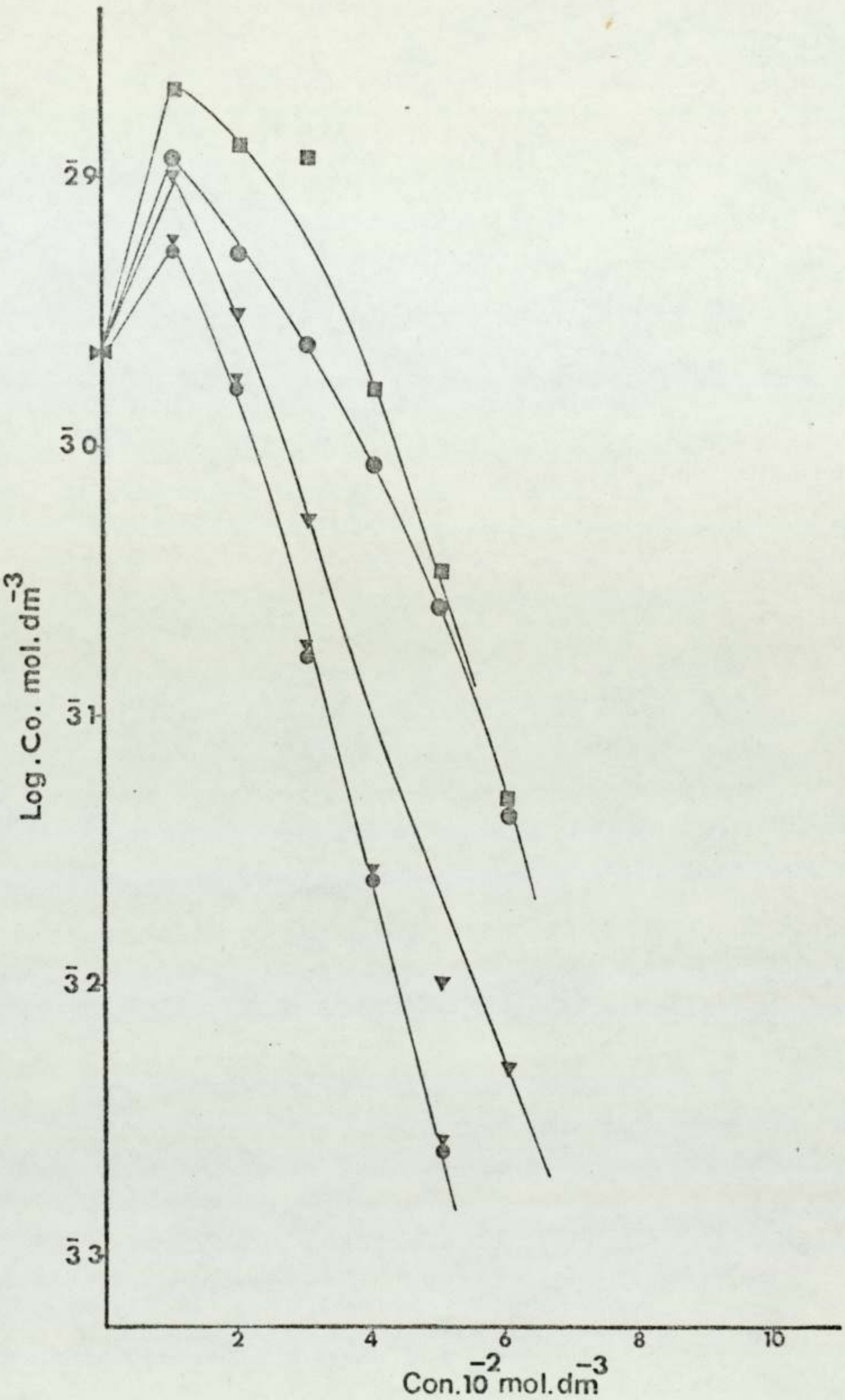


Fig.V.2 Dependence of Log Co of the Cethyltrimethyl ammonium bromide on the various concentration of the aromatic alcohols in Water at 25° C; ▲ Phenol, ● Benzylalcohol, ■ Phenylethanol, and ⧗ Phenylpropanol

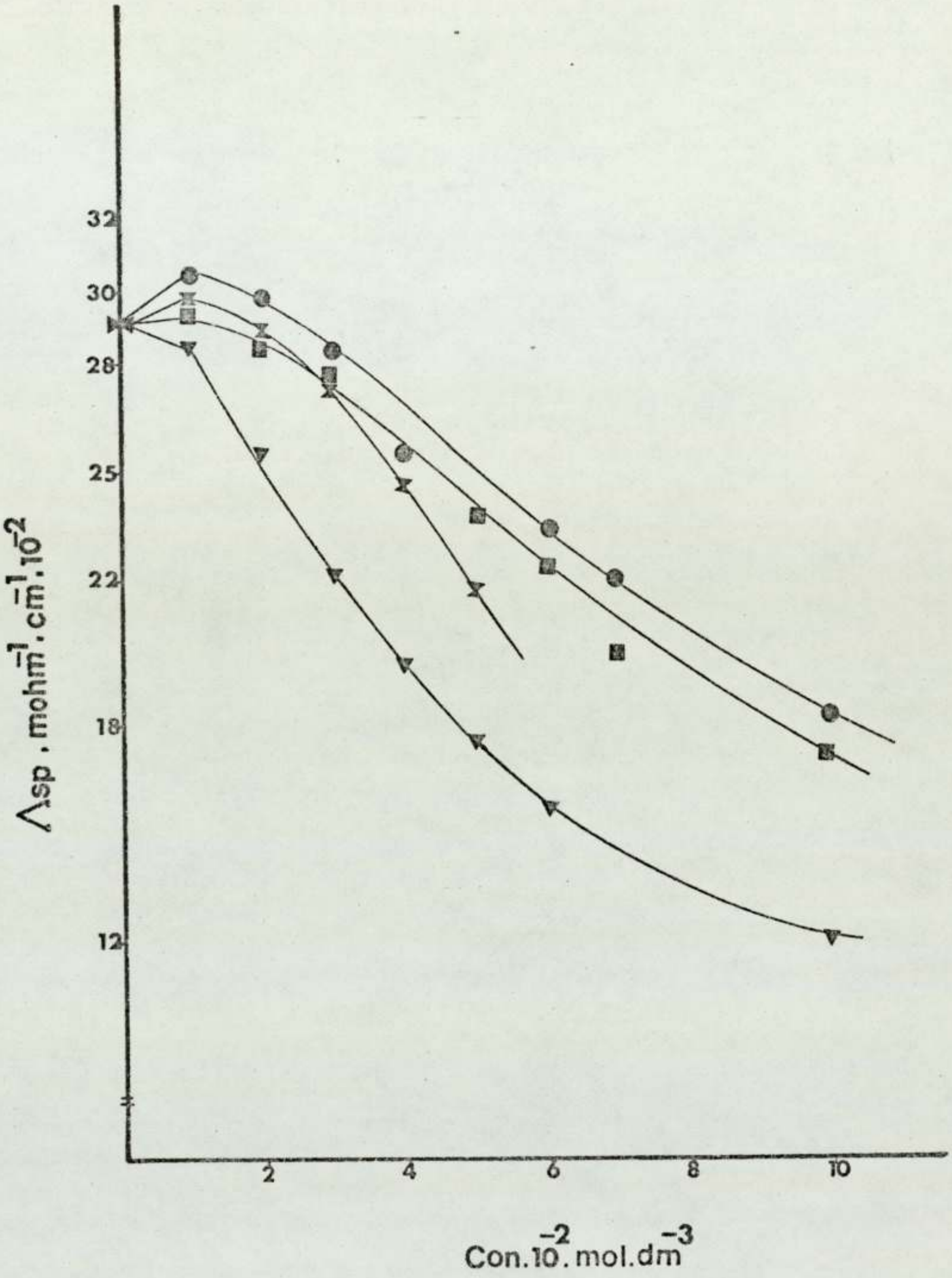


Fig.V.3 The relationship between specific conductivity of the tetradecyl trimethyl ammonium bromide at Co and the concentration of aromatic alcohols in water at 25° C; ▲ Phenol, ● Benzylalcohol, ■ Phenylethanol, and Ϫ Phenylpropanol

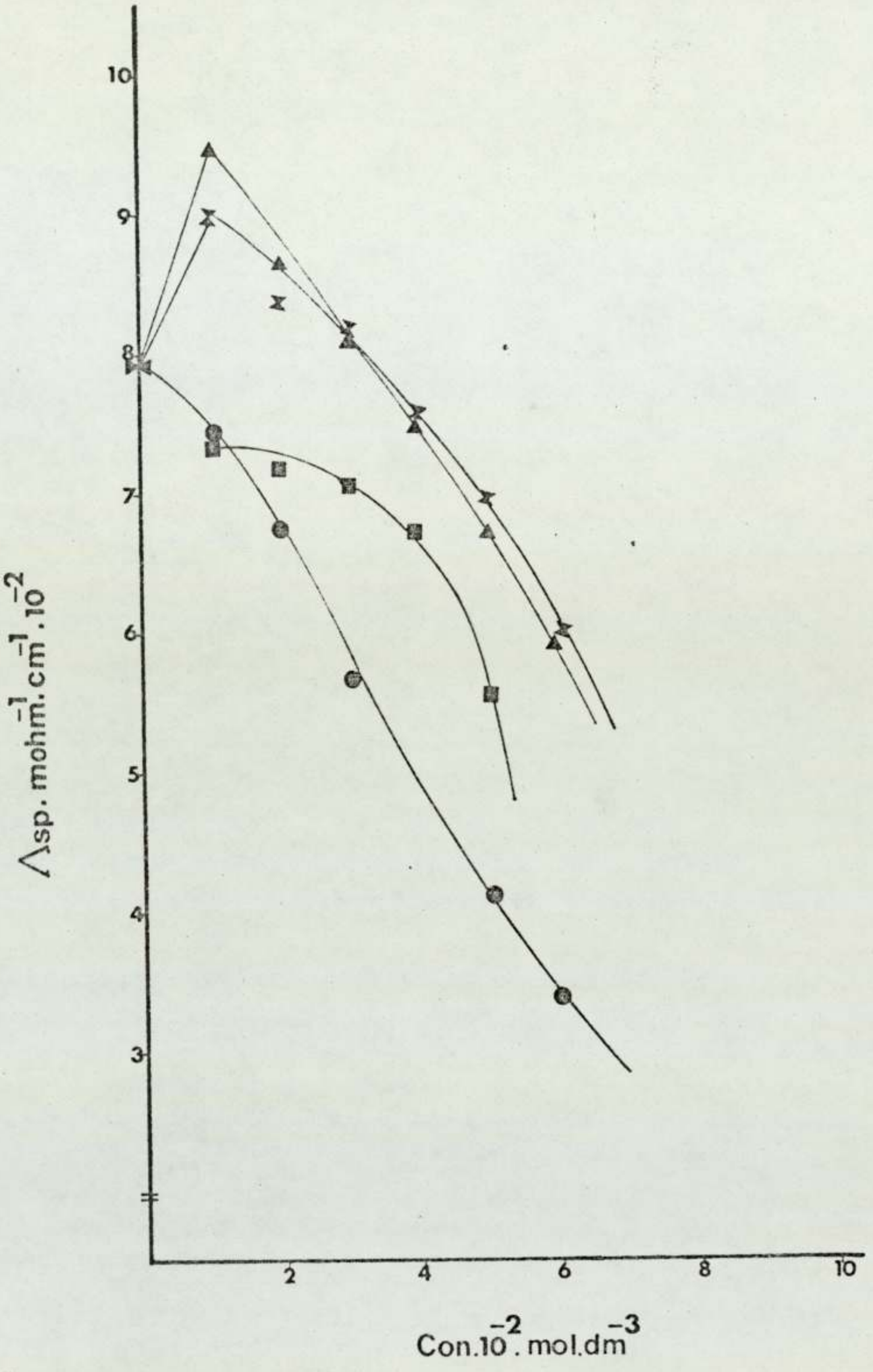


Fig.V.4 The relationship between specific conductivity of the cethyl trimethyl ammonium bromide at Co. and the concentration of aromatic alcohols in water at 25° C; ● Phenol, ▲ Benzylalcohol, ⧗ Phenylethanol, and ■ Phenylpropanol

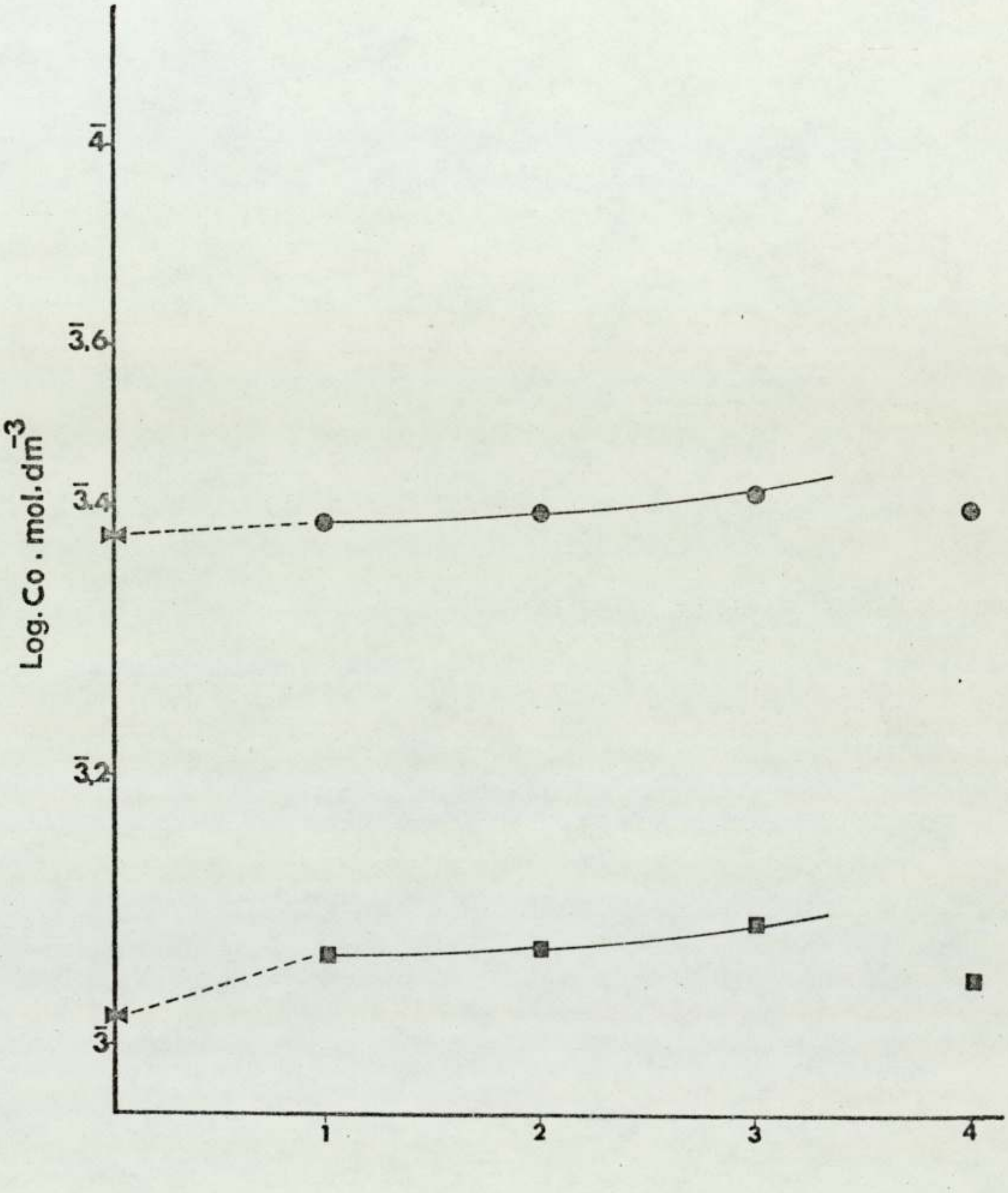


Fig.V.5 Log Co of C_{14}, and C_{16} as afunction of the alkyl chain length of the aromatic alcohol; ● C_{14} , ■ C_{16}

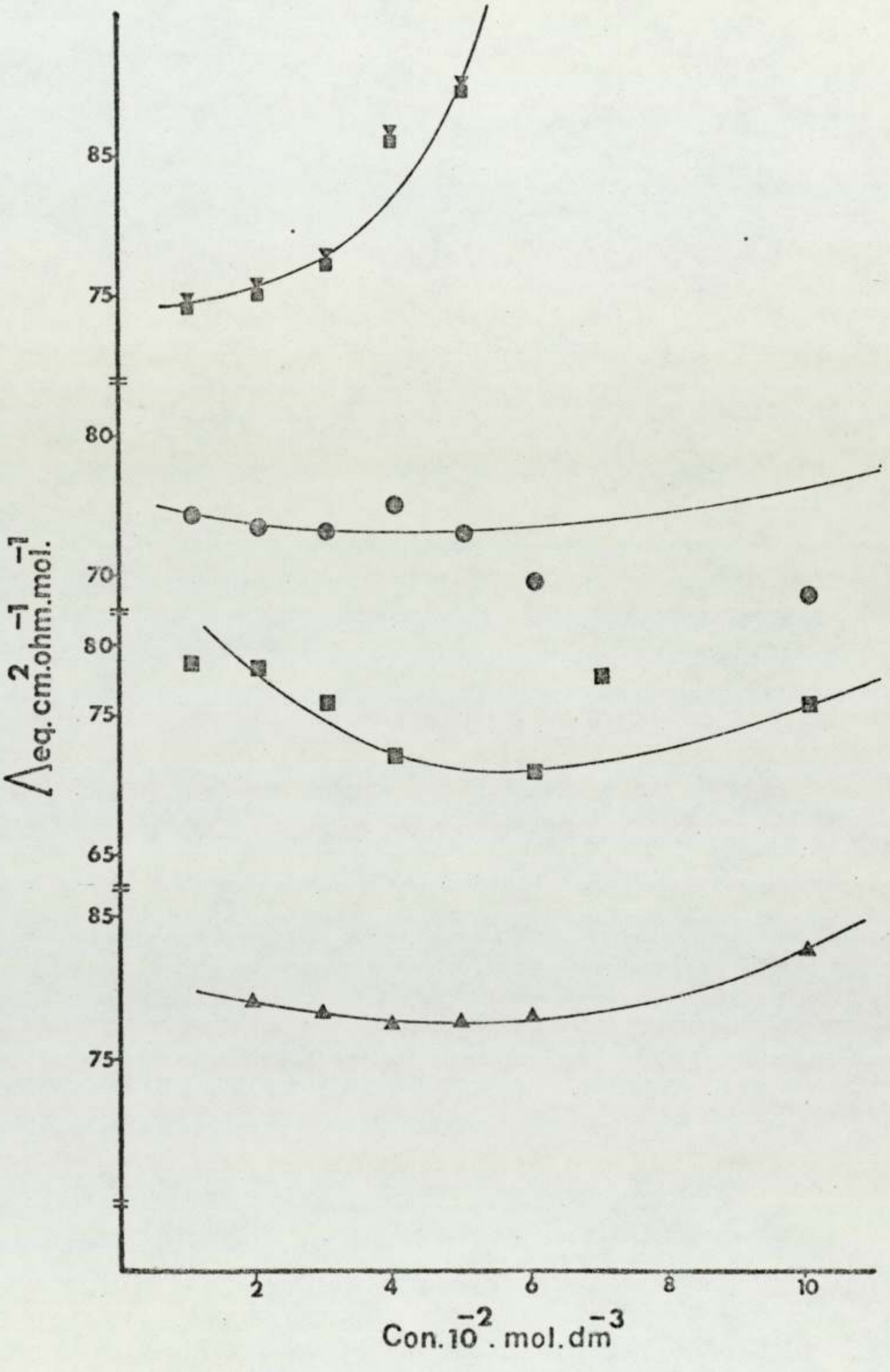


Fig.V.6 Variation of the equivalent conductivity of the tetradecyl trimethyl ammonium bromide at Co with the various concentration of aromatic alcohols in Water at 25° C; ● Phenol, ■ Benzylalcohol, ▲ Phenylethanol, ⧗ Phenylpropanol

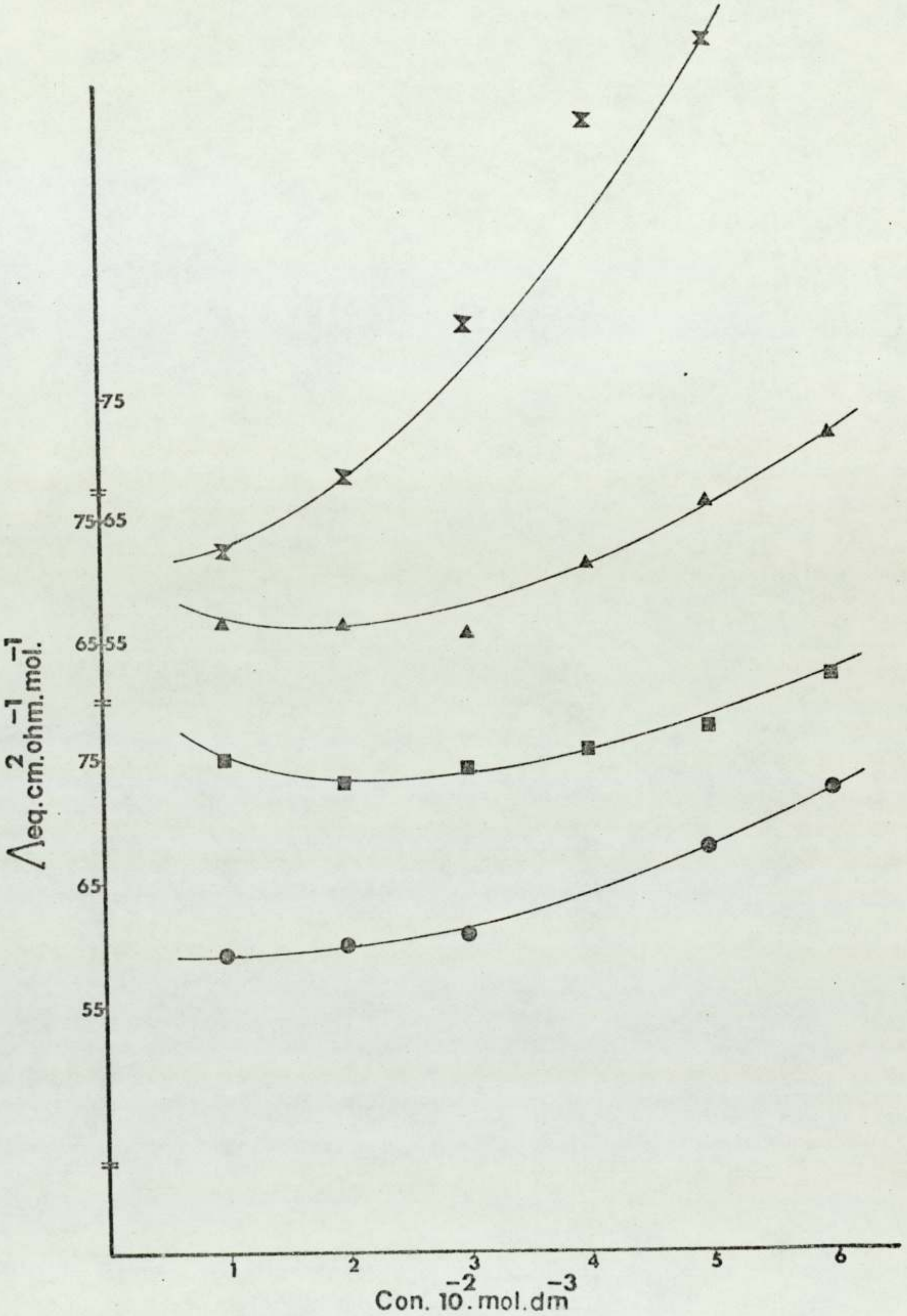


Fig.V.7 Variation of the equivalent conductivity of the cethyltrimethyl ammonium bromide at Co with the various concentration of aromatic alcohols in Water at 25° C; ● Phenol, ■ Benzylalcohol, ▲ Phenylethanol, and ⧗ Phenylpropanol

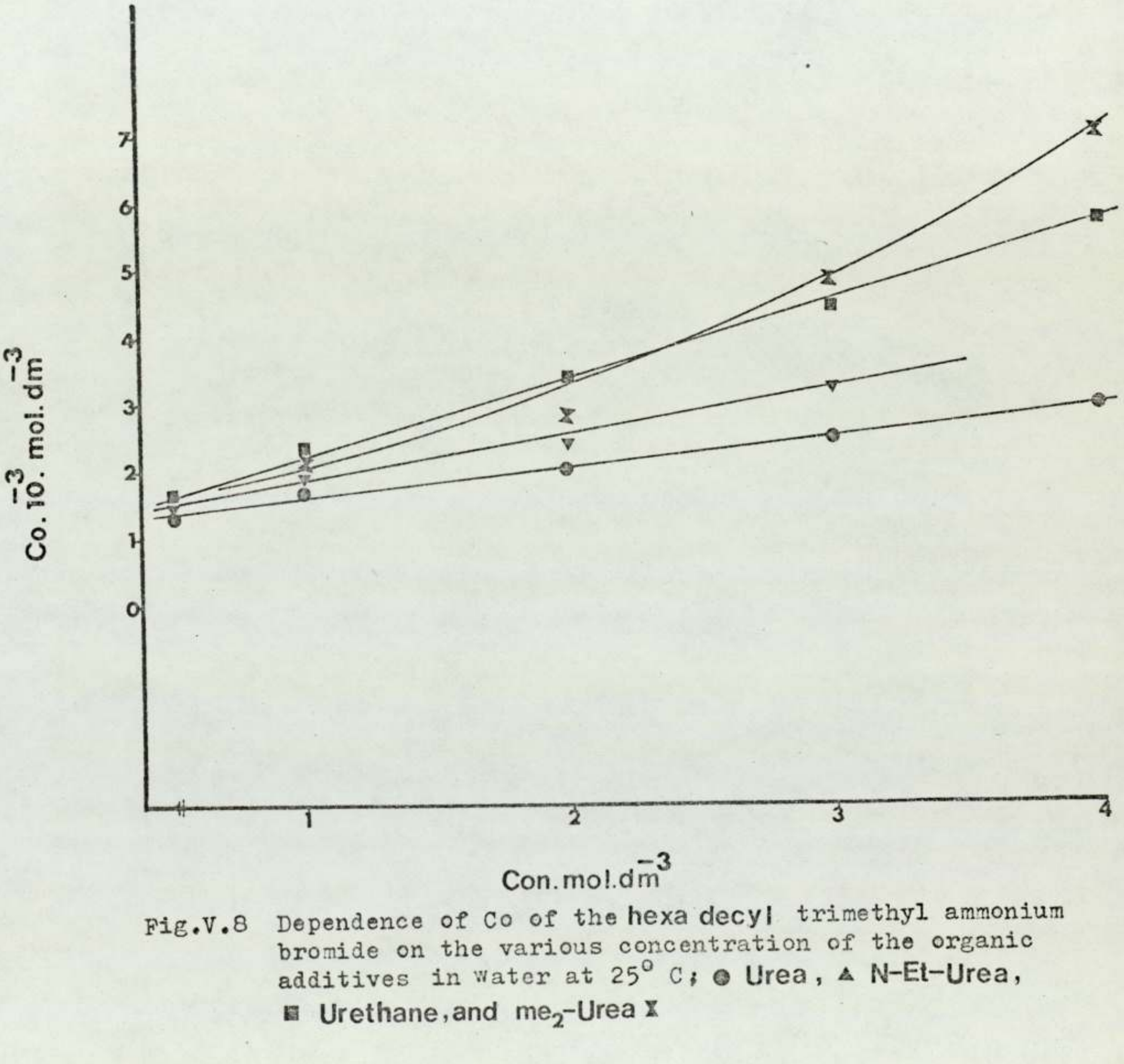


Fig.V.8 Dependence of Co of the hexa decyl trimethyl ammonium bromide on the various concentration of the organic additives in water at 25° C; ● Urea, ▲ N-Et-Urea, ■ Urethane, and me$_2$-Urea ⧗

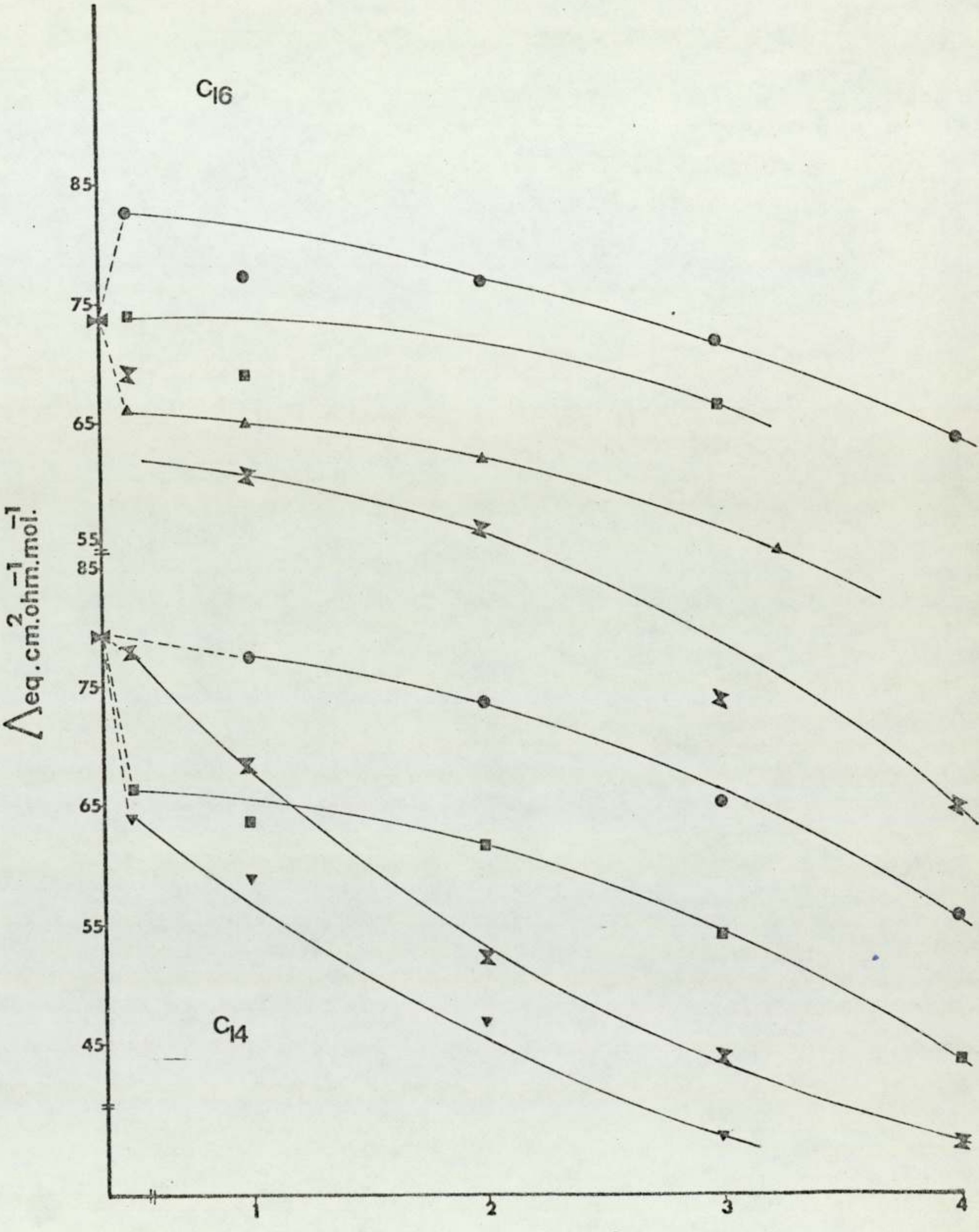


Fig.V.9 Plots of the equivalent conductivity of C_{14} and C_{16} at Co versus concentration of the organic additive in water at 25° C; C_{14} : ● Urea, ■ Urethane, ⧗ me$_2$-Urea, and ▲ N-Et-Urea; C_{16} : ● Urea, ■ N-Et-Urea, ▲ Urethane, and ⧗ me$_2$-Urea

CONDUCTANCE PROPERTIES OF THE MYRISTYL AMMONIUM BROMIDE

IN WATER AND CONTAINING AROMATIC ALCOHOLS AT 25° C

TABLE V.I.1

C mol.dm^{-3}	Λc mohm^{-1}.cm^{-1}	Λsp mohm^{-1}.cm^{-1}	Λeq cm^2.ohm^{-1}.mol^{-1}	Co mol.dm^{-3}
C_{14} H_2O	0.206	0.293	78.975	3.7 x10^{-3}
Phenol				
0.01	0.200	0.284	74.736	3.82x10^{-3}
0.02	0.180	0.256	73.775	3.47x10^{-3}
0.03	0.155	0.220	73.333	3.0 x10^{-3}
0.04	0.138	0.196	75.384	2.6 x10^{-3}
0.05	0.124	0.176	73.333	2.4 x10^{-3}
0.06	0.110	0.156	69.643	2.24x10^{-3}
0.10	0.085	0.121	67.222	1.8 x10^{-3}
Benzylalcohol				
0.01	0.215	0.305	78.608	3.88x10^{-3}
0.02	0.210	0.298	78.627	3.79x10^{-3}
0.03	0.200	0.284	75.936	3.74x10^{-3}
0.04	0.180	0.255	72.034	3.54x10^{-3}
0.06	0.165	0.234	71.341	3.28x10^{-3}
0.07	0.155	0.220	77.193	2.85x10^{-3}
0.1	0.128	0.182	75.833	2.4 x10^{-3}
Ph. ethanol				
0.01	0.210	0.298	73.039	4.08x10^{-3}
0.02	0.20	0.284	79.552	3.57x10^{-3}
0.03	0.195	0.277	78.248	3.54x10^{-3}
0.04	0.180	0.256	77.576	3.3 x10^{-3}
0.05	0.168	0.238	77.780	3.06x10^{-3}
0.06	0.158	0.224	78.596	2.85x10^{-3}
0.10	0.10	0.142	83.041	1.71x10^{-3}
Ph.propanol				
0.01	0.2085	0.296	74.747	3.96x10^{-3}
0.02	0.203	0.288	75.989	3.79x10^{-3}
0.03	0.186	0.264	78.338	3.37x10^{-3}
0.04	0.173	0.245	87.500	2.8 x10^{-3}
0.05	0.153	0.217	90.416	2.4 x10^{-3}

CONDUCTANCE PROPERTIES OF THE CETHLY AMMONIUM BROMIDE IN WATER AND CONTAINING AROMATIC ALCOHOLS AT 25° C

TABLE V.I.2

C $mol.dm^{-3}$	Λc $mohm^{-1}.cm^{-1}$	Λsp $mohm^{-1}.cm^{-1}$	Λeq $cm^2.ohm^{-1}.mol^{-1}$	Co $mol.dm^{-3}$
C_{16} H_2O	0.056	0.0795	73.61	1.08×10^{-3}
Phenol				
0.01	0.0525	0.0745	59.127	1.26×10^{-3}
0.02	0.0475	0.0675	60.267	1.12×10^{-3}
0.03	0.0400	0.0568	60.425	9.4×10^{-4}
0.05	0.0300	0.0426	67.619	6.3×10^{-4}
0.06	0.0240	0.0341	72.553	4.7×10^{-4}
Benzylalcohol				
0.01	0.0670	0.0952	74.961	1.27×10^{-3}
0.02	0.0610	0.0866	73.389	1.18×10^{-3}
0.03	0.0570	0.081	74.380	1.089×10^{-3}
0.04	0.0530	0.0753	76.680	9.82×10^{-4}
0.05	0.0475	0.0675	77.231	8.74×10^{-4}
0.06	0.0420	0.0596	81.644	7.3×10^{-4}
Ph.ethanol				
0.01	0.0635	0.0902	66.406	1.36×10^{-3}
0.02	0.0610	0.0866	66.106	1.31×10^{-3}
0.03	0.0585	0.0831	65.433	1.27×10^{-3}
0.04	0.053	0.0753	71.714	1.05×10^{-3}
0.05	0.049	0.0696	76.567	9.09×10^{-4}
0.06	0.042	0.0596	81.643	7.3×10^{-4}
Ph.propanol				
0.01	0.052	0.074	62.712	1.18×10^{-3}
0.02	0.051	0.072	68.571	1.05×10^{-3}
0.03	0.050	0.071	81.328	8.73×10^{-4}
0.04	0.0475	0.0675	97.543	6.92×10^{-4}
0.05	0.040	0.0568	103.839	5.47×10^{-4}

THE EFFECT OF UREAS AND URETHANE ON THE CONDUCTIMETRIC BEHAVIOUR OF MYRISTYL AMMONIUM BROMIDE IN WATER AT 25° C

TABLE V.I.3

C $mol.dm^{-3}$	Λc $mohm^{-1}.cm^{-1}$	Λsp $mohm^{-1}.cm^{-1}$	Λeq $cm^{2}.ohm^{-1}\,mol^{-1}$	Co $mol.dm^{-3}$
Urea		C_{14}		
1.0	0.258	0.366	77.542	4.72×10^{-3}
2.0	0.28	0.397	73.792	5.38×10^{-3}
3.0	0.31	0.440	65.088	6.76×10^{-3}
4.0	0.35	0.497	55.592	8.94×10^{-3}
Urethane				
0.5	0.255	0.362	75.416	4.80×10^{-3}
1.0	0.260	0.369	73.333	5.4×10^{-3}
2.0	0.325	0.462	58.778	7.86×10^{-3}
3.0	0.290	0.412	47.302	8.71×10^{-3}
4.0	0.310	0.440	40.741	1.08×10^{-2}
N-Et-Urea				
0.1	0.230	0.326	70.869	4.6×10^{-3}
0.5	0.235	0.334	64.231	5.2×10^{-3}
1.0	0.240	0.354	59.000	6.0×10^{-3}
2.0	0.253	0.359	47.236	7.6×10^{-3}
3.0	0.266	0.378	37.425	1.01×10^{-2}
me_2-Urea				
0.5	0.285	0.405	77.885	5.22×10^{-3}
1.0	0.310	0.440	68.750	6.4×10^{-3}
2.0	0.350	0.497	52.315	9.5×10^{-3}
3.0	0.38	0.539	44.180	1.22×10^{-2}
4.0	0.44	0.625	36.764	1.7×10^{-2}

THE EFFECT OF UREAS AND URETHANE ON THE CONDUCTIMERIC BEHAVIOUR OF CETHYL AMMONIUM BROMIDE IN WATER AT 25° C

TABLE V.I.4

C mol.dm^{-3}	Λc mohm^{-1} cm^{-1}	Λsp mohm^{-1}.cm^{-1}	Λeq cm^{2}.ohm^{-1} mol^{-1}	C_o mol.dm^{-3}
Urea	C_{16}			
0.5	0.066	0.094	80.34	1.17×10^{-3}
1.0	0.073	0.104	77.037	1.35×10^{-3}
2.0	0.081	0.115	76.666	1.5×10^{-3}
3.0	0.086	0.122	71.764	1.7×10^{-3}
4.0	0.089	0.126	63.959	1.97×10^{-3}
Urethane				
0.5	0.0735	0.104	66.242	1.57×10^{-3}
1.0	0.101	0.143	65.000	2.2×10^{-3}
2.0	0.140	0.199	62.187	3.2×10^{-3}
3.0	0.160	0.227	54.047	4.2×10^{-3}
4.0	0.175	0.248	43.510	5.7×10^{-3}
N-Et-Urea				
0.5	0.074	0.105	74.285	1.4×10^{-3}
1.0	0.087	0.123	68.333	1.8×10^{-3}
2.0	0.115	0.163	75.814	2.15×10^{-3}
3.0	0.145	0.206	66.452	3.1×10^{-3}
me_2-Urea				
0.5	0.078	0.111	69.375	1.6×10^{-3}
1.0	0.098	0.139	60.434	2.3×10^{-3}
2.0	0.11	0.156	55.714	2.8×10^{-3}
3.0	0.14	0.199	41.458	4.8×10^{-3}
4.0	0.16	0.227	32.428	7.0×10^{-3}

CHAPTER VI - Light Scattering and Micellar Structure of Alkylammonium bromides.

VI.Ia - Theory of Light Scattering by Solutions

VI-Ib - Scattering due to density and concentration fluctuations

VI-Ic - Charge effects in light scattering by colloidal systems

VI-Id - Experimental Procedure

VI-Ie - Light scattering by alkylammonium bromides in water, and solutions containing various additives.

VI-If - Conclusions

VI-Ia - Theory of Light Scattering by Solutions.

According to Debye$^{(245)}$, scattering is due to non-homogeneous molecular structure. In his theory, in order to explain the increase in scattered intensity when a solvent is made inhomogeneous by the addition of a solute, and to derive appropriate conclusions about the number of solute particles in the medium, from the measurement of the light scattered at different angles of observation, he has taken the following considerations into account.

In order to derive the loss of light energy due to its radiation, the particle in the medium was treated as having an electromagnetic field around itself, and fluctuations of the concentration and density has been considered. In this approach the solvent is considered as perfectly homogeneous and its dielectric constant is given by the relation,

$$\epsilon_0 = \mu_0^2 \qquad \text{VI-1}$$

When this medium is influenced by a homogeneous electric field of intensity F, the electric moment of medium (for 1 cm^3 volume) is given by the expression

$$(\epsilon_0 - 1)\ \frac{F}{4\pi} \qquad \text{IV-2}$$

Since the homogeneous field is disturbed by the presence of the particles, the effect of the particles on the homogeneous field has been observed at a point which is at a larger distance from the particle.

In this treatment it has been assumed that (m) and (F) have the same direction. If a volume of solution contains (n) particles per cm^3, its total electric moment in the direction of F, is defined by the expression

$$V\left[(\epsilon_0 - 1)\ \frac{F}{4\pi} + nm\right] \qquad \text{VI-3}$$

In view of this expression the dielectric constant of the solution takes the form

$$\epsilon - \epsilon_0 = 4\pi m \frac{m}{F} \qquad \text{VI-4}$$

In order to derive the radiation field surrounding the particle at large distance, it has been treated in a way that at small distance its electrostatic field is equal to the dipole m vibrating with the frequency of the light.

The electric intensity E, and the magnetic intensity H at a large distance r (large compared with the wave length) are given by the following expressions

$$E = mk_0^2 \quad \frac{\sin v}{r} \quad \mathrm{Cos}(\omega t - n_0 k_0 r)$$

$$H = \mu_0 E \qquad \text{VI-5}$$

where $k_0 = \frac{\omega}{\nu_1} = \frac{2\pi}{\lambda_0}$.

The energy radiated per second through 1 cm^2 of the sphere is given in terms of the time average Poynling's vector.

$$\frac{\nu_1}{8\pi} \mu_0 m^2 k_0^4 \quad \frac{\mathrm{Sin}2v}{r^2} \qquad \text{VI-6}$$

and the total energy loss per second per particle is defined by the relation

$$\frac{1}{3} \frac{\nu_1}{\mu_0} \mu_0^2 \; m^2 \; k_0^4 \qquad \text{VI-7}$$

However he has shown that if a light beam, its intensity equal to the energy carried through 1 cm^2 per second, goes through a solution

$$I = \frac{\nu_1 \; \mu_0^2 F^2}{\mu_0 \; 8\pi} \qquad \text{VI-8}$$

it loses its intensity according to the relation

$$-\frac{dI}{dx} = n \; \frac{1}{3} \; \frac{\nu_1}{\mu_o} \mu_o^2 m^2 k_o^4 = \left(\frac{8\pi \; n k_o^4 m^2}{3F^2} \right) I \qquad \text{VI-9}$$

in the direction of propagation. From the above equation the turbidity is given by the expression

$$\tau = \frac{8\pi}{3} n k_o^4 \; \frac{m^2}{F^2} \qquad \text{VI-10}$$

As can be seen, the turbidity is proportional to the number of particles per unit volume, and with the square of m/F. It is apparent from the above equation that the turbidity measures energy losses and intensities. The substitution of equation (VI-4) into (VI-10) gives the following relation,

$$\tau = \frac{32\pi^3}{3} \; \frac{\mu_o^2 (n_s - n_o)^2}{\lambda^4} \; \frac{1}{n} \qquad \text{VI-11}$$

then it takes the form

$$\frac{\tau}{c} = HM \qquad \text{VI-12}$$

where H is the optical constant which is defined by the expression

$$H = \frac{32\pi^3}{3} \; \frac{n_o^2}{N \; \lambda^4} \left(\frac{n_s - n_o}{c} \right)^2 \qquad \text{VI-13}$$

Since in dilute solution $\mu - \mu_o$ is directly proportional to the concentration, the equation can be rewritten as follows

$$H \; \frac{c}{\tau} = \frac{\partial}{\partial c} \left(\frac{p}{RT} \right) \qquad \text{VI-14}$$

where

$$\frac{p}{RT} = \frac{C}{M} + Bc^2$$

then the following relation is obtained

$$H \; \frac{c}{\tau} = \frac{1}{M} + 2 \; Bc \qquad \text{VI-15}$$

VI.Ib - Scattering due to density and concentration fluctuations.

The fluctuation in density arises from related fluctuation in the polarizability a' of a volume element $\partial V^{(246)}$. The fluctuation behaves as a region of excess polarizability $\delta a'$. The relation between the excess polarizability, and volume element and the turbidity is given by the equation

$$\tau = \frac{128\pi^5}{3\lambda^4}\left[\frac{(\delta a')^2}{\delta V}\right] \qquad \text{VI-16}$$

where $(\delta a')^2$ is the mean square of the excess polarizability corresponding to the volume element δV. The relation of $\delta a'$ with the average dielectric constant of the medium, and the dielectric constant of region exhibiting the fluctuation, can be defined by the expression in terms of δV.

$$\delta a' = \frac{3}{4\pi}\left|\frac{\varepsilon'-\varepsilon}{\varepsilon'+2\varepsilon}\right|\delta V \qquad \text{VI-17}$$

It it is assumed that the fluctuation in region ε' is small, then the above expression takes the form

$$\delta a' = \frac{\delta V \delta\varepsilon}{4\pi\varepsilon} \qquad \text{VI-18}$$

this expression can be related to the turbidity as follows,

$$\tau = \left|\frac{8\pi^3(\delta\varepsilon)^2}{3\lambda^4\varepsilon^2}\right|\delta V \qquad \text{VI-13}$$

This turbidity expression with respect to the dielectric constant (ε) of the medium, where the function of density has been introduced in terms of the temperature and density

$$\tau = \frac{8\pi^3\delta V}{3\lambda_0{}^4}\left[d\left(\frac{\partial\varepsilon}{\partial d}\right)_T\right]\frac{(\delta d)^2}{d^2} \qquad \text{VI-20}$$

where $(\delta d)^2$ is the mean square fluctuation in density, which occurs in the volume element δV. By several computing processes, $(\delta d)^2$ has been evaluated with respect to the thermodynamic relations by the expression,

$$(\delta d)^2 = kT/\beta s \ \delta V \qquad \text{VI-21}$$

The turbidity of the solution can be defined by means of density and concentration fluctuations

$$\tau = \tau d + \tau E \qquad \text{VI-22}$$

The distribution of molecules between the volume elements, and the evaluation of average distribution values gives the magnitude of concentration fluctuations in the volume element. The relation between turbidity and the mean square fluctuation of solute molecule, has been derived in the same way taking into account temperature and density

$$\tau = \frac{8\pi^3}{3\lambda_0} \delta V \left(\frac{\partial \varepsilon}{\partial m}\right)^2_{T,d} (\delta m)^2 \qquad \text{VI-23}$$

VI-Ic - Charge effects in light scattering by colloidal systems.

The scattering of light by small particles is effected by local inhomogenieties of refractive index(245,247), which arise from the fluctuation of density, or concentration which are due to the random thermal motion of solute(247).

The fluctuation in concentration contributes to light scattering proportionally to the magnitude of fluctuation which results in the refractive index. When a colloid particle having charge is treated as a light scattering species, it affects the extent of fluctuations in terms of the requirement of electroneutrality(248). In the case of added gegenions to the system, donnan equilibrium between the fluctuating volume and the bulk solution is established(248,249).

It has been postulated that the turbidity of pure colloidal electrolyte is reduced (p+1) times, when the colloid charge is p. It is apparent that the micelle of ionic surfactant is charged in the aqueous solution and in the presence of ions(248).

In view of the fluctuations theory of light scattering, it has been discussed that the extent of fluctuations is affected by the charge of micelle(248). The presence of monomeric ion reduces the optical efficiency of fluctuations. Consequently the concentration of monomer beyond the critical micelle concentration C_o, is influenced by the equilibrium between monomeric ions and charged micelle(248).

The turbidity of solution is due to the fluctuations in the concentration of solute(245,247,250). As a result of this fact one can assume that the refractive index fluctuates proportionately. In the case of pure association colloid, each mole of micelle is optically equivalent to the degree of association of monomer(248).

Hence, the optical effectiveness of fluctuations of micelles is reduced by a factor of $(1-p/2Nc)$ from Nc to $(Nc-p/2)$(248). Since the turbidity involves intensities rather than amplitudes of vibrations, it has been concluded that it is affected by the square of refractive index increment $\left(\frac{dn}{dc}\right)^2$. Due to this fact, the turbidity of the solution is reduced by $(1-p/2Nc)^2$ (248), and the micellar molecular weight calculated by the Debye method(245) is smaller than the real value.

In the light of this observation, the degree of association has been given by the equation in terms of the Debye relation

$$\frac{1}{M'} = \frac{1}{NA\ M_1} = A \qquad \text{VI-24}$$

The above expression takes the form for the corrected micellar moleculear weight (M)

$$\frac{1}{M} = \frac{1}{NcM_1} = A\left(1 - \frac{p}{2Nc}\right)^2 \qquad \text{VI-25}$$

It has also been given by the following equations for corrected aggregation number, and corrected charge of the micelles(251)

$$Nc = \frac{1}{AM_1} + \frac{2C_0BM_1 + 4\sqrt{2C_0BM_1} - AM_1\sqrt{2C_0BM_1}}{4AM_1 - 2A^2M_1^2} \qquad \text{IV-26}$$

and

$$p = \frac{2\sqrt{2C_0BM_1} + 2C_0BM_1}{2AM_1 - A^2M_1^2} \qquad \text{VI-27}$$

respectively. The uncorrected charge of micelle can be defined by the equation, in terms of the corrected charge and the aggregation number(248)

$$p' = \frac{p(2Nc-p)}{2Nc} \qquad \text{VI-28}$$

VI-Id - Experimental Procedure.

VI-Id$_1$- Materials

The preparation of surface active agents, and purification of aliphatic alcohols which were used in this work has been described in Chapter II. KCl (BDH L.R.grade) was dried in a vacuum oven at about 80-100°C. Double distilled water ($\Lambda w < 1\times10^{-6}$ ohm^{-1} cm^{-1} at 25°C) was filtered several times, through a Millipore filter disc, mean pore size 0.2μ, before using for the preparation of dilute solutions. The solutions were prepared on the molal basis.

VI-Id$_2$-Instrumentation and Measurement.

The refractive index increment (dn/dc) of the solutions was measured by using a differential refractometer. (The Brice-Phoenix, Model BP-2000-V). The instrument was calibrated according to the instrument manual(252).

VI-Id$_2$.A - Calibration.

The calibration of the instrument was made by using a reference solution, whose refractive index difference between solution and solvent is known. As a reference solution, various concentrations of KCl solution were used. Following procedure was employed to calibrate the instrument by using 546 mμ wave length at 25°C.

First both compartments of the differential cell were filled with water, and the glass cover was placed on the cell, then the handle of the rotatable cell holder was turned against the top so that it pointed towards the lamp.

The microscope was focussed on the narrow slit image and the iris diaphram of the projector was set to f:11 (position), then by means of the micrometer drum, the cross hair was set within the eyepiece so that it was aligned with the centre of the slit image. The reading was obtained from the eyepiece scale and the micrometer drum. The process was repeated several times, average (d_1^a) was taken. After that the handle of the cell holder was turned 180° towards the observer, the microscope was refocussed, and the above operation was repeated to obtain the reading at this position (d_2^a).

In order to calculate the solvent zero reading, the average reading (d_1^a) was subtracted from the average (d_2^a). The obtained solvent (water) zero reading (0.0058) is in good agreement with the value (0.006) given by the manufacturer(252).

Following this procedure, the solution compartment was filled with 1 ml calibration solution (KCl), covered with the glass cover, time was allowed for the temperature equilibrium of the solution (15 min.) and its solvent within the cell. After that the cell holder handle was turned towards the lamp housing, and the average reading (d_1) of the solution was recorded. Following this procedure, the cell handle was turned 180° towards observer, and the reading d_2 was determined. The reading for solution (d_2-d_1) was derived by subtracting the average reading for d_1 from the average reading for d_2.

The value of total displacement Δd, corrected for the solvent zero reading was calculated by the equation

$$\Delta d = (d_2 - d_1) - (d_2{}^a - d_1{}^a) \qquad \text{IV-29}$$

the refractive index difference is given by the following relationship

$$\Delta n = Ck.\Delta d \qquad \text{VI-30}$$

By using experimental Δd value 0.8054 (for 0.5964 g/dl standard KCl solution at 25°), and related refractive index difference between standard KCl solution and solvent (e.g.8.17×10^{-4})(252), the calibration constant ($Ck = 1.014 \times 10^{-3}$) was determined for the selected wave length (546 mμ).

VI.Id$_2$.B - Light scattering measurements were made by using a Photo Gonio Diffusometer (Model 4200)(253). The instrument was set and calibrated according to the instrument manual(253).

Initially electrical, optical and mechanical conditions were checked, then the glass scattering standard was placed in the central hole of the rotating plate. After that it was connected with general supply so that the pilot light was on, then the lamp water cooling circuit tap was opened. After a few seconds the high voltage mechanism put into the operation.

The measuring meter needle was set to zero, then was adjusted by using the highest sensitivity position. Following this process finally the needle position was set to the zero reading. The instrument was allowed about 20 minutes for warming up, then was set to the measure position, and the value of the photo tube dark current was checked. After adjusting the zero reading position, the lamp was put into operation. The measuring meter was adjusted for the maximum variation selecting related sensitivity, so that the measuring photo tube was set for maximum sensitivity.

The intensity scattered at 90° by the scattering glass standard is ranging about the intensity scattered by dust free pure benzene. In order to work with a sensitivity corresponding to 50 divisions for the intensity scattered by benzene, the sensitivity position being on I position, the measuring meter was adjusted so that the reading on the division corresponded to the value $(50 \times 0.92 = 46)$. The ratio of the intensity scattered by the glass standard, to the intensity scattered by pure benzene is 0.92 (standard glass constant).

The turbidity of cleaned double distilled water $(\Lambda w < 1 \times 10^{-6}\ \text{ohm}^{-1}\ \text{cm}^{-1})$ was determined $(1.8 \times 10^{-5}\ \text{cm}^{-1})$, and compared with the value given in literature(254) $(1.83 \times 10^{-5}\ \text{cm}^{-1})$ for the wave length used $(546\ m\mu)$.

VI.Id$_2$.B1 - Cleaning the measuring cell and solutions.

All glassware and the measuring cell were filled with a sulfochromic mixture and allowed to stand for about 24 hours. They were then rinsed with dust free distilled water several times. Following this procedure the measuring cell and all glassware were further cleaned using acetone vapour.

Great care was taken in the process of cleaning the prepared dilute solutions. The solution was pipetted into a cleaned glass cylinder, which was fitted with a cleaned filter disc of mean pore size 0.2μ, in the sterilized air condition, then the solution was filtered through the millipore filter under pressure. The process of cleaning the solutions was checked by measuring the dissymmetry of solution.

V.Id$_2$.B2 - Checking the Dissymmetry.

After the calibration of instrument, the scattering glass standard was taken out, and the measuring cell containing the solution was set in its place. Then the intensities scattered by the solution at 60° and 120° angle were measured. The ratio of intensity scattered at 60° to the intensity scattered at 120° by the solution was compared with the standard dissymmetry (1.010) to check the degree of dedusting of the solution.

After the filtration, the concentration of solution was checked by using the differential refractometer. The measured adsorption of material on glassware and millipore used was negligible.

VI.Ie - Light scattering by alkylammonium bromides in water and solutions containing various additives.

VI.Ie1- Light Scattering by the aqueous surfactant solutions.

Light scattering in colloidal solutions depends primarily on the interference effect, which occurs due to dispersed particles(250). If the particle is small compared with the wavelength, each colloidal particle behaves as a light scatter species. As has been discussed, the turbidity of a solution depends on the homogenity of the solution, which is influenced by the fluctuations in concentration and density(245).

Light scattering measurements were made on solutions of the alkylammonium bromides in water, and solutions containing aliphatic alcohols, by using the Photo Gonio Diffusometer(253) at 25°C. The procedure of measurement was performed as described in this Chapter VI.Id. The scattered intensities of solutions was measured at 90° angle, and the Rayleigh ratios for the solutions was calculated, in terms of the scattering glass standard, and the Rayleigh ratio for standard benzene.

The C_0's of systems studied has been determined by plotting S_{90} against concentration ($mol.dm^{-3}$) (Figs.VI.1,3,4). The obtained C_0 value for C_{10} is 6.5×10^{-2} mol dm^{-3}, which is in good agreement with the value obtained from viscosity, and surface tension measurement (6.5×10^{-2} mol.dm^{-3} and 6.0×10^{-2} mol.dm^{-3} respectively).

The C_0 values for C_{12}, C_{14} and C_{16} also agree well with the values obtained from the other methods (Tables VI.I.1, II.I.1,II.I.1.A). The micellar molecular weights of the surfactants in aqueous solution and containing various additives can be derived in terms of the Debye equation (VI-15), which can be rewritten(250) by the relation as follows,

$$\frac{H(C-C_0)}{\tau-\tau_0} = \frac{1}{M}+2B(C-C_0) \qquad \text{VI-31}$$

In order to obtain the apparent molecular weights (AMW) of the micelles, the left side of the above equation was plotted as a linear function of $C-C_0$, and the extrapolation of the obtained curve to $C-C_0 = 0$ gives the intercept, which is equal to $\frac{1}{M}$ according to the Debye relation (Figs.VI.2,VI.5).

Since unassociated surfactant contributes a negligible amount to the total turbidity of a micellar solution, τ_0 is assumed to be equal to the turbidity of solvent. The turbidity of solutions have been evaluated by the equation(246),

$$\tau = \frac{16\pi}{3} \times S_{90} \qquad \text{VI-32}$$

The light scattering measurements of alkylammonium bromides show that the micelles of these surfactants increase in size (molecular weight) (Fig.VI-6, Table VI.I.1.A). The micellar properties of alkylammonium bromides from hydrodynamic data has been discussed in Chapter II. It is concluded that the micelles of surfactants studied in aqueous solutions are spherical, hydrated and small. The increment in micellar molecular weight (AMW) increases as the chain length increases(250) (1.0101×10^4 and 1.5384×10^4 for C_{10} and C_{12} respectively Table VI.I.1.A).

The size of the micelles can be calculated from the micellar density in terms of partial molal volumes, and partial specific volume of the micelles.

The radius of the micelle can be derived by the expression(42)

$$RL = \sqrt[3]{3M/4\pi Nd} \qquad \text{VI-33}$$

However the obtained density values from partial specific volume of the micelles, has been used to calculate radius of the micelles. In order to derive also the radius of micelle from hydrodynamic data the following equation has been applied(174)

$$Rh = (3/4\pi)^{\frac{1}{3}} \; (Vh)^{\frac{1}{3}} \qquad \text{VI-34}$$

The calculated value of radius of micelle for C_{10} by the equation (VI-33), from light scattering data considering (AMW), is lower compared with the radius calculated from hydrodynamic data (16 Å and 21 Å respectively). However the obtained R^c value for C_{10}, taking into account the corrected miceller molecular weight (18 Å) agrees reasonably with the R^o value (Table II.I.4). The difference between the radii obtained by two methods for the other surfactants increases as the chain length increases.

The corrected and uncorrected degree of association of micelles, the effective charge and uncorrected charge has been derived by the equations (VI-26,VI-24,VI-27 and VI-28). It can be seen (Table VI.I.1.A) that the effective charge increases with increasing chain length (14 and 15 for C_{10} and C_{12} respectively), and the difference between uncorrected and the effective charge is 2 for both C_{10} and C_{12}.

As has been discussed in Section (VI.Ib, VI.Ic) in this Chapter, the turbidity of solution is due to inhomogeneties in the refractive index of region, which arise from the fluctuations in concentration and density(245,246,250). The degree of fluctuation is influenced by the charge of micelle(248). As a result of this fact, the optical effectiveness of the micelle is reduced, which affects the turbidity of the solution. The actual value of turbidity of the colloidal solution is effected by the factor of (p+1)(248), when the quantity of micellar charge is equal to p.

The effective charge refers to the equivalent charge under ideal conditions$^{(251)}$. Its value is lower than the true value at the shear surface, which is derived from electrophoretic mobility measurements. The degree of dissociation of micellar charge given by the ratio of micellar charge to the number of monomers, decreases with increasing true number of monomers corresponding to the chain length of surfactant. (Table VI.I.1A, 0.280 and 0.238 for C_{10} and C_{12} respectively). The obtained values corrected for the number of monomers, for the true micellar molcular weights of surfactants (50 and 63 for C_{10} and C_{12}) are slightly higher than the values given in literature (46 and 61.5 for C_{10} and C_{12} respectively)$^{(248)}$.

VI.Ie2 - Light scattering by surfactant solutions containing various aliphatic alcohols.

On the addition of aliphatic alcohols to the system, the micellar properties show deviation from the observed features in aqueous solutions. As has been discussed in Chapter II, the intrinsic viscosity of the micelles increases with increasing chain length. However it decreases for a particular alcohol, when the concentration increases. The increase in viscosity and intrinsic viscosity $[\eta]$ has been discussed in terms of hydrophobic interactions, hydration and electroviscous effect.

As can be seen (Fig.VI.5, Table VI.1.3) on the addition of 1 M C_2H_5OH and 0.5M C_3H_7OH to the aqueous solution of C_{12}, the AMW has considerably increased (5.263×10^4 and 4.0×10^4 respectively) compared with the AMW of C_{12} in aqueous solution (1.5384×10^4). The addition of 0.5M C_4H_9OH shows a similar pattern. However, on the addition of higher concentrations different behaviour has been observed. The AMW decreases when 2M C_2H_5OH, and 1 M C_3H_7OH is added to the aqueous solution (4.167×10^4 and 2.8×10^4 respectively Table VI.I.3)
It is known that the micellar molecular weight increases, when low molecular weight inorganic electrolyte is added to the colloidal system.

The effect of ions on the micellar properties have been extensively examined(150,151,255). The known fact is that the added ion increases the size of micelle and changes the shape of it. Since the physico-chemical nature of alcohol is different than inorganic electrolytes, (e.g. NaCl, NaBr) it does not appear probable that the similar approach could be used for alcoholic solutions of surfactants. As has been discussed, the alcohols penetrates into the micelle through the Stern layer around the kinetic micelle. They decrease the dielectric constant of bulk solution, and Stern layer(179). This effect increases with increasing apolar chain length of the alcohol molecule.

On the other hand alcohols behave as structure promoters at low concentration. However this behaviour tends to the opposite direction, as the concentration increases. The increment towards the alcohol-rich solution state breaks the micelles. It has been definitely established that the aliphatic alcohols enter into the oriented structure of micelles(179,186). Apart from this fact one can conclude that on the addition of alcohol to the system, due to the penetration of alcohol molecule, micellar molecular weight will be increased depending on the degree of solubilization.

The added alcohol decreases the head group repulsion in the micelle because the alcohol molecules orientate themselves between the monomers(186). As the molecules are brought together in the micelles, short range repulsive forces come into operation and corresponding repulsive energy increases.

The decrement in AMW after certain concentration (Table VI.I.3, Fig.VI.6) could be attributed to the solubilization degree of alcohol in the interior of micelle, the dielectric effect of alcohol on Stern layer, the dipole orientations in bulk solution, and hydrophobic interactions between possible orientations in the Stern layer, and in the interior of micelle between hydrocarbon groups.

However the penetration of alcohol into the micelle changes the structure and shape of micelle. The change in $[\eta]$ of micelles confirms also the idea that the micelle shape is changed by the addition of solute to the system.

On the addition of alcohol to the system, the $[\eta]$ deviates from the value (0.025 g/dl) given by Einstein for rigid spherical uncharged particles(126,127). The obtained $[\eta]$ for a micelle on the addition of 1 M C_2H_5OH is lower ($0.044 g.dl^{-1}$) compared with the value from aqueous solution ($0.069 g.dl^{-1}$). It decreases with increasing concentration. The observed lower values of $[\eta]$ for micelles is due to the decrease in hydration and electroviscous effects. The addition of C_3H_7OH and C_4H_9OH shows a similar behaviour.

Hence on the addition of alcohols, the deviation from ($0.025 g.dl^{-1}$) could be attributed to the change in axial ratios of the micelles. It is a known fact that the increase in axial ratio of the particle, increases the intrinsic viscosity(169;256). The axial ratio of micelles decreases as the alcohol concentration increases (4.1 and 3.3 for 1 M C_2H_5OH and 2M C_2H_5OH respectively). The semi axis of revolution A_b and equatorial radius A_a of the micelles has been calculated taking into account the density of micelle and micellar molecular weight (AMW).

Since the axial ratios of the micelles, compared with the values given by Mehl et al.(169) and Scheraga(170) in terms of the shape function, and light scattering and viscosity data support the assumption of prolate type of micelle, it has been concluded that the micelles are rod (prolate) type rather the other shapes. On the addition of 1 M C_2H_5OH to the aqueous solution, the dimensions of the micelles have changed considerably (70 Å and 17 Å for A_a and A_b

respectively, Table II.I.5).

The dissymmetry measurements (at 60° and 120°) indicate also that the slight deviation from standard dissymmetry (1.01) is due to the increase in molecular size and shape (1.04 and 1.054 for 1 M C_2H_5OH, and 2 M C_2H_5OH respectively. Table VI.I.2.A).

On the addition of alcohols to the system (Figs.VI.3, VI.4, Tables VI.I.2,A,B,C) the Rayleigh ratio and turbidity decreases as the concentration of alcohol increases (0.842×10^{-5} cm^{-1} and 1.4101×10^{-4} cm^{-1} for 4×10^{-2} mol dm^{-3} containing 1 M C_2H_5OH compared with 1.0385×10^{-5} cm^{-1} and 1.7391×10^{-4} cm^{-1} in aqueous solution of 4×10^{-2} mol.dm^{-3} surfactant respectively).

The effect of a second solvent on the light scattering properties, has been examined in terms of the density and concentration fluctuations, and the adsorption of low molecular weight species on the solute(257,258).

The parameter which measures the change in composition of the mixture surrounding the particles due to the selective adsorption has been discussed by Ewart et al.(257). This view has been employed by Parfitt-Wood(259,260) to methanol-water and ethanol-water mixed systems. They have concluded that if the optical efficiency of the fluctuations of the second solvent, related to the concentration fluctuation Rayleigh ratio of the liquid mixture is small, then its extra term on the fluctuations could be neglected.

According to their view the optical effect of concentration fluctuations of the secondary solvent on the micelles may be neglected. They have examined the effect of methanol as secondary solvent, on light scattering properties of SDS by adding 0.06-0.27 mole fraction alcohol to the system. They have observed that in a methanol-water mixture of mole fraction of methanol 0.12, the micellar molecular weight (AMW) decreases(260). The decrement increases with increasing mole fraction of alcohol, and they have also discussed the absence of micelle at 0.27 mol fraction of alcohol(260). Herrmann-Benjamin(261) found similar behaviour on the addition of ethanol to a non-ionic system. The observed decrement in turbidity is due to the change in mean square density and concentration fluctuations in the refractive index increment. Since the alcohols behave as structure making at low concentration due to the apolar side of molecule(97), it is reasonable to assume that, even if they decrease the dielectric constant of solution, they will behave in the same manner in the Stern layer.

The optical efficiency of fluctuations of the secondary solvent on micelles contributes also to the change in the Rayleigh ratio, and decrement in the turbidity. On the other hand the effect of adsorbed solutes also plays a unique role in the changing light scattering properties of surfactant solutions.

As has been observed by Parfitt-Wood(260), in high concentration alcohols behave as structure breakers then, due to this fact, they destroy the micelles, consequently as concentration of alcohol is increased no critical change is observed in the turbidity-concentration curve.

However, in the mixed systems, the corrected micellar number, and the effective charge has also been calculated (33 and 28 (corrected) and 30.3 and 25.6 (uncorrected) for 1 M C_2H_5OH and 2M C_2H_5OH respectively) (Table VI.I.3).

The increase in effective charge could be attributed to the increase in molecular size, and the effect of alcohols on the hydration of micelles. The decrement in hydration of micelles and increment in repulsive energy(186) due to the penetration of alcohol into the micelle, could cause more adsorption of the counter ions in the Stern layer. This effect could also be taken as a possible reason for increase in the effective charge, because of an increase in the concentration of counter ions in the Stern layer. The difference between effective charge and uncorrected charge (8 and 2.7 for 0.5 M C_3H_7OH and 1 M C_3H_7OH respectively) arises from the fluctuations in the solution(248,251). The degree of dissociation of the micellar charge decreases as the concentration increases (0.296 and 0.220 for 0.5 M C_3H_7OH and 1 M C_3H_7OH respectively Table VI.I.3).

As it can be seen, the addition of aliphatic alcohols to the aqueous solution of C_{12} has changed the light scattering properties of the micelles. The main effect arises from the change in the density and concentration fluctuations. The effect of alcohol as a secondary solvent on those fluctuations, and the optical efficiency of micelles plays also an important role in the observed features of micelles.

VI.If - Conclusions.

The light scattering by alkylammonium bromides in water, and solutions containing various aliphatic alcohols has been examined at 25°C. The observations indicate that the micellar molecular weight increases, as the hydrocarbon chain length increases. Since fluctuations in density, in concentration and charge on the micelle effect the optical efficiency of micelles and the turbidity of the solution, in view of these facts the true micellar number and the effective charge of the micelles, has been observed.

Secondly the effect of aliphatic alcohols on the micelles has been studied, by adding various concentration to the aqueous system. The addition of alcohols first increased (AMW) then it decreased (AMW) with increasing concentration. In addition to this behaviour, they affected the turbidity of the solution in terms of changing the fluctuations in the bulk solution, and the kinetic properties of micelles. The effective charge has also increased, then it decreased with increasing concentration of alcohol. The change in micellar properties is presumably due to the interference effect of alcohol on fluctuations, and electrokinetic properties of micelles in terms of structure promoting and breaking behaviour.

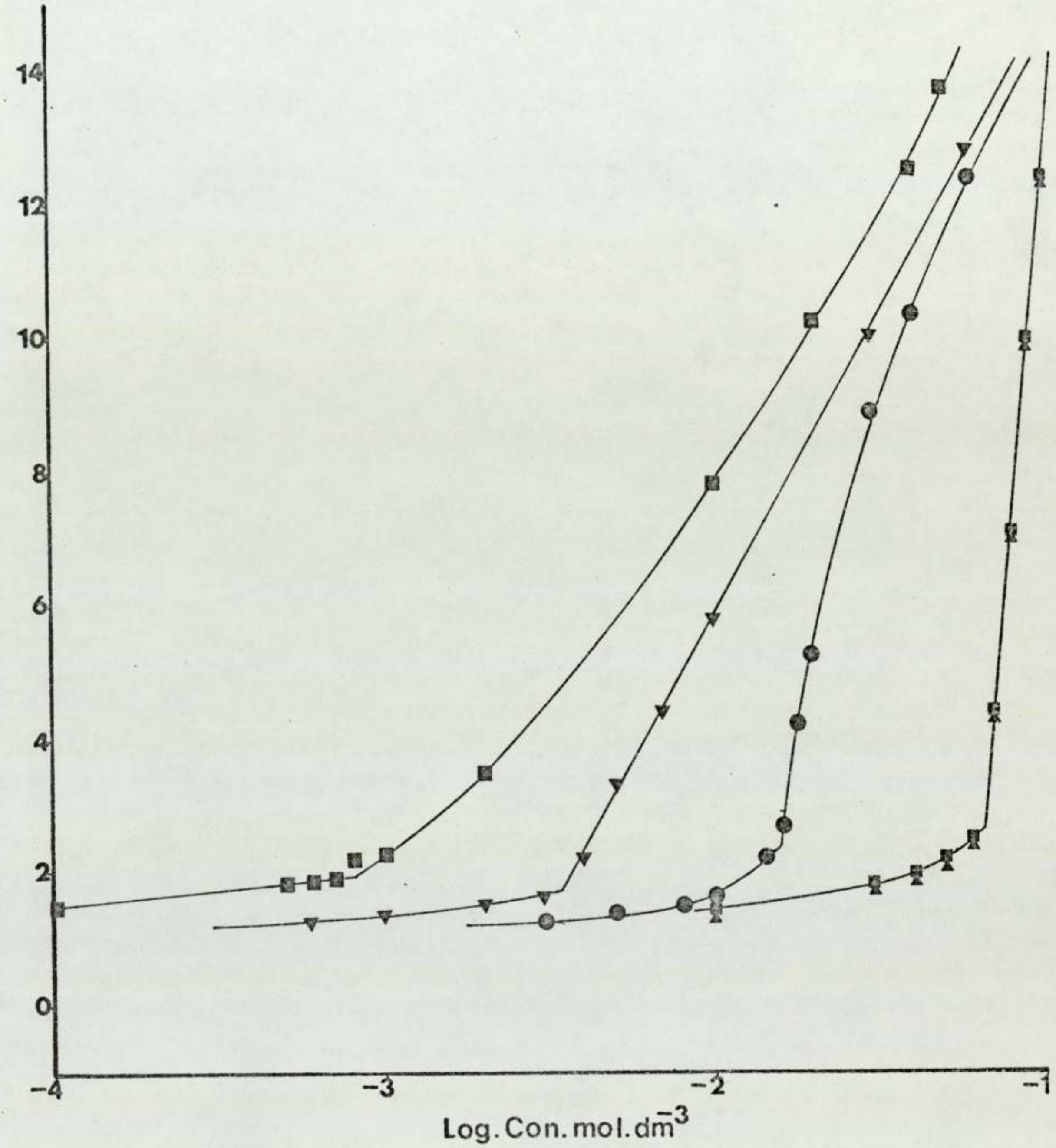


Fig. VI.I Scattering at 90° by aqueous solutions of the alkyltrimethyl ammonium bromides at 25° C; ⧗ C_{10}, ● C_{12}, ▼ C_{14}, and ■ C_{16}

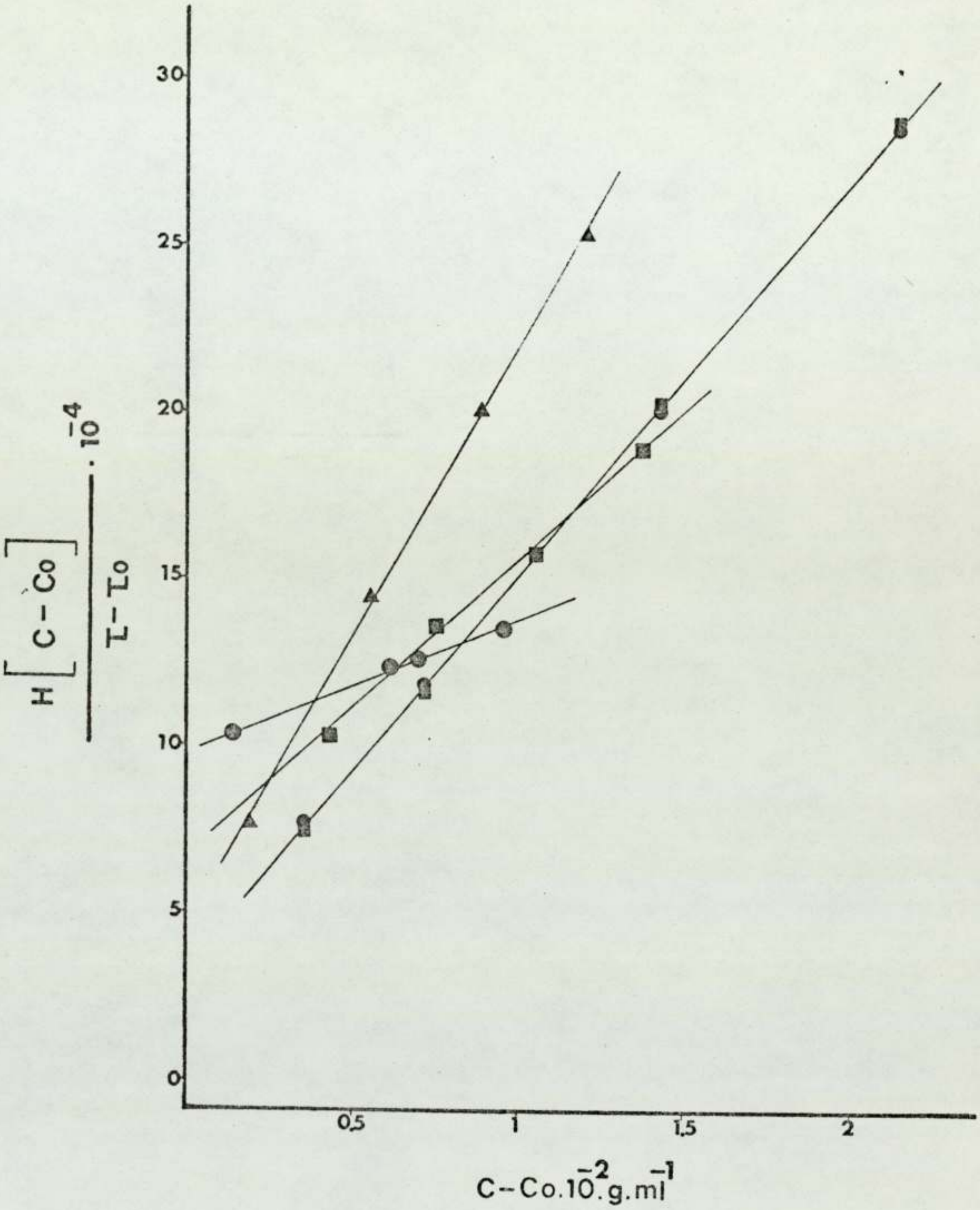


Fig.VI.2 Debye plots of the alkyltrimethyl ammonium bromides in water as a function of C-Co at 25° C; ● C_{10}, ■ C_{12}, ▲ C_{14}, and ● C_{16}

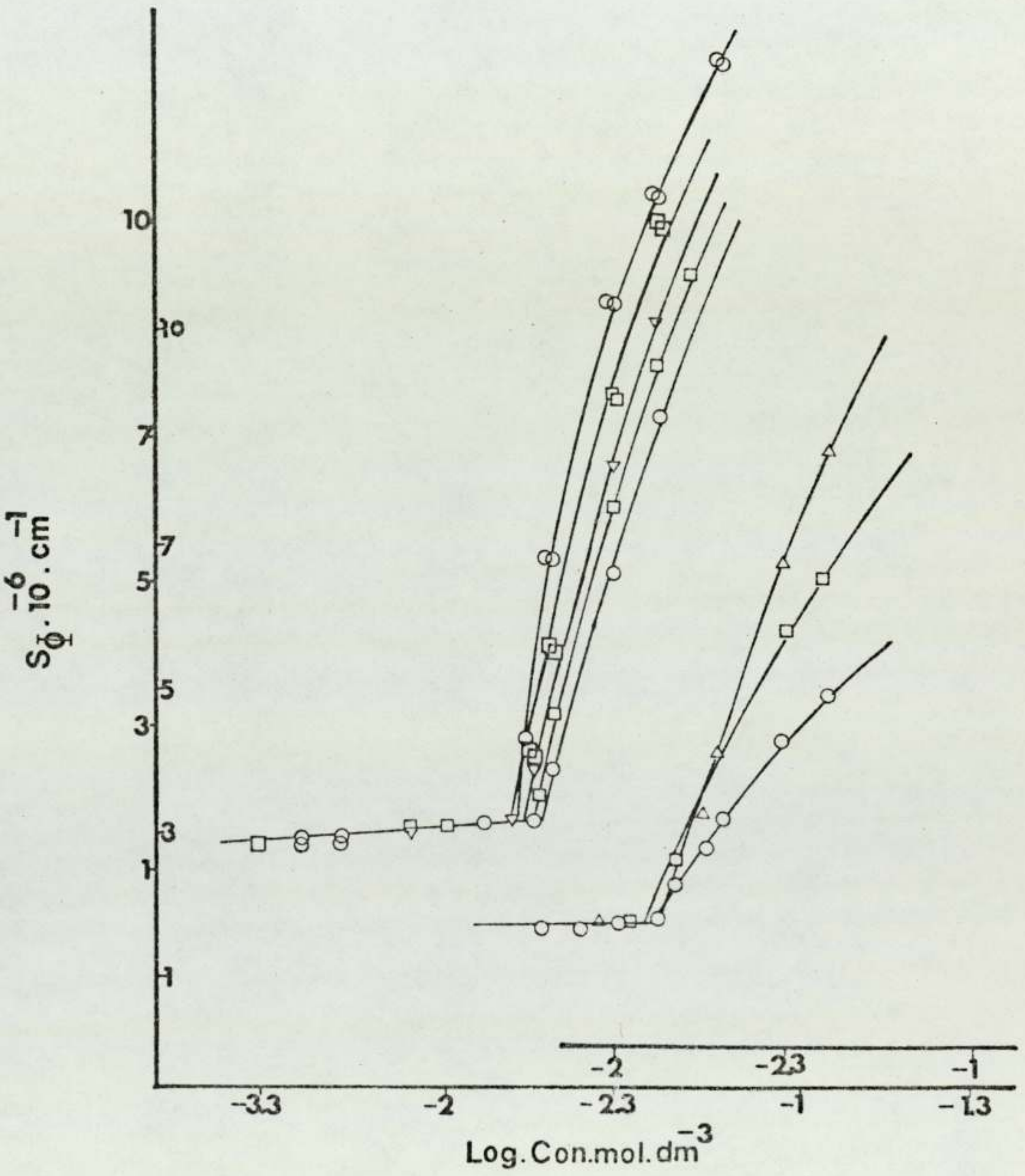


Fig.VI.3 Dependence of the scattering at 90° by dodecyltrimetyl ammonium bromides on the various concentration of methanol and ethanol in water at 25° C; Me-OH: ○○ H_2O. ⧉ 1M, ▽ 2M, □ 3M, and ○ 4M; Et-OH: △ 1M, □ 2M, and ○ 2.8M

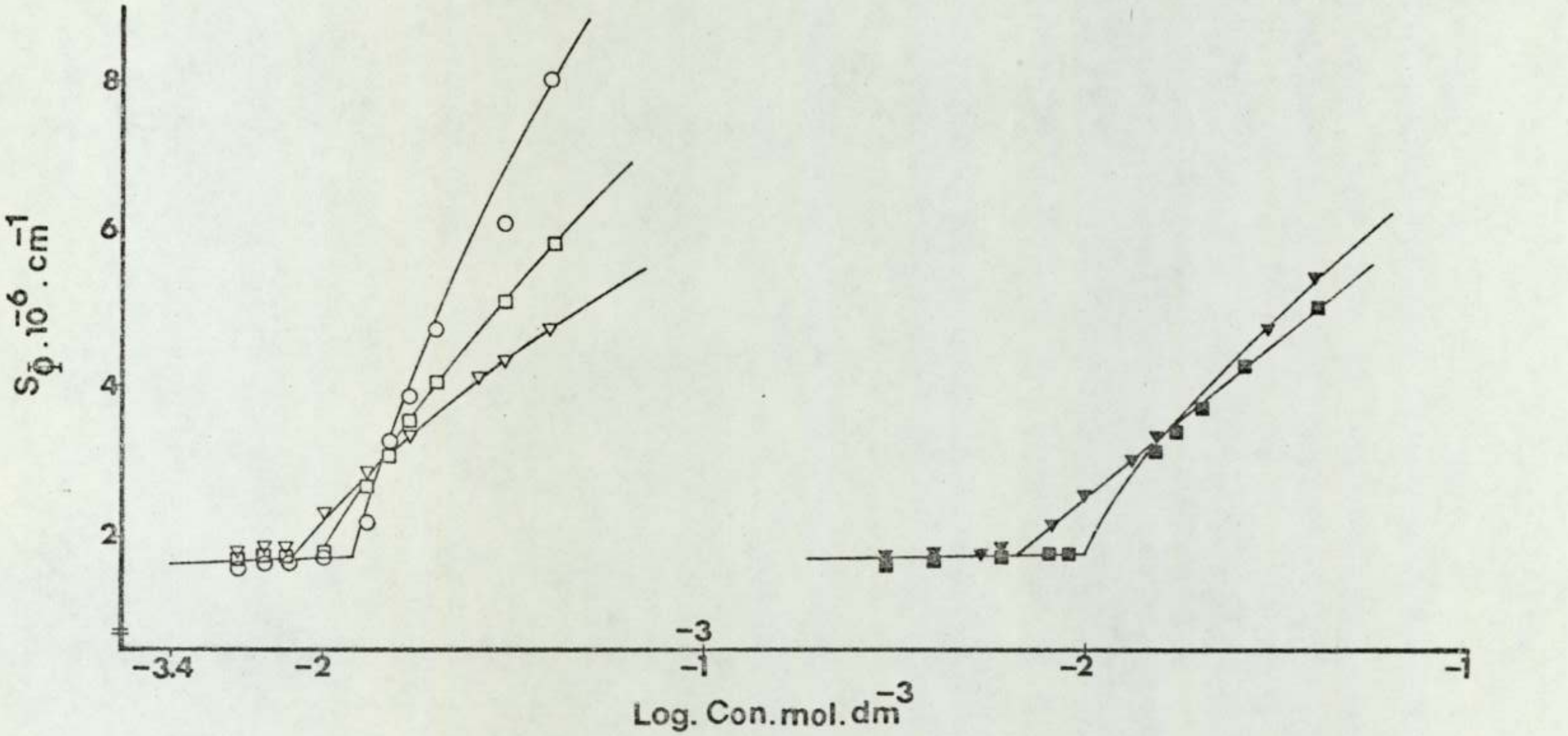


Fig. VI.4 Dependence of the scattering at 90° by dodecyltrimethyl ammonium bromides on the various concentration of propanol and butanol in water at 25° C; Pr–OH: ○ 0.5M, □ 1M, and △ 1.5M ; Bt–OH: ▲ 0.5M, ▨ 1M

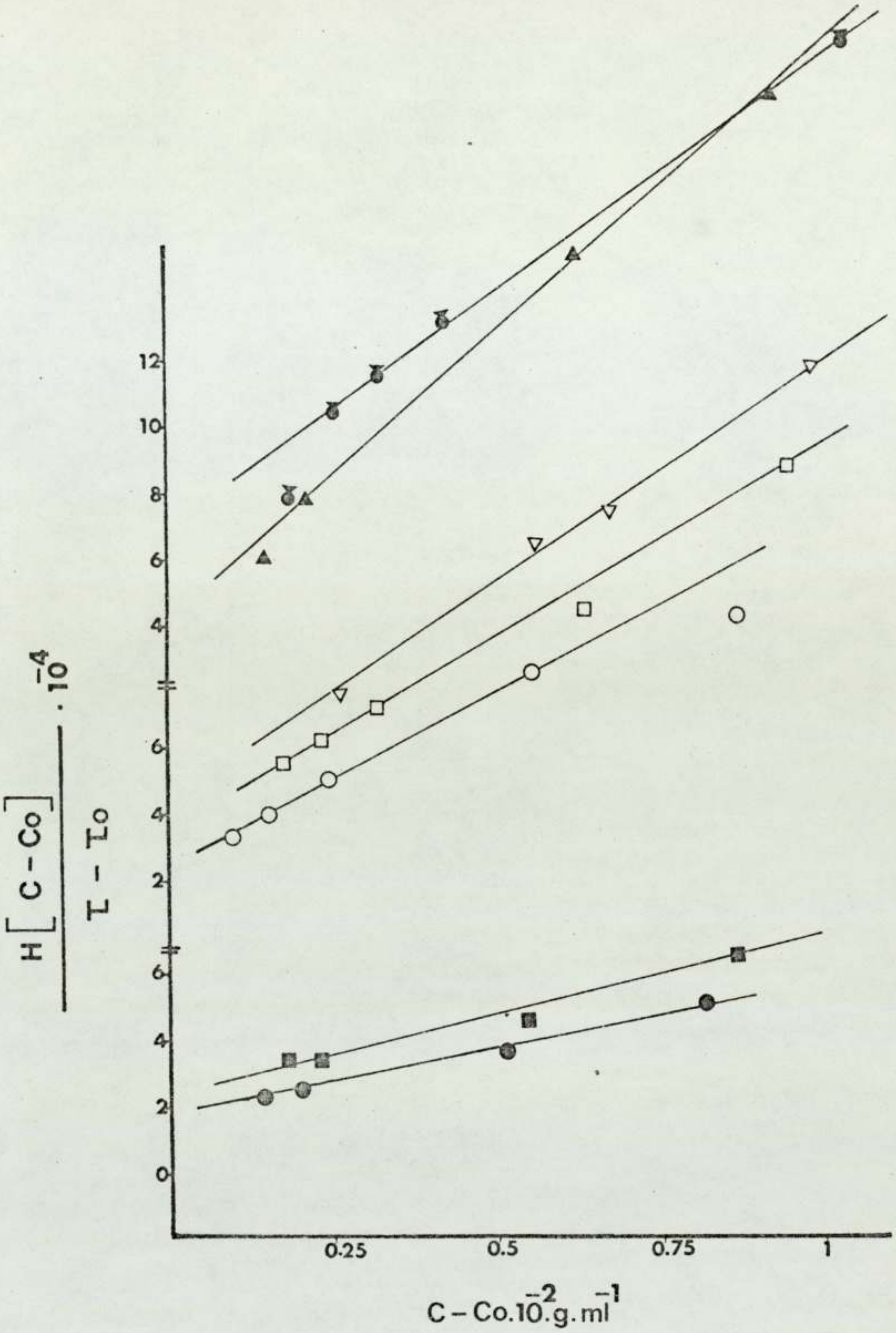


Fig.VI.5 Debye plots of the dodecyltrimethyl ammonium bromidecontaining various concentration of the aliphatic alcohols in water as a function of C-Co at 25° C; Et-OH: ● 1M, ■ 2M; Pr-OH: ○ 0.5M, □ 1M, and △ 1.5M; Bt-OH: ▲ 0.5M, ⧗ 1M

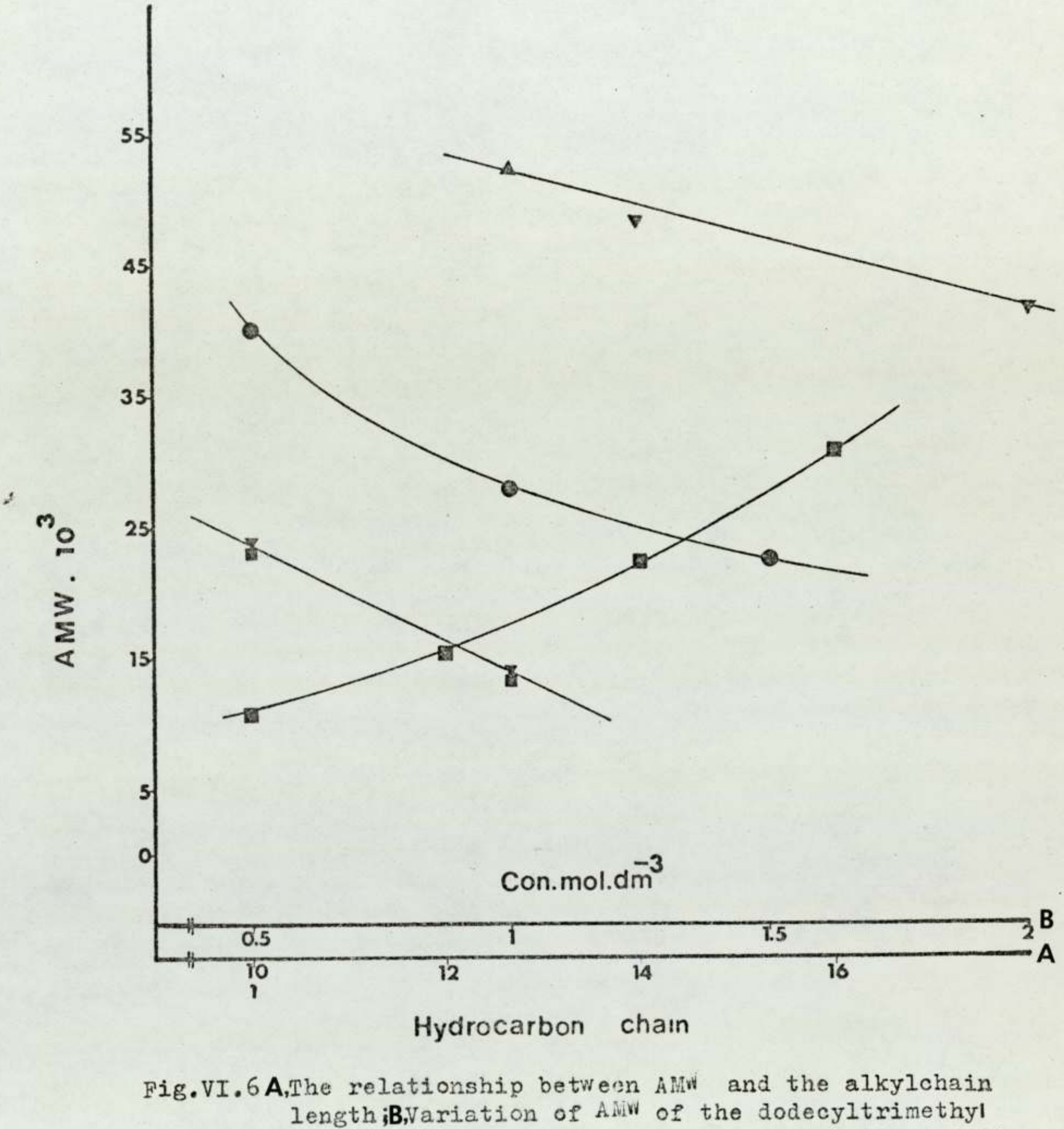


Fig.VI.6 **A**,The relationship between AMW and the alkylchain length;**B**,Variation of AMW of the dodecyltrimethyl ammonium bromide with various concentrations of the aliphatic alcohols at 25° C;**B** ▲ Et-OH , ● Pr-OH, and ▼ Bt-OH ; A ■ AMW

LIHGT SCATTERING BY ALKYLAMMONIUM BROMIDES
IN AQUEOUS SOLUTIONS AT 25° C

TABLE VI.I.1

C mol.dm^{-3}	$S_{\emptyset}$ $.10^{-5}.cm^{-1}$	τ $.10^{-4}.cm^{-1}$	D_R	ΔI ml . g^{-1}	H	C_o mol.dm^{-3}
C_{10}						
1 x 10^{-1}	1.2420	2.0799	1.02	0.152	2.52	6.5 x 10^{-2}
9 x 10^{-2}	1.0122	1.6951				
8 x 10^{-2}	0.7130	1.1940				
7 x 10^{-2}	0.4451	0.7454				
6 x 10^{-2}	0.2532	0.4241				
5 x 10^{-2}	0.2147	0.3595				
4 x 10^{-2}	0.1962	0.3285				
3 x 10^{-2}	0.1869	0.3130				
1 x 10^{-2}	0.1526	0.2555				
C_{12}						
6 x 10^{-2}	1.2372	2.0720	1.02	0.155	2.63	1.55x 10^{-2}
5 x 10^{-2}	1.150	1.9258				
4 x 10^{-2}	1.0385	1.7391				
3 x 10^{-2}	0.8964	1.5012				
2 x 10^{-2}	0.5343	0.8950				
1.8x 10^{-2}	0.4200	0.7034				
1.6x 10^{-2}	0.2691	0.4510				
1.4x 10^{-2}	0.2268	0.3798				
1 x 10^{-2}	0.1613	0.2701				
8 x 10^{-3}	0.1461	0.2450				
5 x 10^{-3}	0.1384	0.2320				
3 x 10^{-3}	0.136	0.2277				
C_{14}						
6 x 10^{-2}	1.249	2.0922	1.03	0.157	2.72	8 x 10^{-4}
5 x 10^{-2}	1.0848	1.8166				
4 x 10^{-2}	0.9164	1.5346				
3 x 10^{-2}	0.7664	1.2835				
2 x 10^{-2}	0.7183	1.2030				
7 x 10^{-3}	0.4498	0.7533				

5 x 10^{-3}	0.3407	0.5710				
4 x 10^{-3}	0.2249	0.3766				
3 x 10^{-3}	0.1662	0.2783				
2 x 10^{-3}	0.1499	0.2510				
1 x 10^{-3}	0.143	0.2395				
C_{16}						
6 x 10^{-2}	1.3713	2.2965	1.03	0.157	2.72	8 x 10^{-4}
5 x 10^{-2}	1.1662	1.9530				
4 x 10^{-2}	1.2530	2.0984				
3 x 10^{-2}	0.7992	1.3384				
2 x 10^{-3}	0.3566	0.5972				
1 x 10^{-3}	0.2339	0.392				
8 x 10^{-4}	0.239	0.4003				
6 x 10^{-4}	0.175	0.2931				
5 x 10^{-4}	0.1813	0.3036				

MICELLAR DIMENSIONS OF THE ALKYLAMMONIUM BROMIDES IN WATER

FROM LIGHT SCATTERING MEASUREMENT

TABLE VI.I.1.A

S.A.A	A	B g.ml	AMW	N_A	N_c	p	$\frac{p}{N_1}$	p'
C_{10}	$9.9\ x10^{-5}$	$4\ x10^{-3}$	10101	36	50	14	0.280	12
C_{12}	$6.5\ x10^{-5}$	$8.5x10^{-3}$	15384	50	63	15	0.238	13.2
C_{14}	$4.42x10^{-5}$	$1.7x10^{-2}$	22624	67	82	16	0.195	14.4
C_{16}	$3.2\ x10^{-5}$	$1.2x10^{-2}$	31250	86	93	8	0.086	7.6

LIGHT SCATTERING DATA FOR THE DODECYL TRIMETHYL AMMONIUM BROMIDE IN WATER CONTAINING ALIPHATIC ALCOHOLS AT 25° C

TABLE VI.I.2

C mol.dm^{-3}	$S_Ø$ .10^{-5} cm^{-1}	τ .10^{-4} cm^{-1}	D_R	C_o mol.dm^{-3}
		1M ,Me-OH		
4.0x10^{-2}	1.0033	1.6802	1.04	1.5 x10^{-2}
3.0x10^{-2}	0.7599	1.2730		
2.0x10^{-2}	0.4116	0.6893		
1.7x10^{-2}	0.2604	0.4361		
1.5x10^{-2}	0.1779	0.2979		
1.3x10^{-2}	0.1726	0.2891		
1.0x10^{-2}	0.1652	0.2766		
8.0x10^{-3}	0.1642	0.2749		
4.0x10^{-3}	0.1544	0.9586		
		2M		
4.0x10^{-2}	0.8646	1.4479	1.04	1.67x10^{-2}
3.0x10^{-2}	0.6584	1.1030		
2.0x10^{-2}	0.3321	0.5562		
1.8x10^{-2}	0.2491	0.4172		
1.6x10^{-2}	0.1952	0.3269		
1.4x10^{-2}	0.1683	0.2820		
1.0x10^{-2}	0.1653	0.2768		
7.0x10^{-3}	0.1660	0.2780		
5.0x10^{-3}	0.1483	0.2484		
		3M		
4.0x10^{-2}	0.8054	1.3487	1.05	1.8 x10^{-2}
3.0x10^{-2}	0.6038	1.0142		
2.0x10^{-2}	0.2881	0.4825		
1.8x10^{-2}	0.2126	0.3560		
1.6x10^{-2}	0.1781	0.2983		
1.3x10^{-2}	0.1639	0.2745		
1.0x10^{-2}	0.1618	0.2710		
8.0x10^{-3}	0.1625	0.2721		
6.0x10^{-3}	0.1529	0.2561		

TABLE VI.I.2.A

C mol.dm^{-3}	S$_{\varnothing}$ .10^{-5}.cm^{-1}	τ .10^{-4}.cm^{-1}	D$_R$	ΔI ml.g^{-1}	H	C$_o$ mol.dm^{-3}
			4M			
4.0x10^{-2}	0.7362	1.2330	1.04	0.035	0.135	1.8 x10^{-2}
3.0x10^{-2}	0.5107	0.8553				
2.0x10^{-2}	0.2480	0.4153				
1.7x10^{-2}	0.1807	0.3030				
1.5x10^{-2}	0.1660	0.2780				
1.3x10^{-2}	0.1550	0.2596				
9.0x10^{-3}	0.1550	0.2596				
4.0x10^{-3}	0.1581	0.2647				
			1M, Et-OH			
4.0x10^{-2}	0.8420	0.4101	1.04	0.0794	0.693	1.35x10^{-2}
3.0x10^{-2}	0.6811	1.141				
2.0x10^{-2}	0.4198	0.7030				
1.8x10^{-2}	0.3320	0.5559				
1.5x10^{-2}	0.2157	0.3612				
1.3x10^{-2}	0.1813	0.3040				
1.0x10^{-2}	0.1881	0.3150				
8.0x10^{-3}	0.1757	0.2942				
5.0x10^{-3}	0.1673	0.2802				
			2M			
4.0x10^{-2}	0.6640	1.1120	1.054	0.077	0.65	1.2 x10^{-2}
3.0x10^{-2}	0.5951	0.9966				
2.0x10^{-2}	0.3669	0.6144				
1.8x10^{-2}	0.3101	0.5193				
1.5x10^{-2}	0.2750	0.4610				
1.3x10^{-2}	0.1764	0.2954				
1.0x10^{-2}	0.1800	0.3014				
8.0x10^{-3}	0.1800	0.3014				
4.0x10^{-3}	0.1800	0.3014				

TABLE VI.I.2.B

C mol.dm^{-3}	$S_{\varnothing}$ $.10^{-5}$ cm^{-1}	τ $.10^{-4}$ cm^{-1}	D_R	ΔI ml.g^{-1}	H	Co mol.dm^{-3}
2.8 M						
$4.2\text{x}10^{-2}$	0.4472	0.7489	1.05	-	-	$1.3\text{x}10^{-2}$
$3.0\text{x}10^{-2}$	0.4353	0.7289				
$2.0\text{x}10^{-2}$	0.3181	0.5330				
$1.8\text{x}10^{-2}$	0.2816	0.4720				
$1.5\text{x}10^{-2}$	0.2116	0.3543				
$1.3\text{x}10^{-2}$	0.1850	0.3098				
$1.0\text{x}10^{-2}$	0.1832	0.3070				
$8\ \text{x}10^{-3}$	0.1756	0.2941				
$5\ \text{x}10^{-3}$	0.1672	0.280				
0.5M, Pr-OH						
$4\ \text{x}10^{-2}$	0.8007	1.3410	1.02	0.107	1.24	$1.2\text{x}10^{-2}$
$3\ \text{x}10^{-2}$	0.6142	1.0286				
$2\ \text{x}10^{-2}$	0.4794	0.8030				
$1.7\text{x}10^{-2}$	0.3887	0.6510				
$1.5\text{x}10^{-2}$	0.3146	0.5268				
$1.3\text{x}10^{-2}$	0.2258	0.3781				
$1\ \text{x}10^{-2}$	0.1812	0.3034				
$8\ \text{x}10^{-3}$	0.1763	0.2952				
$4\ \text{x}10^{-3}$	0.1675	0.2810				
1 M						
$4\ \text{x}10^{-2}$	0.5822	0.9750	1.06	0.102	1.13	$9.5\text{x}10^{-3}$
$3\ \text{x}10^{-2}$	0.5100	0.8541				
$2\ \text{x}10^{-2}$	0.4056	0.6792				
$1.7\text{x}10^{-2}$	0.3516	0.5888				
$1.5\text{x}10^{-2}$	0.3101	0.5193				
$1.3\text{x}10^{-2}$	0.2798	0.4685				
$1\ \text{x}10^{-2}$	0.1823	0.3053				
$8\ \text{x}10^{-3}$	0.1772	0.2967				
$4\ \text{x}10^{-3}$	0.1683	0.282				

TABLE VI.I.2.C

C mol.dm^{-3}	S_0 $.10^{-5}.cm^{-1}$	L $.10^{-4}.cm^{-1}$	D_R	ΔI ml.g^{-1}	H	C_o mol.dm^{-3}
1.5M						
4×10^{-2}	0.47340	0.7930	1.02	0.098	1.085	8.25×10^{-3}
2.6×10^{-2}	0.4073	0.6821				
1.3×10^{-2}	0.2812	0.4710				
1×10^{-2}	0.2312	0.3872				
9×10^{-3}	0.1921	0.3220				
7×10^{-3}	0.1732	0.2901				
5×10^{-3}	0.1701	0.285				
0.5M, Bt-OH						
4×10^{-2}	0.5412	0.9063	1.03	0.120	1.48	1.0×10^{-2}
3.8×10^{-2}	0.4735	0.7930				
2.6×10^{-2}	0.4300	0.7201				
1.7×10^{-2}	0.3450	0.5777				
1.5×10^{-2}	0.3320	0.5559				
1.3×10^{-2}	0.2910	0.4873				
1.0×10^{-2}	0.20	0.3350				
9×10^{-3}	0.1801	0.3020				
6×10^{-3}	0.1751	0.2932				
5×10^{-3}	0.1742	0.292				
1M						
4×10^{-2}	0.515	0.8624	1.02	0.112	1.37	6.6×10^{-3}
2×10^{-2}	0.369	0.6180				
1.7×10^{-2}	0.337	0.5644				
1.5×10^{-2}	0.316	0.5292				
1.3×10^{-2}	0.312	0.5225				
1×10^{-2}	0.256	0.4287				
8×10^{-3}	0.2234	0.3741				
6×10^{-3}	0.1802	0.3020				
4×10^{-3}	0.1723	0.2885				
2×10^{-3}	0.1651	0.2765				

MICELLAR DIMENSIONS OF THE DODECLYTRIMETHYL AMMONIUM BROMIDE IN WATER CONTAINING ALCOHOLS FROM LIGHT SCATTERING MEASUREMENT

TABLE VI.I.3

A	B g.ml	AMW	N_A	N_C	p'	p	$\frac{p}{N}$	C $mol.dm^{-3}$
Et-OH								
1.9×10^{-5}	3.75×10^{-3}	52630	170	202	30.3	33	0.163	1 M
2.4×10^{-5}	5.0×10^{-3}	41670	135	162	25.6	28	0.173	2 M
Pr-OH								
2.5×10^{-5}	1.06×10^{-2}	40000	130	179	45	53	0.296	0.5 M
3.6×10^{-5}	1.1×10^{-2}	28000	91	114	22.3	25	0.220	1 M
4.4×10^{-5}	1.3×10^{-2}	22730	74	94	18.80	21	0.223	1.5 M
Bt-OH								
4.2×10^{-5}	1.73×10^{-2}	23800	77	104	25	29	0.278	0.5 M
7.0×10^{-5}	1.33×10^{-2}	14280	46	58	10.57	12	0.207	1 M

CHAPTER VII - Micellar Properties of Polyoxyethylene Monohexadecyl ethers in aqueous solution and containing additives.

VII.Ia - Viscometric measurements on dilute aqueous solutions of n-alkylpolyoxyethylene surfactants.

The micellar structure of non-ionic surfactants has not been extensively examined, in contrast to the investigations on the micellar structure of ionic surfactants. Kushner-Hubbard(262) have discussed the negative solubility coefficients of non-ionic surfactants in aqueous solution, in terms of the interactions of surfactant with solvent molecules. However the deviation of $[\eta]$ of the micelles from the Einstein value ($0.025\ g.dl^{-1}$) has been interpreted by means of the change in micellar shape, and the solvent effect on the surfactant molecules.

Due to this fact, the solubility of the surfactant molecules in water have been attributed to the hydration phenomenon, which occurs due to the affinity of the oxyethylene chain to water molecules.

The effect of the hydrophilic group of the surfactant molecule on the stability of non-ionic surfactants in solution has been studied by Reich(263). According to his view, the cross-sectional area of the hydrophilic group of a non-ionic surfactant plays an important role preventing the association of individual molecules. However, this view has been strengthened(188) by including the heat of hydration, and the configurational entropy terms of the flexible hydrophilic chain.

The factors which are involved in non-ionic micelle formation in aqueous solution have been also investiged by Schick et al.(172). Their observations indicate that the degree of association of the monomers depends on the length of both hydrophilic, and hydrophobic groups. They have also concluded that the aggregation number of non-ionic micelles decreases as the ethylene oxide chain length increases.

On the other hand, the extent of hydration of non-ionic surfactants in aqueous solutions has been examined by Schott(176), taking into account its role in the stability of their aqueous solutions.

The study of dilute aqueous solution of non-ionic surfactants was carried out by measuring the absolute viscosities of the surfactants at 25°C, using a U-tube viscometer and the C_o in aqueous surfactant solution was determined as described in Chapter II. As can be seen in Fig.VII.1, the relative viscosity increases with increasing EO chain length (1.0059 and 1.0083 for 5×10^{-4} mol.dm^{-3} of $C_{16}E_{10}$, and $C_{16}E_{18}$ respectively Table VII.I.1). The increase in relative viscosities of the cationic surfactants in aqueous solutions, and containing various additives has been discussed (Chapter II) in terms of hydration, electroviscous effect, particle shape and hydrophobic interactions.

In aqueous solution of non-ionic surfactants, since there are not the electrical forces involved in the molecular interactions of the non-ionic surfactant with water molecules, the increase in viscosity can be attributed to the possible hydration of molecules, change in particle shape, and the hydrophobic interactions of ethylene-oxide chain length, and hydrophobic group with water molecules(172,176,262). This long range interaction increases water structure around the non-polar and polar groups. The aggregation of monomers due to these interactions moves the nonpolar part of the molecule to the thermodynamically favourable to nonpolar region, reducing hydrocarbon water interface, and the release of energy involved in this process causes a physico-chemical change at certain concentration of the aqueous surfactant solution, which is C_o (5.6×10^{-5} mol.dm^{-3} and 1.4×10^{-5} mol.dm^{-3} for $C_{16}E_{10}$, and $C_{16}E_{60}$ respectively Tables VII.I.1, VII.I.1.A).

The C_o decreases as the EO chain length increases (Figs.VII.2, VII.5). The discrepancies in C_o values between this work and the literature values will be discussed in one of the sections of this chapter. The intrinsic viscosity of the micelles was determined in the same way as described in Chapter II. As can be seen in Fig.VII.8 (Table VII.I.1.B) the $[\eta]$ increases as the EO chain length increases (0.039 g.dl^{-1} and 0.117 g.dl^{-1} for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively).

The increment in $[\eta]$ is due to the hydration, the change in the shape, and size of the micelles(172,176). No clear picture has yet been obtained of how the hydration is affected by the ethylene oxide chain length. Elworthy-Macfarlane(264) have discussed that the hydration of non-ionic surfactants is due to a trapping of water molecule in the mesh of oxyethylene chain length. According to their view the hydration of the micelles depends on the length of the hydrophilic group, its degree of contraction, and on the geometry of the micelle.

The obtained higher intercepts on $\frac{\eta_{sp}}{\phi}$ versus ϕ curve have been discussed in terms of micellar asymmetry, the increase in temperature effects and the radial length of the micelle occupied by the polyoxyethylene chain. This increase induces the trapping of water molecules, in the mesh of polyoxyethylene chains. It has been also shown(265) that the micellar asymmetry develops at a higher temperature, and the higher Huggins constant, and the negative second virial coefficient B have been used as an indication of the asymmetry of the micelles.

However, the hydration of polyoxyethylene surfactant has been determined in terms of crystal density and specific volume of anhydrous non-ionic surfactants(175). The calculated g. water/g surfactant decreases with increasing ethylene oxide chain length (1.152 g /g.surfactant, 0.38 g /g.sur.for $C_{16}E_{10}$,$C_{16}E_{60}$ respectively, Table VII.I.6). These results are contrary to the values given by El Eini et al.(266).

On the other hand, the Huggins constants of the surfactant molecules in aqueous solution were calculated as described in Chapter II. The Huggins constant ($\simeq 2.0$) is given by Tanford(327) and Schott(176) as an indication of sphericity of the uncharged rigid particles. In view of this observation the calculated Huggins constant are 5.84, 4.98 and 4.63 for $C_{16}E_{10}$, $C_{16}E_{18}$ and $E_{16}E_{60}$ respectively (Table VII.I.1.B).

As can be seen, there is considerable deviation from the value $\simeq 2.0$. Since the electrical forces and surface charge do not exist in the systems used, this deviation and high $[\eta]$ values of micelles can be attributed to the change in micellar shape, size, hydrophobic interactions and the hydration. In the light of this consideration, this view can be expanded to investigate the above properties of micelles in aqueous solution.

The intrinsic viscosity $[\eta]$ of micelles of $C_{16}E_{10}$ is $0.039\ g.dl^{-1}$ (Table VII.I.1.B). This value of $[\eta]$ is less compared with $[\eta]$ of the spherical micelles of C_{10} (cationic surfactant, $0.06\ g.dl^{-1}$, Table II.I.1). The increase in $[\eta]$ in ionic surfactant solutions has the contributions from electroviscous effect, hydration and shape of the micelles. If it is assumed that the increment in $[\eta]$ due to electroviscous effect is not significant, then one can conclude that the hydration of the micelles is the dominant factor beside the shape of the micelle.

In view of this assumption,when the $[\eta]$ value of micelles of C_{16} is compared with the $[\eta]$ of the micelles of $C_{16}E_{60}$, as can be seen (Tables VII.I.1.B, II.I.1.A) the difference is $0.021\ g.dl^{-1}$. If the micelles of both surfactants are spherical, and only the hydration effect is a major factor, with the size of micelles for increase in $[\eta]$, then one can say considering Einstein's theory that the increase in $[\eta]$ of micelles of polyoxyethylene monohexadecyl ethers should be higher compared with the small spherical micelles of ionic surfactants, since the hydration is a function of the polyoxyethcylene chain length,as this part of micelles is involved in the trapping of water molecule(264).

It is apparent that even though the non-ionic surfactant ($C_{16}E_{60}$) has the same hydrophobic surface area compared with the cationic surfactant (C_{16}TAB), and a long oxyethelere chain the increase in $[\eta]$ is not significant (0.096 g.dl^{-1} and 0.117 g.dl^{-1} for C_{16} and $C_{16}E_{60}$ respectively). In the light of this approach we can examine the possible shape of the micelles. When the oxyethylene chain length is increased, while the hydrocarbon surface is constant, it causes an increase in penetration, and greater density in the packing of the polyoxyethylene chains in the outer shell(176). This tighter network holds less water molecules than the more open network of shorter chains. The long chain length promotes the water of hydration of micelles to be squeezed out(176). However the hydration of micelles has also been discussed in view of the geometry of micelle, and the length of the hydrophilic group(264).

It has been concluded that since the hydrocarbon chain lengths are parallel to one another along the long axis of the rod type of micelle, the volume per monomer in which water molecules are trapped is smaller than in the spherical case. On the other hand, on the assumption of the state of very closely packed hydrophilic groups, which are very close to the hydrocarbon region (micellar core), water molecules may come into contact with the hydrocarbon region. This contact could increase the interfacial tension on the hydrocarbon-polyoxyethylene interface, causing the change in the micellar shape and size(265) (elongation).

In view of these facts, the shape of the micelles was examined in terms of hydrodynamic, and light scattering data and the approach was based on the elongated type of micelle. The shape function of the micelles of the non-ionic surfactants was calculated using equation (II-44), taking into account the specific volume of the monomer at C_0, which was calculted from corresponding partial molal volumes of the micelles. The calculated shape function of the micelles are (4.3) and (14.57) for $C_{16}E_{10}$ and $C_{16}E_{60}$ (Table VII.I.6).

These results also confirm that the deviation from the Einstein value for spherical particles 0.025 g.dl^{-1} is due to one of these facts, which is the change in micellar shape. These obtained results were compared with the table given by Mehl et al.(169) and Scheraga(170). In those tables this shape function (4.152) corresponds to the axial ratio (3.5) for prolate, while (4.382 corresponds to the axial ratio (4.5) for oblate. In view of these reported values for prolate and oblate particles, the obtained shape functions were substituted into equation (II-45,II-46), in order to derive the axial ratio of the semi axis of revolution to equatorial radius of the micelles.

The observation in this work indicates that the axial ratios of the micelles fit well to the prolate type shape. The axial ratio (3.7) for $C_{16}E_{10}$ corresponds the shape function (4.3) which is very close to the shape function for prolate given by Mehl et al.(169) and Scheraga (170).

On the other hand the higher axial ratio of the prolate micelles of $C_{16}E_{60}$ (10.4) corresponds to the shape function of the micelles (14.57) agreeing well with the value of axial ratio of the prolate particles (10.0) corresponding to the shape function (13.634), which is very close to the shape function determined for $C_{16}E_{60}$.

In the case of oblate/ obcets, the shape function 14.80 corresponds to an axial ratio 20 which is considerably higher than the observed value. The dimensions of the micelles were calculated in terms of the density of micelles, and micellar molecular weight (from light scattering data). The obtained partial specific volumes of the monomers from corresponding partial molal volumes are 0.91361 ml/g and 0.8020 ml/g at 25°C for $C_{16}E_{10}$, and $C_{16}E_{60}$ respectively (Table VII.I.2).

From this observation, it is apparent that the density of micelles are higher than the density of liquid hexadecane at 25°C at constant pressure. But the pressure in the interior of the micelle is not known. It is reasonable to assume that the core of micelles has some amount of water molecules. Similar type of results were obtained for the density of the cationic micelles from the partial molal volumes of the corresponding micelles. The view of the interior of micelles containing water molecules has also been confirmed by some investigators(162,163,164,165).

However, the observed micellar dimensions are 130 Å and 35 Å for Aa, and Ab of $C_{16}E_{10}$ (Table VII.I.6), and the equatorial radius of micelles increases as the EO increases, while the semiaxis of revolution decreases (198 Å and 19 Å for Aa, and Ab of $C_{16}E_{60}$. The obtained shape function, and partial specific volume were used to calculate the hydrated volume of the micelles, in terms of the equation (II-36) (0.642×10^{-18} ml and 0.295×10^{-18} ml for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively, Table VII.I.6).

As can be seen, the hydrated volume of micelles decreases as the EO chain length increases. This observation confirms also that the hydration of non-ionics, decreases as the hydrophilic chain length increases. This is due to the change in configurational orientation of the polyoxyethylene group. These experimental results are contrary to the hydration phenomenon, which have been observed by several investigators(172,176,263,264,265) in aqueous non-ionic systems. The observed dehydration of micelles (decrement in hydration) can be discussed in terms of the prolate shape of the micelles, which are less hydrated than the spherical micelles, and very close packing of the long ethylene oxide chains near the hydrocarbon region (micellar core) which squeezes water molecules out from the outer shell of the micelles.

VII.Ib - Partial Molal volumes of Polyoxyethylene Monohexadecyl ethers in aqueous solution.

The volumetric properties of short chain alcohols have been investigated by Friedman-Scheraga(211), in terms of the environmental effects on the partial molal volumes of the alchols, as the alcohols transfer from a hydrocarbon environment to an aqueous region. On the other hand Corkill et al.(217) have determined the partial molal volume properties of ionic, and non-ionic surfactants below the C_o, and above the C_o considering molecular structure of surfactants. They have concluded that the methyl group remote from the hydrophilic group contributes to an increase of P.M.V, while the additional methylene group which is close to a hydrophilic centre gives a negative contribution to P.M.V.

However, in aqueous systems the involved volume change due to the alkyl chain length has been interpreted by Nemethy and Scheraga(5), in terms of the pertubation of water molecules by alkyl chain length, introducing negative volume change.

When $\partial\overline{V}_2{}^E/\partial X_2$ passes through a minimum for a given solute at a given concentration, and at low temperature becomes negative(80), this behaviour can be attributed to the decrement effect per mole of solute to the total volume of the system, as the concentration of solute increases. It is apparent that the solute-solute effects play an important role even in very dilute solution. However it has been shown that the slope of the curve $\overline{V}_2(X_2)$ depends on the ratio of polar to nonpolar groups in the solute molecule(213).

This observation indicates that the negative slope of curve $\overline{V}_2(X_2)$ decreases in magnitude as the polar group increases. However in the case of a very polar solute, the slope of the curve is near to zero. In the light of this work one can say that as the nonpolar nature of the solute decreases, its ability to influence water structure at long range decreases(213).

However in the case of alcohols in water $\partial\overline{V}_2{}^E/\partial X_2$ becomes more negative moving to lower X_2, as the nonpolar group of alcohol increases in size. This behaviour is maximum in t-butyl group which is of a size that is more favourable to clathrate-type structure stabilization(116).

The structuring effects of mixed solutes can be examined considering another aspect of their volumetric behaviour, which is their ability to shift the temperature of maximum density of water. The observed positive temperature of maximum density of water in lower alcohols, ethers, and ketones supports the idea that positive $\Delta\theta$ corresponds to a stabilization of the intermolecular structure of water(215). This view is strengthened by the observation for D_2O $\theta = 11°$, which is thought due to stronger hydrogen bonds in this liquid.

Since the formation of micelles involves the transfer of monomers from aqueous region to nonpolar environment$^{(217)}$ and the observed micelle formation (Chapter IV) was accompanied by a volume change at C_0, the partial molal volume properties of non-ionic surfactants were also investigated by the same approach. The partial molal volumes of non-ionic surfactants below the C_0, and above the C_0 were calculated at 25°C as described in Chapter IV(Figs.VII.10, VII.11). As can be seen in Table VII.I.2, the $\overline{V}_1$ is higher than the $\overline{V}_0$ in all non-ionic surfactants studied. (620.05 ml/mole and 624 ml/mole for $C_{16}E_{10}$ below the C_0 and above the C_0 respectively). However the $\overline{V}_1$ increases as the EO chain length increases (964.5 ml/mole and 2316.6 ml/mole for $C_{16}E_{18}$ and $C_{16}E_{60}$ respectively).

The observed $\overline{\Delta V_1}$ during the micelle formation (i.e. the volume change due to transfer of monomers to nonpolar environment) shows a decrement as the EO chain length increases (Table VII.I.2 3.95 ml/mole and 2.0 ml/mole for $C_{16}E_{10}$ and $C_{16}E_{30}$ respectively). Corkill et al.$^{(217)}$ have also observed similar behaviour for n-alkylsulphinyl alkanols at 25°C. $\Delta\overline{V}_1$ decreases also as the hydrophilic group increases (3.2 ml/mole and 2.7 ml/mole for n-alkylsulphinyl alkanols ($C_6SO(CH_2)_nOH$) containing two and four $-CH_2-$ group in hydrophilic group).

The increment in $\overline{V}_1$ is 29 ml/mole ($\overline{V1D^\circ}$) per ethylene oxide chain length ($-CH_2-CH_2-O-$). It is apparent that at C_0 each addition to the EO chain length gives an increase in $\overline{V}_1$ as the environment of the monomers is changed. However Corkill et al.$^{(217)}$ showed that the increment in partial molal volume above the C_0 is higher than below the C_0 (17.3 ml/mole and 15.8 ml/mole respectively for $C_2SO(CH_2)_2OH$.

It is apparent that as the hydrophilic group increases while the hydrophobic surface area is constant, the volume change is positive

(1.5 ml/mole). On the other hand, in this work the observation indicates that the change in $\overline{V}_0$ per (-CH_2-CH_2-O-) group is lower than the change in $\overline{V}_1$ (Table VII.I.2, 28.7 ml/mole). The increment in partial molal volume per (-CH_2-CH_2-O-) is shown in Fig.VII.12. The difference between $\overline{V}1D^\circ$ and $\overline{V}IC^\circ$ is 0.3 ml/mole. This increment can be interpreted by the affinity of ethylene oxide chain length for water molecules, which causes the hydration. The number of water molecules bound per monomer of micelles, and the number of water molecules in core of micelles might be the reason for the increase in partial molal volume during micellization(267).

However the observed volume change at C_0 (0.3 ml/mole) is less compared with the value (1.5 ml/mole) given by Corkill et al.(217) This can be interpreted taking into account the particle shape of the micelles, and monomers since polyoxyethylene monohexadecyl ethers have a long hydrophobic group. It has been observed that the prolate type micelle is less hydrated than the spheroid micelle. Although the alkyl chain length appears more expanded in the core of the micelle than in the normal liquid form(217), the less increment in partial molal volume change can be attributed to the hydrophilic groups, which are closely packed near the hydrocarbon region (micellar core) squeezing water molecules out from the outer shell of the micelles(176).

Corkill et al.(217) have also shown that the methylene groups near to the hydrophilic centre show a contraction in the micellar state, as opposed to the expansion of the alkyl chain during the change of environment.

This is due to retention of the aqueous environment of methylene groups, which are in the proximity with the hydrophilic group on micellization. The increment in $\overline{V}_1$ during micellization as function of the alkyl chain length has been also discussed in terms of the retention of hydrocarbon-water contact by the methylene groups near to the hydrophilic centre in the micellar state.

A nuclear magnetic resonance study in several surface-active agents(268), and the measurements of the thermodynamic parameters of micellization have indicated a similar pattern. These facts confirm that the hydration of hydrophilic group, and the methylene groups near to the hydrophilic centre plays a unique role in the increment in $\overline{V}_1$ during the micellization.

VII.Ic - Light scattering from Polyoxyethylene Monohexadecyl ethers in aqueous solution and containing organic additives.

VII.Ic1- Light scattering from polymer single solvent systems.

A polymer solution at infinite dilution is considered to contain (n) solute molecules in a unit volume dV, and when it is illuminated by an unpolarized beam, each particle behaves as a dipole with a moment $p = \alpha' E$, under the influence of the electric field E of the incident beam. The intensity of scattered light at an angle of observation $\Phi = 90°$ by the (n) independent particles can be given by an equation(269)

$$R_{90} = \frac{8\pi^4 n}{\lambda_0^4} (a')^2 \qquad \text{VII-1}$$

For the dilute polymer solutions a' can be evaluated from the dielectric constant or the refractive index $\overline{n}$ ($D = \overline{n}^2$)

$$a' = \frac{\overline{n}^2 - \overline{n}_0^2}{4\pi n} \qquad \text{VII-2}$$

If the medium is infinitely dilute, $\overline{n}$ is a linear function of the solute concentration

$$\overline{n} - \overline{n}_0 = c \frac{d\overline{n}}{dc} \qquad \text{VII-3}$$

where $\frac{d\overline{n}}{dc}$ is the refractive index increment of the solution as a function of the polymer concentration. The number of particles per unit volume can be defined taking into account the molecular weight, and Avagadro number by $c = nM/N_0$ then the relation between a', and the optical properties of the system can be derived by combining equation (VII-2) and (VII-3),

$$a' = \frac{\bar{n}_o M}{2\pi N_o} \frac{d\bar{n}}{dc} \qquad \text{VII-4}$$

and substituting equation (VII-4) into equation (VII-1) the Rayleigh ratio becomes

$$R_{90} = \frac{2\pi^2 \bar{n}_o^2}{\lambda_o^4 N_o} \left(\frac{d\bar{n}}{dc}\right)^2 cM \qquad \text{VII-5}$$

At an angle of observation Φ, when the Rayleigh ratio R_Φ for unpolarized light is corrected for light depolarization, then equation (VII-5) becomes

$$R_\Phi = K \left(\frac{d\bar{n}}{dc}\right)^2 cM \; (1+\text{Cos}^2\Phi) \qquad \text{VII-6}$$

where

$$K = \frac{2\pi^2 \bar{n}_o^2}{\lambda_o^4 N_o}$$

However at a given angle Φ, the Rayleigh ratio for unpolarized light can be written taking into account the particle function

$$\frac{R_\Phi}{1+\text{Cos}^2\Phi} - K \left(\frac{d\bar{n}}{dc}\right)^2 \left[\frac{1}{{}^1/_{Mp\Phi} + 2BC}\right] \qquad \text{VII-7}$$

The equations described above are applicable to the dilute aqueous polymer solutions composed of a polymer dissolved in only one solvent. It is quite evident that when a third component is added to the system it brings local modifications of the refractive index, which affects the scattering by particles. In this case, when the turbidity or (scattering) is extrapolated to zero concentration of polymer, the results show deviation due to the second solvent or precipitant, which cannot be explained by the change in the refractive index increment of solution alone. Ewart et al.$^{(257)}$ have studied the light scattering of polymer systems containing additives. According to their observations of the polystyrene in benzene-methanol system, the value of Hc/τ extrapolated to zero concentration of polymer differs considerably from $(Hc/\tau)_{c=0}$ determined in pure benzene, and varied with the concentration of methanol.

Ewart et al.(257) have defined light scattering in terms of turbidity in the polymer systems containing various concentrations of organic additive by

$$\tau = \frac{8\pi^3}{3\lambda_0^4 N_0} \left(\frac{\epsilon - \epsilon_1}{c} \right)^2 M \qquad \text{VII-8}$$

ϵ and ϵ_1 are the dielectric constant of solution, and the dielectric constant of the medium surrounding the spheres. In the case of a mixed polymer solution ϵ_1 is no longer equal to the dielectric constant ϵ of the mixed solvent outside the polymer, due to the selective adsorption of the good solvent on the polymer, causes a modification of the binary solvent composition in the vicinity of the particle.

When the solvent composition is defined by the volume fraction ϕ of a good solvent, then the turbidity can be expressed by the relation

$$\left(\frac{\tau}{c} \right)_{c=0} = \frac{32\pi^3 \bar{n}^2}{3\lambda_0^4 N_0} M \left(\frac{d\bar{n}}{dc} + \alpha_a \frac{d\bar{n}}{d\phi} \right)^2 \qquad \text{VII-9}$$

where $d\bar{n}/d\phi$ represents the variation of the refractive index of the solution with the composition of the solvent. The parameter (α_a) represents the variation of composition of the binary solvent surrounding the particle

$$\alpha_a = - \frac{d\phi}{dc} \qquad \text{VII-10}$$

In other words, α_a is directly related to the preferential adsorption phenomena, which characterizes the variation of solvent composition $\frac{d\phi}{dc}$ in the vicinity of the polymer.

VII .Ic2 - Micellar properties of polyoxyethylene monohexadecyl ethers from Light Scattering Data

VII .Ic.2A Aqueous solution of Polyoxyethylene Surfactants

The scattering intensities of non-ionic surfactants in aqueous solution, and containing various concentration of aromatic alcohols, urea and urethane was observed by using the Photo Gonio Diffusometer(253), Model 4200 as described in Chapter VI. The observed scattering intensity is almost constant at low concentration, and does not change significantly as the concentration increases (Fig.VII.13). But at a critical concentration (5.2×10^{-5}mol.dm^{-3} and 3.4×10^{-5} mol.dm^{-3} for $C_{16}E_{10}$ and $C_{16}E_{18}$ respectively. Table VII.I.3), the slope of $S\phi_{90}$ - concentration curve markedly changed. The observation also confirms the results obtained from the hydrodynamic measurements that the C_0 decreases as the EO chain length increases (Fig.VII.8). The molecular weight of the micelles was calculated using the Debye relation (equation VI-31), and employing procedure as described in Chapter VI (Fig.VII.14). The degree of association of monomers decreases as the hydrophilic group increases. As can be seen in Table VII.I.6, the micellar molecular weight decreases as the hydrophilic chain increases in length.

The decrease in micellar size is due to the decreased affinity of the monomer for water (4.26×10^5 and 2.22×10^5 for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively). The micellar dimensions were calculated as described in this chapter. The observation indicates that the axial ratio of the prolate type of micelle increases as the dimensions of the micelle increases (3.7 and 7 for the axial ratio of A_a/A_b for $C_{16}E_{10}$ and $C_{16}E_{30}$ respectively Table VII.I.6), since the major axis A_a increases as the EO chain length increases. The particle scattering function PΦ was calculated using the Debye relation given by the equation(263)

$$\frac{Hc}{\tau} = \frac{1}{MP\Phi} + 2BC \qquad \text{VII-11}$$

when the dimensions of the scattering particles are big enough to compare with the wave length of the light in the medium (λ). The particle scattering function plays an important role for the scattering intensity of the particles. If the particle is larger than about $\lambda/20$, corresponding roughly to 200-270 Å, the light scattered from different points of the particle reaches the observer with different phases, consequently the scattering intensity is diminished due to interference. In view of this fact the calculated particle scattering function of the micelles ($P^{-1}\Phi$) is 1.456 and 0.337 for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively Table VII.I.6. The scattering function decreases sharply as the EO chain length increases, but the decrement in $P^{-1}\Phi$ after 30 EO chain length is not considerable (Fig.VII.22), which is due to the decrease in MW and minor axis (A_b) of the prolate micelle.

VII.I.c2B- Solution containing Aromatic alcohols.

When an aromatic alcohol is added to aqueous surfactant solution, the scattering intensity increases (0.3056×10^{-5} cm^{-1} for 1×10^{-4} mol.dm^{-3} $C_{16}E_{18}$ containing 0.01M phenol Table VIII.I.4.) As can be seen in Fig.VII.15 the scattering intensity increases gradually as the concentration increases. At a certain concentration the slope of the curve considerably increases.

On the addition of 0.01 phenol, the increase in C_0 is not significant compared with the aqueous surfactant solution (3.45×10^{-5} mol.dm^{-3} and 3.4×10^{-5} mol.dm^{-3} for $C_{16}E_{18}$ containing 0.01M phenol and in aqueous solution respectively.) However the addition of 0.02M phenol increased C_0 (3.6×10^{-5} mol.dm^{-3}). The further increase in concentration of second solvent shifts the C_0 to a lower value, as observed in cationic systems.

On the other hand the effect of phenol on C_0 was observed using surface tension measurement. The observation also indicates that C_0 increases up to 0.03M, then it decreases with increasing concentration (4.2×10^{-5} mol.dm^{-3}; 4.4×10^{-5} mol.dm^{-3} and 4.5×10^{-5} mol.dm^{-3} for $C_{16}E_{18}$ containing 0.01M, 0.02M and 0.03M phenol respectively Table VII.I.4, Fig.VII.17.)

As discussed in a previous section the addition of a third component alters the refractive index of the solvent which affects the scattering phenomena. The distribution of molecules in any unit volume element will vary with the time because of thermal motion of the molecules, and consequently each particular region will differ from its neighbours.

Thus the local density of the solvent around the molecule is constantly changing due to the possible selective adsorption of a third component such as phenol or benzyl alcohol on polyoxyethylene mono ether molecules. In such a state the refractive index of the solvent around the molecule is different from the refractive index of the bulk solution due to the density and concentration fluctuations in the solvent near to particles.

Ewart et al.(257) have showed that in the polystrene-benzene 80% - methanol 20% ststem, the solvent 1 (benzene) is preferentially adsorbed on polystrene ($\alpha_a = 0.405$) as the second virial coefficient and limiting viscosity number decreases. Tuzar-Kratochvil and Cowie-Bywater(270) have observed similar behavior of component 1 (solvent) for the adsorption on the polymer.

However Read(271) has used polystyrene-benzene (1) - cyclohexane (2) in order to investigate the preferential adsorption in the system. He has concluded that benzene is adsorbed on polystyrene rather than cyclohexane.

In view of these facts, it is reasonable to assume that the possible adsorption of aromatic alcohol on the non-ionic surfactant used is a major factor for an increase in $S\phi_{90}$ and turbidity of solution.

However when 0.01M benzyl alcohol is added to the aqueous solution of $C_{16}E_{18}$, the turbidity increases (5.1546×10^{-5} cm^{-1} for 1×10^{-4} mol.dm^{-3} of $C_{16}E_{18}$ Table VII.I.4.B, Fig.VII.15). The increment in turbidity also has a contribution from the density and concentration fluctuations in the refractive index of the solvent surrounding the particle.

It is apparent that the optical efficiency of aromatic alcohols give contributions which raise the Rayleigh ratio consequently turbidity.

The change in fluctuations in density and concentration is directed by the static dielectric constant of the aromatic alcohols. The decrement of static dielectric constant of the solution increases with increasing $-CH_2-$ group in substituted alcohol chain length.

The optical efficiency of fluctuations of the alcohols as second solvent on micelles contribute to an increase in Rayleigh ratio. Similar behaviour is observed when benzyl alcohol or phenylethanol is added to the system. But the effect of phenylethanol on C_o differs appreciably from that of the lower alcohols. The addition of 0.01M phenylethanol has increased C_o considerably (3.58×10^{-5} mol.dm^{-3}) compared with the observed values for lower alcohols. (Table VII.14D, Fig.VII.15A).

This behaviour can be attributed to the structure promoting effect of the alcohol due to an increase in the nonpolar nature of the alcohol molecule. On the addition of aromatic alcohol to the system hydrophobic interactions occur between the OH groups of alcohol and water molecules, interactions also occur between the hydrcarbon group and benzene ring through π electron clouds, and polyoxyethylene group and water molecules. These play an important role in micelle formation.

The hydrophobic interactions between these groups increase the complex type association of polyoxyethylene surfactants with aromatic alcohols in the system as discussed in Chapter V in the case of cationic surfactants. The alcohols behave as structure makers at low concentration. This effect is quite clearly observed through the increase in C_o as the hydrophobic character is increased. The increase in C_o at low concentration of added alcohol can be discussed in the light of structure promoting behaviour of alcohols and their complex type association through hydrophobic interactions with non-ionic surfactants.

However the solubility of aromatic alcohols also plays an important role in the increase of C_o. But, when the concentration of additive is increased, the observed behaviour is changed to the opposite direction. The decrement in C_o probably arises from the increase in structure breaking effect of the alcohol molecules, and the decrement in solubility of alcohols in bulk solution and in the interior of the micelles. Due to these effects C_0 is shifted to the lower value with decreasing free energy of micellization as observed on addition of propanol and butanol to the cationic system (Chapter II).

The light scattering observation indicates that the micellar molecular weight increases as the concentration of additive increases (4.88×10^5 and 6.45×10^5 for $C_{16}E_{18}$ containing 0.01M and 0.02M phenol respectively. Table VII.I.7. Fig.VII.19). In the case of phenol the increase in MW is nonlinear while the increase is linear on the addition of benzyl alcohol and phenylethanol.

The observed dissymmetry is higher (1.05 and 1.06 for $C_{16}E_{18}$ containing 0.01M and 0.02M phenol respectively) compared with the standard (1.01). The dissymmetry of the micelles increases as the $-CH_2-$ group increases (1.07 and 1.08 for $C_{16}E_{18}$ containing 0.01 benzyl alcohol and phenylethanol respectively, Tables VII.I.4.B, VII.I.4.D). The observation indicates that the size of micelle is changed with addition of alcohol. In order to observe the size and shape of the mixed micelle, the oblate shape was taken into account as well as the prolate type micelle as an alternative model shape.

Disregarding the helical nature of the polyoxyethylene chain, the carbon-carbon bonds (1.5 Å) with the bond angles of 110° and carbon bonds (1.5 Å) were used to calculate the extended length of monomeric unit which is 3.5 Å, [redacted], then the extended length of $C_{16}E_{18}$ was determined taking into account the length of the hydrophobic and hydrophilic groups of surfactant (approximately 90°A),

The observation of the dimensions of oblate type micelles was carried out in view of Harkins's(168) approach, in order to estimate the semi-axis revolution and equatorial radius (A_a). Since the diameter of the rod type micelle is twice the length of monomer molecule and it can be approximated to the oblate shape, the monomer extended length (90 Å) was used as the length of semi-axis (A_b) revolution for computing (A_a).

Considering this approach one can calculate the equatorial radius taking into account the density of the micelle. The obtained value is 52 Å for semi-axis (A_a). As a result of this fact, the following argument can be put forward to examine the possibility of an oblate shape for the mixed micelles. It was observed that in aqueous solution the micelle of $C_{16}E_{18}$ is prolate type. The observed dimensions are 153 Å and 30.5 Å for (A_a) and (A_b) respectively.

When the aromatic alcohol is added to the system micellar size changes. If the micellar shape changes from prolate type to oblate shape with addition of alcohol, the molecular dimensions of the micelles must expand in two dimensions. It is assumed that it occurs in this system. Although the extended length of the monomer was used, the semi-axis (A_b) is 90°A while A_a is 52 Å. As far as the dimensions of the micelle are concerned, the observed lengths do not fit well into the oblate shape if the structure of the interior of the micelle is considered.

If the length of semi-axis (90°A) is compared with the semi-axis $(A_b = 30.5)$ of $C_{16}E_{18}$ in aqueous solution it is considerably high, on the other hand the equatorial radius $(A_a = 52$ Å$)$ is lower compared with the radius $C_{16}E_{18}$ (153 Å). However it is unlikely that the addition of any aromatic alcohol studied to the system will cause such a change in the dimensions of micelles (i.e. as in the case of added 0.01M phenol).

As observed with aqueous non-ionic surfactants, the semi-axis A_b does not change significantly as the molecular weight of micelle increases. The difference between the semi-axes of $C_{16}E_{10}$ and $C_{16}E_{30}$ is 10 Å which is due to the increase in the degree of coiling of hydrophilic group. The degree of coiling increases as the EO increases. In view of Peterlin's(291) theory the calculated effective length of $C_{16}E_{18}$ is 74 Å. If the effective length is compared with the extended length one can calculate that the degree of coiling in solution is 1.176.

It is quite evident that the expansion of micellar size is more favourable along the long axis (equatorial) rather than in both lengths.

However if the effective length of $C_{16}E_{18}$ is considered, then the semi-axis of equatorial diameter can be calculated in the same way as discussed above. The obtained (A_a) is 56 Å. Considering both extended and effective length of the monomer molecule, the calculated lengths of the oblate shape show that the hydrocarbon groups and benzene rings are located near the centre of the micelle causing a two dimensional change in shape from prolate to oblate.

If the axial ratio of the micelle is considered, (1.73 and 1.36 for the considered extended and effective lengths respectively) one can say that the shape of micelle is close to the spherical shape. If the shape of micelle is assumed to be oblate, the volume of micelle will be equal to that assumed for the other shape (prolate). If this is the case the monomer will be closely packed in the interior of micelle, which is not favourable if the interior of micelle is considered.

If one considers all the hydrocarbon chains and benzene rings are attracted towards the micellar centre effecting a two dimensional change in shape, with an increase in spherical volume, this can be in error due to the fact that the hydrocarbon chains cannot approach each other more closely than about 5 Å(158). On the other hand, the free volume of monomer will oppose the close packing in the interior of the micelle.

However in this work this type of change is found unrealistic in view of the geometry of the particles, the free volume of the hydrocarbon groups and the limitation on the closest distance between hydrocarbon groups. On the other hand to bring the hydrocarbon groups near the centre changing the dimensions will require extra energy.

In view of the above discussions, the prolate shape was considered as a possible shape of micelle. The density of hexadecane at 25°C was used to calculate the length (A_a) of micelle on the assumption that the semi-axis of revolution does not change (as discussed in this section for non-ionic surfactants in aqueous solution).

The calculated (A_a) of prolate micelles of $C_{16}E_{18}$ containing additives increases with increasing MW (260 Å and 1108 Å for $C_{16}E_{18}$ containing 0.01M and 0.08M phenol respectively. Table VII.I.7). Due to increase in micellar size the particle scattering function of micelles was taken into account to observe its effect on scattering intensity of particles on micellar state.

As can be seen in Table VII.I.7 and Fig.VII.22 $P^{-1}\Phi$ does not change significantly up to 0.05M phenol (0.623 and 1.074 for $C_{16}E_{18}$ containing 0.01M and 0.05M phenol respectively) as the concentration increases, then it gradually increases.

However in the case of benzyl alcohol and phenylethanol after 0.04M and 0.03M respectively the increase in $P^{-1}\Phi$ is greater in magnitude compared with $C_{16}E_{18}$ containing phenol. Since large dissymmetries were not observed and the concentration of monomer is low in the systems studied, it was assumed that depolarizations of the solutions and Cabannes factor were negligible.

VII.Ic3 - Non-ionic surfactant solution containing urea and urethane.

The addition of urea and urethane to the aqueous solution of non-ionic surfactant increase C_0 (6.8×10^{-5} mol.dm^{-3} and 6.25×10^{-5} mol.dm^{-3} respectively. Table VII.I.5, Fig.VII.18). It is quite evident that on the addition of urea or urethane the structural order of water molecules is changed. The effect of urea on water structure was discussed taking into account the structure maker or structure breaker approaches which were postulated by different investigators.

As can be seen in Table VII.I.5 the Rayleigh ratio and turbidity increase when 1M urea and 0.7M urethane is added to the system ($\tau = 6.8008 \times 10^{-5}$ cm^{-1} and $\tau = 6.262 \times 10^{-5}$ cm^{-1} for 1×10^{-4} mol.dm^{-3} $C_{16}E_{18}$ containing 1M urea and 0.7M urethane respectively).

The increase in turbidity is due to possible adsorption of additive on the surfactant molecule and the change in density and concentration fluctuations in the refractive index of the solvent near to the surfactant molecule. On the other hand the interaction of non-ionic surfactant with urea or urethane through hydrophobic interactions also plays a unique role in the increase in scattering intensity and consequently in turbidity.

In this work, it is believed that urea and urethane participate in mixed cluster formation with water molecules to accommodate the surfactant molecule more efficiently than the water clusters around the non-polar and polar groups.

It is apparent that the participation of both additives in cluster formation arises from their ability to increase the structure of water molecules through hydrophobic interactions. On the addition of urea and urethane, the light scattering observation indicates that the MW increased (2.5×10^6 and 3.33×10^6 respectively, Table VII.I.7, Fig.VII.20).

Although the added concentration of urethane is less than urea, the increase in MW is higher compared with the $C_{16}E_{18}$ containing 1M urea. This is due to the chemical structure of urethane which has an extra oxygen atom instead of nitrogen atom. It is known that the hydrophilic group readily associates with water molecules in terms of hydrophobic interactions which might be the reason for the higher MW.

On the other hand, the observed dissymetry is higher in both cases (1.05) than unity (1.01). The micellar dimensions were calculated as described in this section. The obtained lengths of micelles are 1332 Å and 1774 Å for 1M urea and 0.7M urethane respectively. Since the length of micelles is higher than $\lambda/20$, the particle scattering function is higher compared with $C_{16}E_{18}$ containing aromatic alcohols (12.77 and 6.723 for urea and urethane respectively).

Due to this fact the scattering intensity is affected considerably because of the increase in size of the micelles.

VII.Id - Critical Micelle concentrations of polyoxyethylene Monohexadecyl Ethers in aqueous solution.

VII.Id1- Purification of surfactants.

The commercial impure non-ionic surfactant (100g) was mixed in a separating funnel with 100 ml 5N aqueous solution of sodiumchloride(272). This mixture was then equilibrated with an equal volume of ethylacetate (BDH A.R)(134). The mixture was shaken for 15 minutes to separate the free polyethylene glycol from the non-ionic surfactant molecules. After the separation of layers the organic layer which contains the non-ionic surfactant, and the aqueous layer containing polyoxyethylene glycol were collected. This procedure was repeated several times, then the organic solution was reextracted several times by 100 ml 5N sodium chloride to remove the remaining free polyethylene glycol. Following this process the organic solution which contains non-ionic surfactant was evaporated on a water bath and dried under vacuum.

The obtained surfactant was dissolved in acetone, filtered to remove remaining sodium chloride, evaporated and dried under vacuum. The purity of the non-ionic surfactants was checked using surface tension measurements (Du Nouy tensiometer, as described in Chapter II) and the above procedure was repeated until a fine intersection was obtained on the surface tension concentration curve.

VII.Id2 - The characterization of Non-ionic Surfactants by NMR spectrometer.

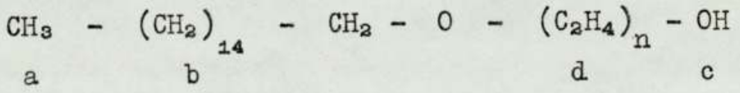
The non-ionic surfactants were characterised using a A-60A NMR spectrometer(273). The instrument was set according to the instrument manual. The non-ionic surfactant was characterized in terms of the hydrophilic group assuming that the hydrophobic group was known and did not vary. The specifications of the instrument used were the operating frequency (60 MHz), the magnetic field strength (14.092 G), the average R-F field at sample (0.005 to 0.5 mG), the sample tube size (4.28 mm ID), the resolution (0.3Hz).

The sensitivity of the instrument was sufficient to detect a

0.007 molar concentration of hydrogen nuclei occurring in a single line of less than 0.6 Hz natural line width. The integral reproducibility was 1% electronic accuracy in integrating circuit. Spectral reproducibility after 24 hours warming up was, in an environment with temperature variation $\leq \pm 1$°C (1 Hz/hr), the average deviation for five successive 250-sec scans (0.4 Hz) in the temperature change $\leq \pm 3$° (2 Hz/hr) and corresponding average deviation for successive 250-sec scans (0.6 Hz). Resolution 0.3 Hz was less than 0.6 Hz in 16 hours run. The calibrated instrument was used according to the instrument manual.

The spectra of a 10% CCl_4 solution of non-ionics surfactants were recorded at 25°C using (TMS) as internal reference at a sweep width 500 cps using 250 sec-sweep time at spectrum amp.(10), integral amp.(80), filter band width (14) and R-F field (0.03).

The manufacturer's(274) code A_{10},A_{18},A_{30} and A_{60} show the approximate value of ethylene oxide unit. Carbon tetrachloride was chosen as a solvent because it contains no interfering protons, and the selected internal reference gives a single sharp line of a relatively high value of the magnetic field due to its hydrogen atoms being equivalent. The obtained spectrum was interpreted in the following manner: the theoretical formula;



$$\underset{a}{CH_3} - \underset{b}{(CH_2)_{14}} - CH_2 - O - \underset{d}{(C_2H_4)_n} - \underset{c}{OH} \qquad \text{VII.i-1}$$

Since each step in the integral corresponds to the number of protons giving a signal in the spectrum, in order to determine the number of protons which correspond to the various functional groups in the NMR spectrum, the functional groups in the molecule were denoted by the letters (a,b,c,d). The absence of signals other than those identified as due to internal reference, or alkyl polyoxyethylene surfactant is also the indication of the relative purity of the compound (purified non-ionic surfactant spectrum).

The number of protons present in the polyoxyethylene group of non-ionics (impure and purified) was calculated using the ratios of the integrals of the $(-CH_2-CH_2-O-)_n$ peak to the integral of the hydrophobic group (known) of the molecule. As can be seen in Table VII.I.8, the calculated total of protons of the $(-CH_2-CH_2-O-)$ group is 125 and 294 for $A_{10}$and,A_{60} respectively. However the c alculated number of moles of $(-CH_2-CH_2-O-)$ group from NMR spectrum for non-ionic surfactants are shown in Table VII.I.8.

VII.Id3 - <u>Volumetric method</u>.

In order to check the ethylene oxide content of the surfactant molecule, which was determined by NMR measurement, a titration procedure was employed(275) in the following manner;

A. 1.00g surfactant was weighed into a 100 ml beaker, then 25 ml of DMF (BDH), and 5 ml benzene (BDH A.R) were added to the flask. The sample was dissolved by swirling, and the temperature (25°C) was kept constant using an ice bath. Double distilled water was added from a 50 ml burette in about 2 ml increments, and the flask was swirled after each addition. Since the temperature rises due to the heat of solution hydration, the flask was kept in the ice bath after each addition of water to maintain the solution at 25°C.

When the solution on the addition of water becomes turbid before swirling, the quantity of titrating water was reduced to 0.5 ml. At a certain concentration the end point of titration was reached, and the volume of water was recorded. If the ethylene oxide chain length of the surfactant has the number of $(-CH_2-CH_2-O-)$ unit which was calculated from NMR spectrum, then a linear relationship must be observed between the volume of titrant, and number of ethylene oxide group. It is reasonable to consider that A_{10} and A_{18} can be easily purified with the liquid distribution method employed since the excess of $(-CH_2-CH_2-O)$ group impurity is 2.3 mole, and 4.3 mole for A_{10} and A_{18}. When the corresponding titrants of the surfactants are plotted versus ethylene oxide groups, as can be seen in Fig.VII.9 a straight line plot is obtained. If A_{60} has 60 ethylene oxide group, then the titrant volume must be on the volume of titrant-EO group plot. As is seen in Fig.VII.9 there is a linear relationship between the volume of titrant and corresponding EO chain length. This procedure confirms also that the non-ionic surfactants contain the exact number of moles of ($-CH_2-CH_2-O$) group, which was determined by NMR spectrometer.

VII.Id4 - Cloud Point Relation in aqueous surfactant solution.

When the temperature of a non-ionic solution is increased to a certain temperature, it becomes turbid in a narrow temperature range. This temperature is called the cloud point.Hydration is rather sensitive to temperature, and when the temperature is increased at a certain temperature dehydration occurs, as a result of this the polyoxyethylene surfactant becomes less soluble at increased temperatures.

The mechanism of clouding phenomenon is not yet clear. It has been discussed(158) that the micellar weight of a non-ionic surfactant becomes larger with increasing temperature,then at a certain temperature the micelles grow so large that the solution becomes turbid. This temperature might be called the cloud point. When the micelles become larger, phase separation occurs as the result of the formation of giant aggregates which finally separate from the water phase. The cloud points of the non-ionic suefactants was determined as follows.

A 1.00g surfactant was dissolved in 100 ml of water, and cooled in an ice bath until the solution was clear, then the temperature was raised slowly until the solution became turbid. As can be seen in Table VII.I.1.B the cloud point of the surfactant increases with increasing ethylene oxide chain length (50 °C and 79,60 °C for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively). It has been discussed(158) that the non-ionic surfactant having a longer hydrophilic group indicates a higher cloud point, and capacity to hydrate. However the obtained cloud points indicate that the observed low value is due to the less hydration of the surfactant molecule, which causes a decrement in solubility. The g.water/g.surfactant quantity decreases ith (Table VII.I.6) increasing EO group. As a result of this fact, the dehydration is reached at low temperature, which is due to the less amount of hydrated water molecules bound to the surfactant molecule.

VII.Id5 - The critical micelle concentration of non-ionic surfactants in aqueous solution.

The micelle formation in aqueous solution for non-ionic surfactants resembles that of the ionic surfactants. The C_o in general is lower than for ionic surfactant. It has been discussed that the C_o increases as the hydrophilic group increases when the concentration data are expressed in units of weight per volume. However, Carless et al.(276) and Schick et al.(172) have found that the C_o decreases with increasing chain length when the concentration is increased on a molal basis. On the other hand Elworthy-Macfarlane(264,277) and Corkill et al.(278) have discussed the increment in C_o with increasing ethylene oxide chain length.

In this work, the C_o of non-ionic surfactants in aqueous solution was measured, using viscosity, surface tension and light scattering methods. The observations indicate that the C_o decreases as the ethylene oxide chain length increases (5.6×10^{-5} mol.dm^{-3}, 6.0×10^{-5} mol.dm^{-3} and 5.2×10^{-5} mol.dm^{-3} for $C_{16}E_{10}$ corresponding the viscosity, surface tension and light scattering measurements respectively. Tables VII.I.1 and VII.I.3). As is seen in Fig.VII-4 the surface tension of non-ionic surfactant (i.e. $C_{16}E_{10}$) decreases gradually as the concentration decreases. After reaching certain concentration, it increases with increasing concentration. The observed minimum on the surface tension - concentration curve is due to the impurities. After the purification of surfactants as is seen in Fig.VII.5, the minimum on the surface tension-curve does not occur.

On the other hand the C_o of non-ionic surfactant ($C_{16}E_{10}$) was observed in terms of the aqueous solution, which was prepared on weight-volume basis. As seen in Fig.VII.7, the C_o of $C_{16}E_{10}$ is dl^{-1} which is equivalent to 5.85×10^{-5} mol.dm^{-3} .The adsorption of surfactant on to glassware was also examined. It was observed that the adsorption only occurs in small quantities (Fig.VII.6), which does not affect the C_0 value. Corkill et al.$^{(279)}$ have discussed that homogenous non-ionics in the solution are not stable. The minimum on the surface tension-concentration curve, and the gradual decrementin the surface tension above the C_0 as the concentration increases have been discussed by Elworthy et al.$^{(280)}$ in terms of impurity of the non-ionics in aqueous solution. The observation of C_0 of the surfactants, and the question of decrement in C_0 as the hydrophilic group increases, can be expanded to obtain a reasonable explanation about the phenomenon.

Staudinger$^{(281)}$ has postulated two types of structure for polyoxyethylene chains which are zigzag and meander configurations. He has concluded that at a low degree of polymerization, the chain exhibits a zigzag structure, and the chain contraction increases with increasing ethylene oxide chain length. The oxygen atoms of the main polyoxyethylene groups attract each other, the magnitude of this attraction increases considerably beyond a degree of polymerization of 9, consequently it causes chain contraction.

Rösch$^{(282)}$ has given an alternate explanation. According to his view the contraction is due to electrostatic attraction. Marchal-Benoit$^{(283)}$have shown that the individual dipole moments (dipole moment of dimethylether of oxyethylene unit) diminish with increasing length of the polymeric chain. Rösch's$^{(282)}$ explanation of the contraction of polyoxyethylene is supported by the fact that it is based on intramolecular, coaxial electrostatic attraction. Ionic surfactants also exhibit zigzag chain configurations. The only difference between the paraffin chain and oxyethylene groups is the presence of a hetero atom. This hetero atom, ether oxygen causes dipole attractions towards the neighbouring methylene groups, and consequently exerts electrostatic forces to the polyoxyethylene chain.

When the oxyethylene chain length is increased, the large electrical moment in the coaxial direction contracts the chain length (ethylene oxide) and transforms it to the meander configuration. The meander configuration is less extended than the zigzag configuration. It has been shown(284) by X-Ray investigation that the zigzag configuration is transformed to the meander configuration at a degree of polymerization of 20 to 40. In bulk state, with surface active derivatives of polyoxyethylene, the change in modification is obtained at a degree of EO unit of 15 to 20.

The width of polyoxyethylene chain in the meander configuration is 4.5 Å, while it is 2.5 Å in the zigzag configuration. The related cross-sectional area is 28 $Å^2$ for the meander chain, and 19 $Å^2$ for the zigzag chain(284).

The helical configuration of the polyoxyethylene polymers has also been put forward to analyse the orientation of the hydrophilic group. Miyazawa et al.(285) have measured the polarized infrared spectra of crystalline films of polyoxyethylene glycol in the region 3500-400 cm^{-1}. The structural configuration of polyethylene glycol has been discussed in terms of the equations for the helical parameters. The model which has been introduced has seven repeating units, and two helical turns per fibre period of 19.25 Å. On the other hand, the internal rotation angles for the helical model have been calculated to be 60° for c-c bond and 191.5° for the c-o bond.

Tadokoro et al.(286) have studied the molecular structure of polyoxyethylene oxide $(-CH_2-CH_2-O-)_n$ by X-Ray diffraction and infrared adsorption spectroscopic methods. They have concluded that the polyoxyethylene molecule has a helical structure in the crystalline state, which contains seven chemical units and two turns in the fibre period of 19.3 Å. The calculated trans, trans and gauche conformations are related to the corresponding internal rotation angles of the molecule, which are 64.58 and 188.5° for $(O-CH_2-CH_2-O)$ and $(-CH_2-CH_2-O-CH_2-)$ respectively.

Yoshihara et al.(287) have also examined the molecular structure of polyoxyethylene at various temperature using infrared spectroscopic method. They have shown that the results they obtained are in good agreement with the results given in literature for the helical structure of polyoxethylene oxide.

VII.Id6 - Configurations of the polyoxyethylated molecules in solution.

Due to Brownian motion particles, or polymer segments, are driven forward by collisions with the moving molecules in the medium(288). Because of this fact, fluctuations in tension take place within the polymer molecule. This behaviour causes cooperative motion of segments in the molecule, and consequently the polymer chain is pulled in, and out of a number of configurations. Debye-Bueche(289) have calculated root- mean-square end to end distances, taking into account Einstein's theory. A permeable sphere of radius Rs has been considered as a polymer molecule, which occupies average space. They have further assumed that this sphere contains a uniformly distributed system of resisting points. The permeability of the sphere has been accounted for by a hydrodynamic factor $\phi(\sigma)$. The dimensions of the polymer molecule has been given by the relation,

$$(\overline{Rs}^2)^{\frac{1}{2}} = (36/10)^{\frac{1}{2}} \left[300M[\eta] \big/ 4\pi \, No \ \phi(\sigma) \right]^{3/2} \qquad \text{VII-12}$$

Kirkwood-Riseman(290) have examined the random-coil model. This theory allows the hydrodynamic interaction of the molecular segments in terms of inhibited flow through the chain. The polymer dimension has been defined by an equation

$$\begin{aligned} [\eta] &= (6\pi^3)^{\frac{1}{2}} \, No \ be^3 \ Z^{\frac{1}{2}} \times Fo(X)/3600M_o \\ \left(\overline{Rs}^2\right)^{\frac{1}{2}} &= be \ Z^{\frac{1}{2}} \end{aligned} \qquad \text{VII-13}$$

Peterlin(291) has introduced a model of a polymer molecule with the random distributed chain elements. Due to the molecular elements, it has been considered that the solvent flow through the molecule is hindered.

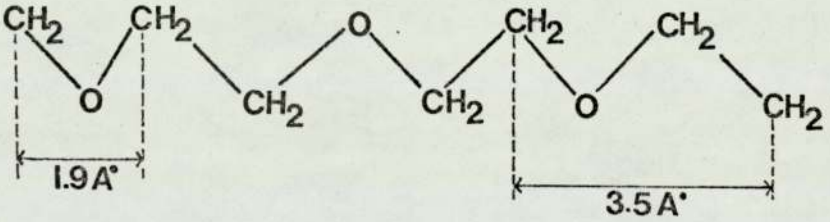
The transition from a free draining coil to an impermeable coil has been discussed by means of the intrinsic viscosity.

The dimension of the polymer has been given by

$$(\bar{R}s^2)^{\frac{1}{2}} = 1.52 \times 10^{-8} (\cot\alpha)^{\frac{1}{3}} M^{\frac{1}{2}}. \qquad \text{VII-14}$$

VII.Id7 - The proposed configurations of Polyoxyethylene surfactants in aqueous solution.

As has been discussed in this section, the polyoxyethylene non-ionic surfactant of a lower degree of polymerization exists in zigzag configuration. If the length of ethylene oxide group is considered to be in this configuration, then one can calculate (approximately) that the zigzag chain length of EO unit of $C_{16}E_{10}$ is 35 Å. The configuration can be illustrated as follows(284)

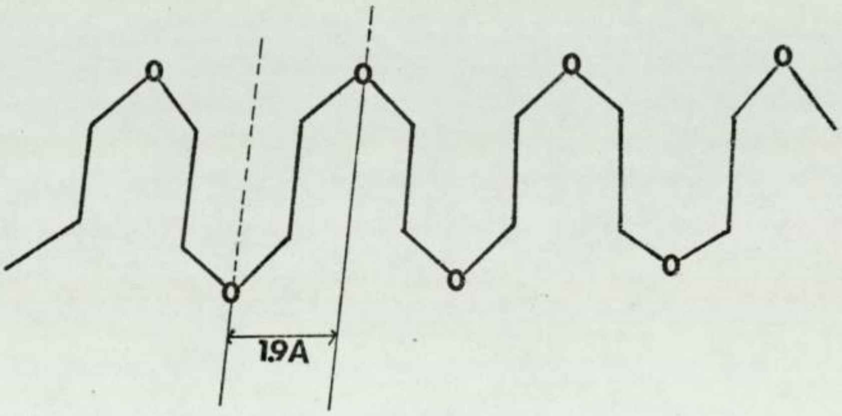


VII.i.2

The hydration of polyoxyethylated surfactants shows that the extent of hydration decreases as the hydrophilic chain is increased. On the other hand the cloud points of the non-ionics are lower. This is also an indication of the hydration and solubility of the surfactant molecules. With the observed non-ionics, the water of hydration does not require the higher temperature for it to be released, in other words, the temperature shows that the hydrated number of water molecules are less. However one can say, considering the above view that the lower non-ionic surfactant should have a higher cloud point, since it has a higher quantity of hydrated water molecules. The lower cloud point of $C_{16}E_{10}$ (50 °C) comparing $C_{16}E_{60}$ (79.60 °C) is due to the difference in the configurational orientations in aqueous solution.

When the degree of polymerization is increased, due to the increase in length, the large electrical moment in coaxial direction causes contraction of the hydrophilic chain length and transforms it to the meander configuration(284). It is believed that the meander configuration of oxyethylene groups exist in higher oxyethylated non-ionics in aqueous solution. If the length of the unit oxyethylene group is of the order of 1.9 Å, then the length of the hydrophilic group is approximately 118 Å. Taking into account the zigzag configuration of the hydrophobic group (22 Å), one can calculate the length of the $C_{16}E_{60}$ which is 140 Å.

The extended length of a monomeric unit is obtained in terms of the length of the oxyethylene unit (3.5 Å) which is 232 Å. When the polyoxyethylene length is increased at constant hydrocarbon area it exerts inter penetration, and greater density in packing of oxyethylene group occurs due to the random coiling, which is entropically favourable. If the hydration of oxyethylene groups, increases with the increasing of hydrophilic chain length, then the polyoxyethylene chain must be in extended configuration. However, the observed results of hydration of non-ionics are contrary to the above considerations. The meander configuration of higher polyoxyethylene surfactants can be illustrated(284) as follows



VII.i.3

If it is assumed that the surfactant molecules in aqueous solution exist in a combination of zigzag (hydrophobic group) and meander configuration, then the difference between the extended length, and configurational length can be used as a parameter to interpret the molecular dimensions of the surfactants. This approach can be extended, taking into account Peterlin's theory(291). Peterlin has examined the polymer molecule in solution, and has concluded that the molecules resemble a loosely coiled chain. On the other hand, due to the chain elements near the centre have greater density, it has been considered that the flow of solvent through coil is impeded towards the centre rather than periphery. Because of this fact the solvent is partly immobilized in the centre part of the coil configuration. This situation, according to his view, is reflected in the dependence of the intrinsic viscosity. When the flow is totally hampered, he has shown that the intrinsic viscosity, and sedimentation coefficient increase in proportion to the square root of the moleculear weight M, or the degree of polymerization considering the mean distance of the two chain elements. The effective length shows the same square root dependency upon the number of links involved. The relation between intrinsic viscosity and statistical coil effective length has been defined by an equation

$$[\eta] = \frac{\pi}{4} \frac{a_o A_o^2}{M_o} \frac{N}{1 + 1.2(6/\pi)^{\frac{1}{2}} (a_o/A_o) N^{\frac{1}{2}}} \qquad \text{VII-15}$$

In this approach It is considered that the effective length, and the resistance of the molecule do not depend on the way in which the flexibility of the molecule is taken into account. In order to know how many statistically independent fundamental units are joined to form segments, the valency angles and the rotational hindrance can be used in terms of the parameter $\xi = \frac{Z}{N}$.

He has introduced(291) an equation, by means of the slope of the plot $M/[\eta]$ against $M^{\frac{1}{2}}$, the uncertain factor 1.2 and Avagadro number by

$$Re = \left(3^{1/6}\ 2^{5/6}/\pi^{\frac{1}{2}}\right)\left(1.2\ \mathrm{Cot}\alpha/\mathrm{No}\right)^{\frac{1}{3}}\ M^{\frac{1}{2}} \qquad \text{VII-16}$$

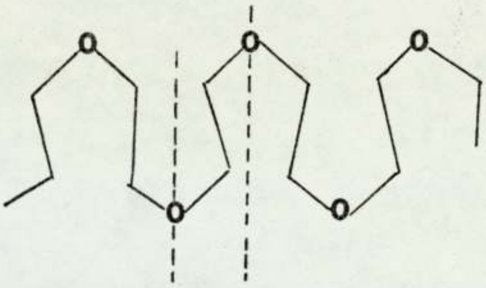
$$Re = 1.52 \times 10^{-8}\ (\mathrm{Cot}\alpha)^{\frac{1}{3}}\ M^{\frac{1}{2}}$$

Although the factor (1.2) found for higher linear polymer is uncertain, in the light of the above discussion, one can calculate the effective length of the linear polymer in terms of the slope α, and molecular weight of the polymer. As can be seen in Fig.VII.21 there is a linear relationship between $M/[\eta]$ and $M^{\frac{1}{2}}$. The slope of the line has been substituted into equation (VII-16) to obtain the effective length of the molecule. The derived approximate effective length of $C_{16}E_{60}$ is 120 Å. It is 20 Å less than the straight meander length of $C_{16}E_{60}$ (140 Å).

If the extended length (232 Å) of molecule is compared with the straight meander length and effective length, there is considerable decrement in the length of the molecule in the aqueous solution. If the configuration of polyoxyethylene in aqueous solution is assumed in the meander type of configuration and straight (this assumption is contrary with the observed hydration quantity) then the degree of coiling can be calculated which is (1.16). The degree of coiling of MW of 5×10^4 is equal to 20 in water at 35°C (Flory-Fox theory)$^{(292)}$. If the degree of coiling is considered to be proportional with the $M^{\frac{1}{2}}$ then the degree of coiling is obtained to be (1.15), which is very close to the observed value.

Due to the coiling of polyoxyethylene group the surface area of the hydrophilic group will be decreased because of the reducing surface area, then because of being in meander configuration nearly half of the oxygen atoms of oxyethylene group will be inside the coiled configuration. When the degree of polymerization is high (i.e. $C_{16}E_{60}$), the dipole contraction increases, which is equal to 4.2×10^{-4} dyne for $C_{16}E_{60}$.

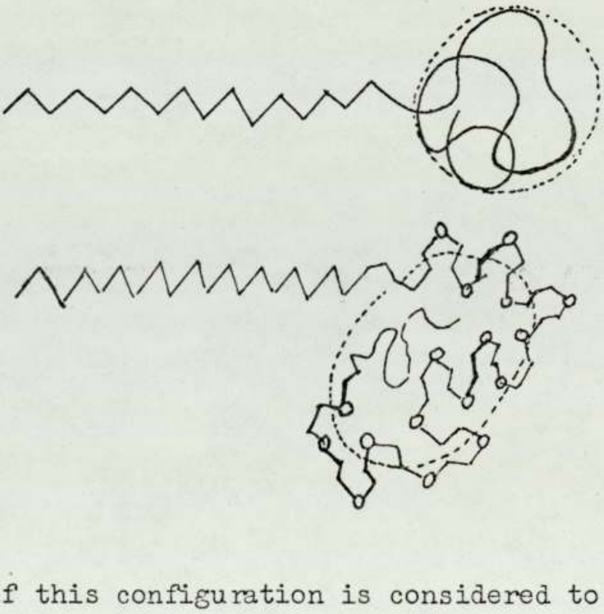
Consequently the length between (-O-CH_2-CH_2-O) group as illustrated



VII.i.4

will be reduced. In view of this treatment it is reasonable to postulate that the contact area of the hydrophilic group with water molecules will be reduced. The existence of some quantity of water in the interior of the configuration will stabilize the coiled meander configuration through hydrophobic interaction with oxygen atom.

Whatever the geometry of the configuration of the head group of surfactant is, the minimum one third or half oxygen atoms of the hydrophilic group will be the inside of the coiled head group. The geometry of the possible configurations can be illustrated such a s,



VII.i.5

If this configuration is considered to have constant density, the solvent to penetrate only partially and to be spherical, then the radius of the head group theoretically can be calculated. It is reasonable to consider that the hydrophobic group in zigzag configuration is not much affected due to contraction, because of not having hetero atoms like oxygen, then the diameter of the head group can be obtained, taking into account the effective length (120), the radius of the sphere is 49 Å. The volume occupied by the head group is 493000 Å^3, the volume which the meander unit can accommodate is 8216 Å^3. Due to this fact the whole molecule of non-ionic surfactant increases its hydrophobicity. The increase in hydrophobic surface area decreases C_0, the extended length of C_{16} is approximately equal to 25 Å which is one fourth of the diameter of the configuration of the spherical head group. It is apparent that the hydrophobic group has increased the surface area four times bigger than the hydrocarbon chain length. Because of the increment in hydrophobicity, C_0 shifts to a lower value, and the solubility of the surfactant tends to reverse direction (decrement in solubility)(172,292)

In the case of $C_{16}E_{30}$,$C_{16}E_{18}$ and $C_{16}E_{10}$ the zigzag configuration of oxyethylated hydrophobic group is considered. The obtained effective length is 91 Å; 74 Å, and 60 Å and the degree of coiling is 1.39 and 1.14 for $C_{16}E_{30}$,$C_{16}E_{18}$ and $C_{16}E_{10}$ respectively Table VII.I.6.

In the case of $C_{16}E_{10}$ the effective length is equal to the zigzag length of the molecule. This observation indicates that $C_{16}E_{10}$ does not coil in aqueous solution which is reasonable, since the hydration of oxyethylene group is high. The decrement in C_0 for lower polyoxyethylated surfactants can be discussed in the same way as performed in this section.

VII.Ie - Conclusions.

The micellar properties of non-ionic surfactants in aqueous solution and containing additives, were examined in terms of viscosity, surface tension and light scattering techniques, taking into account the adsorption of molecules on glassware. The observations show that the C_0 decreases with increasing ethylene oxide chain length, and the observed adsorption does not affect the C_0. The C_0 of the non-ionic surfactant ($C_{16}E_{10}$) was also examined on a weight volume basis. The obtained value of C_0 confirmed also the results observed by the mol.g. volume basis.

The decrement in C_0 was discussed in terms of the coiling of the polyoxyethylene group decreasing its hydrophilic surface area. The examination of this phenomenon was carried out on the basis of zigzag, and meander configuration of polyoxyethylene chains in aqueous solution, employing Peterlin's theory. In view of Peterlin's approach the calculated effective lengths are less than straight configurational lengths of the hydrophilic groups. The degree of coiling, and the dipole contraction force decreases with decreasing degree of polymerization.

This observation indicates that the hydrophilic group is coiled, considerably reducing its contact area with water molecules. Due to this fact the hydrophobicity of the molecule is increased because of the considerable number of ether oxygen atoms remaining inside the configuration of the head group. When the hydrophilic character of the molecule is reduced because of the existence of the coiled configuration, the hydrophobic surface area is increased, which decreases the affinity of the molecule for the water molecules, then the solubility of non-ionic decreases, consequently the C_0 shifts to a lower value as the hydrophobicity increases.

The observed quantity of hydration is decreased as the hydrophilic group increases, which is contrary to the concept of the hydration of the polyoxyethylene surfactant given in literature. The amount of water molecules hydrated per g. surfactant decreases with increasing ethylene oxide chain length. The intrinsic viscosity of micelles increases with increasing hydrophilic chain length. Although the relative viscosity of the aqueous solution of non-ionic surfactant is high, the increment in intrinsic viscosity is not significant compared with cetyltrimethyl ammonium bromide. The major contribution for the increment in intrinsic viscosity arises from particle shape and size of the micelles. The other factors involved are hydration, and hydrophobic interactions between nonpolar, polar and water molecules. In view of hydration and light scattering data it was concluded that the micelles were of prolate type.

The cloud points of the non-ionic surfactants increase with increasing ethylene oxide chain length. However the observed cloud points are not high compared with the values given in literature. These results confirm also that the amount of hydrated water molecules by non-ionic surfactants are not significant. The micellar molecular weight decreases as the hydrophilic chain length increases, with decreasing semi-axis of revolution of the micelles.

The partial molal volumes of the non-ionic surfactants increase below the C_o, and above the C_o as the hydrophilic group increases. It is quite evident that the formation of micelles is accompanied by volume change during the micellization. The increment in partial molal volume of the monomer is the indication of the volume change, when the monomer is transferred from aqueous environment to a nonpolar region. The increment in partial molal volume of the micelles decreases with increasing ethylene oxide chain length.

The micellar properties of non-ionic surfactants have also been observed by adding organic additives to the system. The effect of aromatic alcohols, urea and urethane was examined by means of light scattering technique. The scattering intensity of mixed solutions is high compared with that of aqueous surfactant solution. The increment in turbidity was discussed taking into account the change in density and concentration fluctuations in the refractive index of the solution near to the solute particle, and selective adsorption of the additive on polymer molecule. It is also believed that the effect of alcohols on the optical efficiency of the micelles plays a unique role for the increment in turbidity. The effect of alcohols on C_o was interpreted in terms of hydrophobic interactions between possible orientations, the degree of solubility of alcohols, and the structure breaker and maker character of the alcohol molecules. The C_0 increases when 0.01M alcohol is added to the system. As the concentration of alcohol increases, the behaviour of alcohol on C_0 tends to reverse direction as was observed for the cationic systems. The micellar molecular weight increases with increasing concentration of alcohol, and $-CH_2-$ group of alcohol chain length, and the observed shape of micelle is prolate type.

The addition of urea and urethane has considerably changed the micellar properties of non-ionic surfactants. The C_0 increased in both cases. But the increment in C_0 is higher on the addition of 1M urea to the system compared with the urethane. The increment in scattered intensity and turbidity was also discussed. The effect of concentration and density fluctuations on the solvent molecules near the solute, and the preferential adsorption of the organic solute on the surfactant molecule. The increment in turbidity is higher when the 0.7M urethane is added to the system. This is due to more polar character of the urethane than the urea.

It is believed that in both cases, the additives take an active part in the mixed cluster formation in terms of the hydrophobic interactions with water molecules. It is further assumed that these additives are structure promoters since the mixed clusters are larger than water clusters, which readily accommodate the large hydrophobic group inside the cavity.

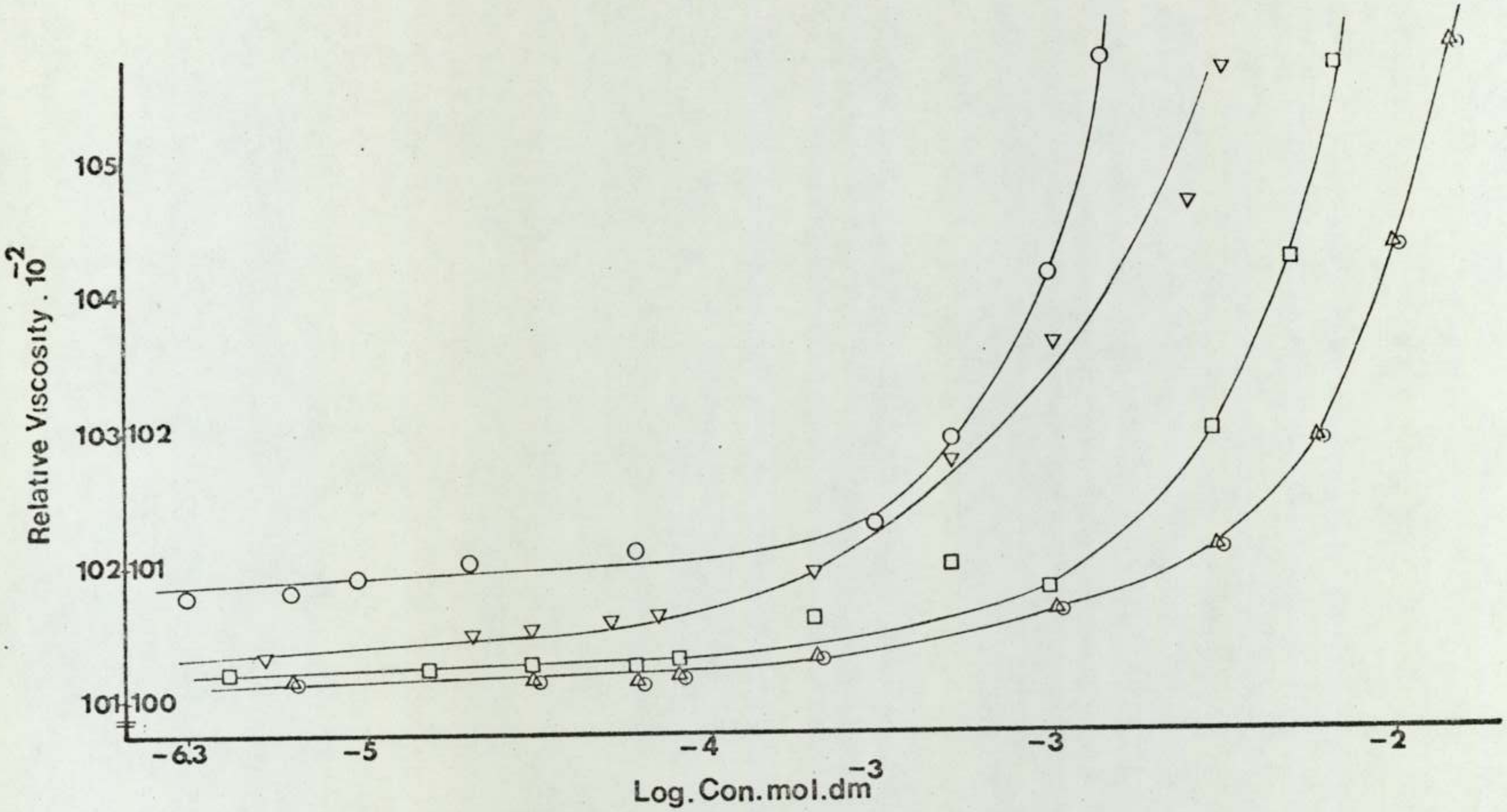


Fig. VII.1 Plots of relative viscosities of the polyoxyethylene mono hexadecyl ethers in water at 25° C; ⦻ EO_{10}, □ EO_{18}, △ EO_{30}, and ○ EO_{60}

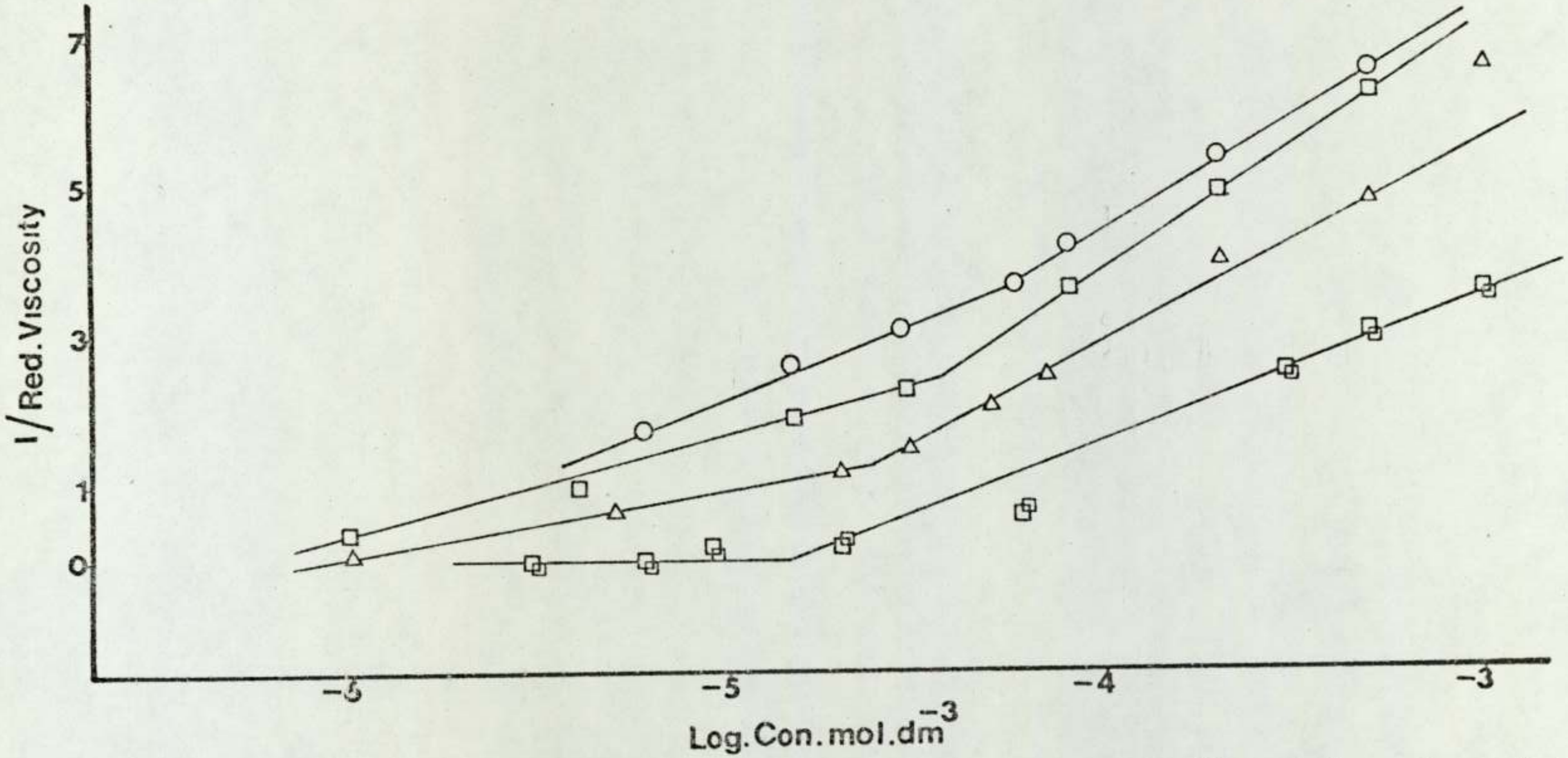


Fig. VII.2 Reciprocal reduced viscosities as a function log. concentration of the polyoxyethylene mono hexadecyl ethers at 25° C; ○ EO_{10}, □ EO_{18}, △ EO_{30}, and ⊞ EO_{60}

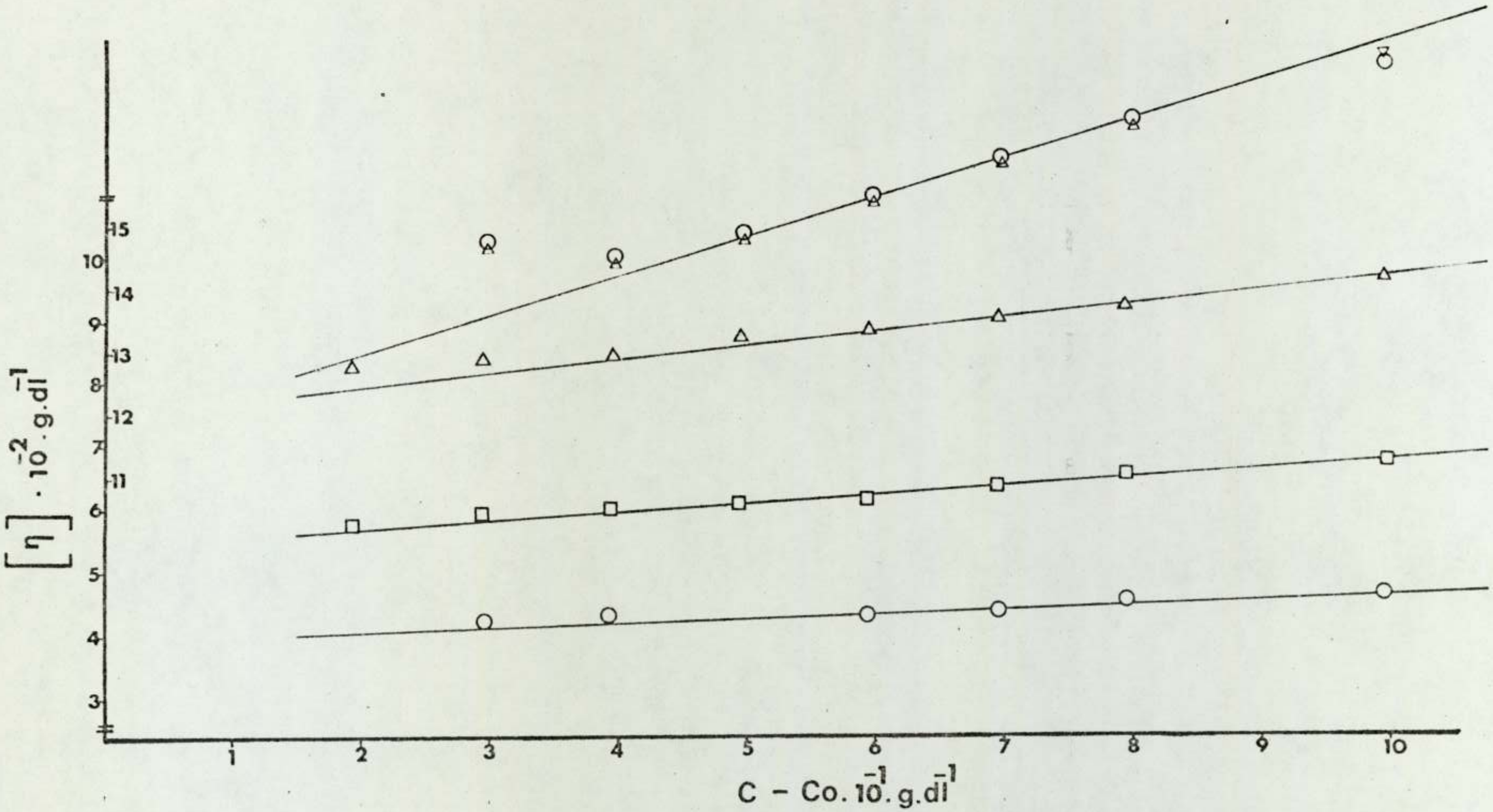


Fig. VII.3 The intrinsic viscosity of micelles versus concentration for the polyoxyethylene mono hexadecyl ethers in water at 25° C; ○△ EO$_{60}$, △ EO$_{30}$, □ EO$_{18}$, and ○ EO$_{10}$

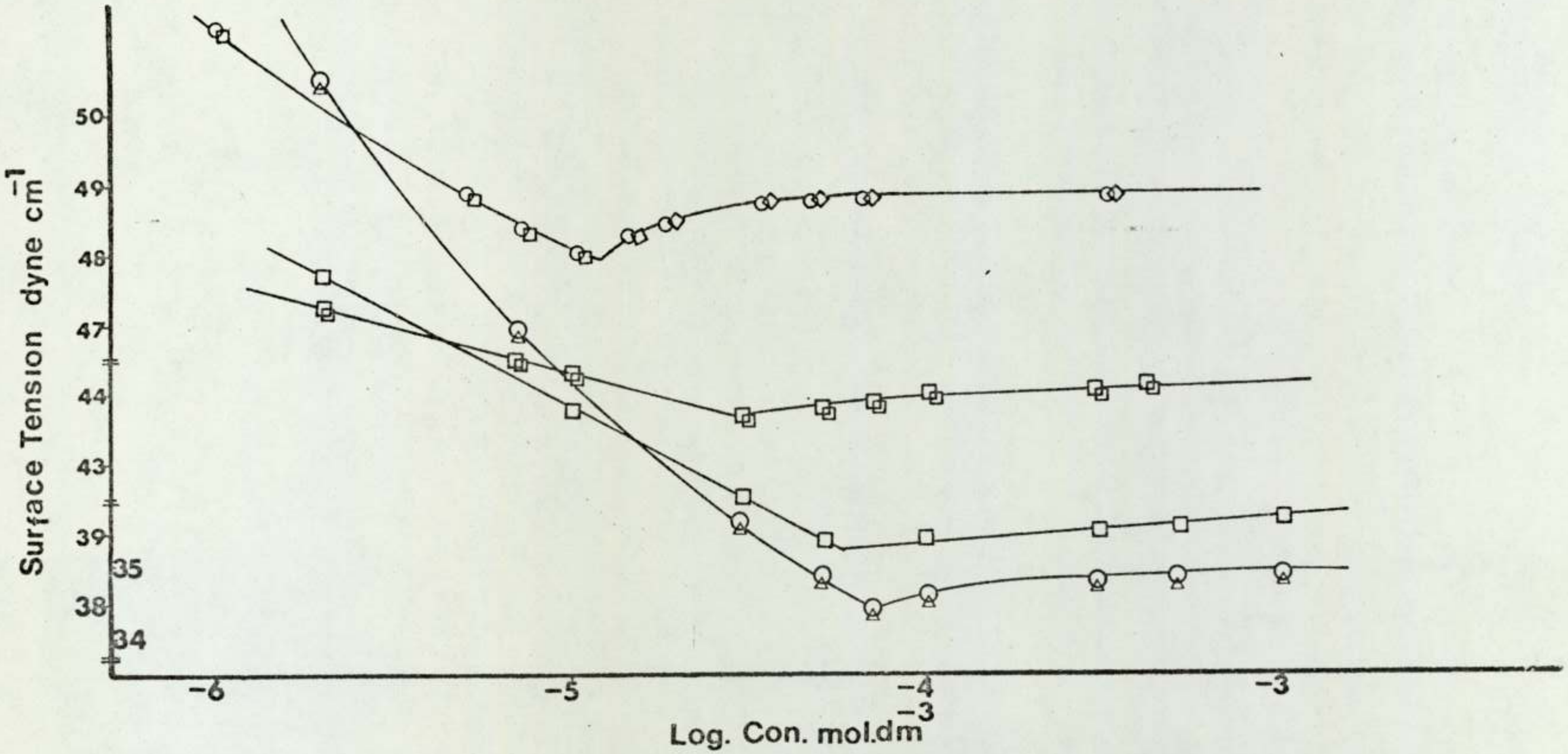


Fig. VII.4 Plots of surface tension versus log. concentration for the impure polyoxyethylene mono hexadecyl ethers in water at 25° C; ○◇ EO_{60}, ⊞ EO_{30}, □ EO_{18}, and ○△ EO_{10}

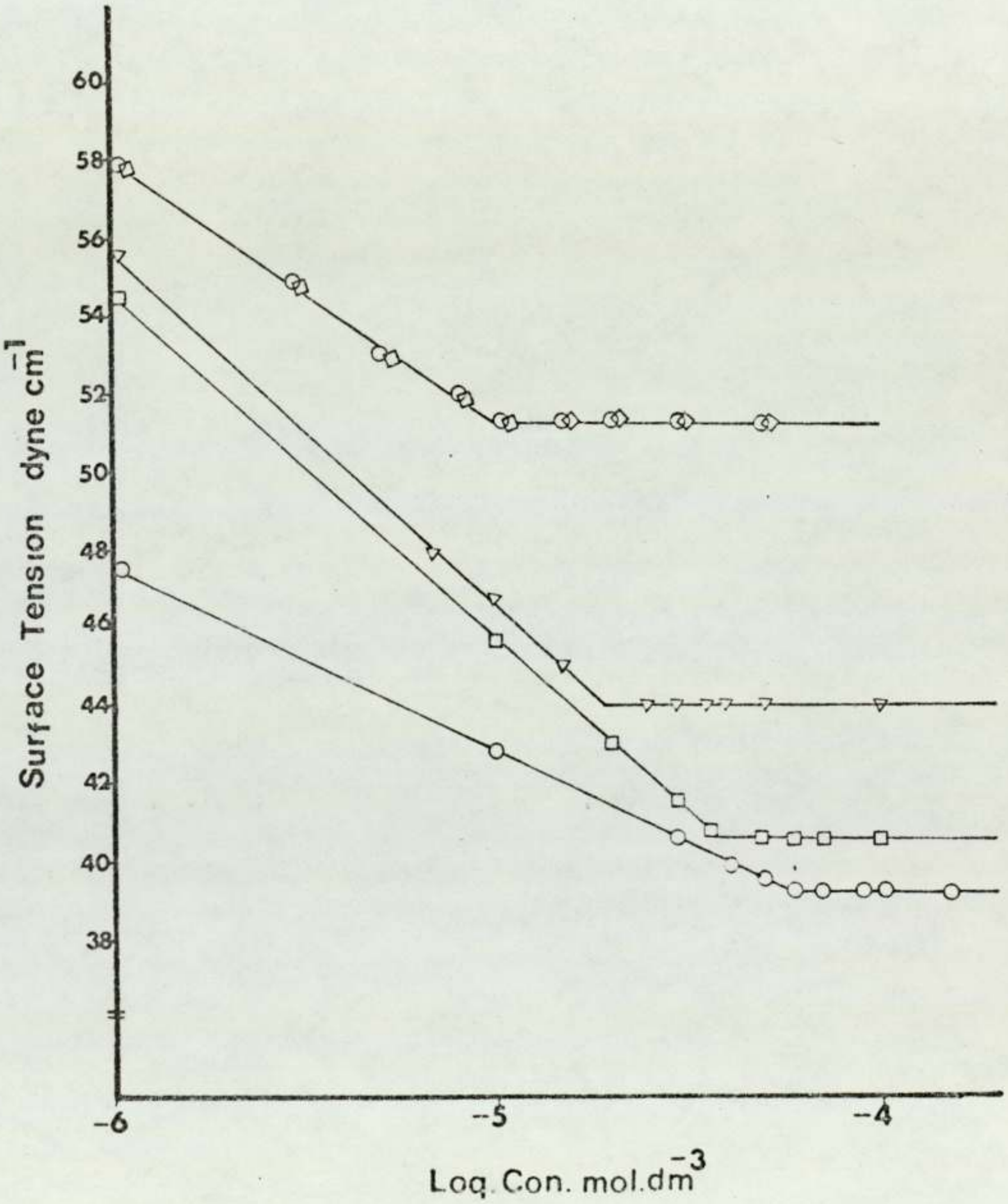


Fig.VII.5 Plots of surface tension versus log. concentration for the purified polyoxyethylene mono hexadecyl ethers in water at 25° C; ○◇EO_{60}, △ EO_{30}, □ EO_{18}, and ○ EO_{10}

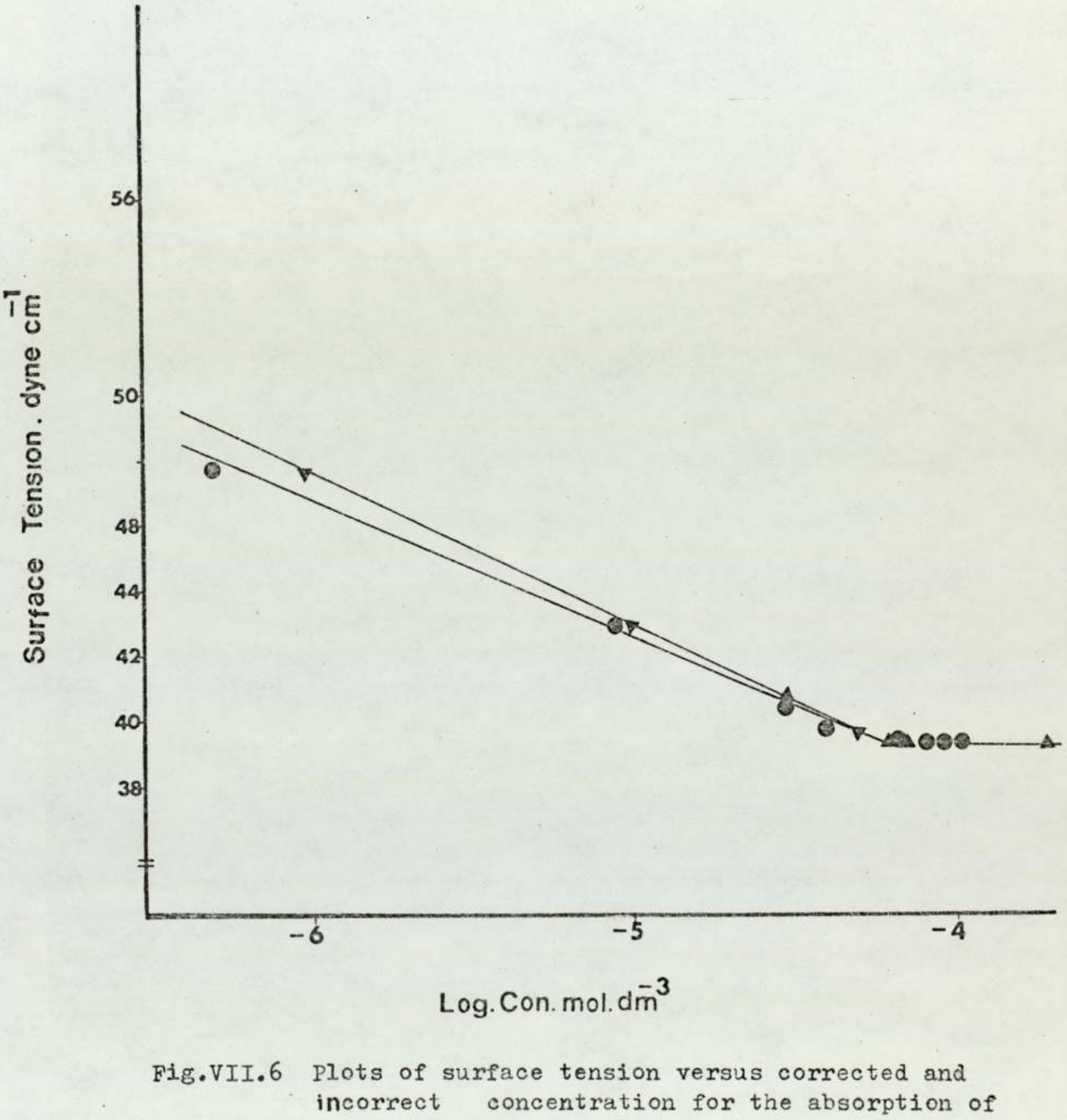


Fig.VII.6 Plots of surface tension versus corrected and incorrect concentration for the absorption of polyoxyethylene mono hexadecyl ether (A 10) on glassWear in water at 25° C; ● Incorrect con. ▲ corrected

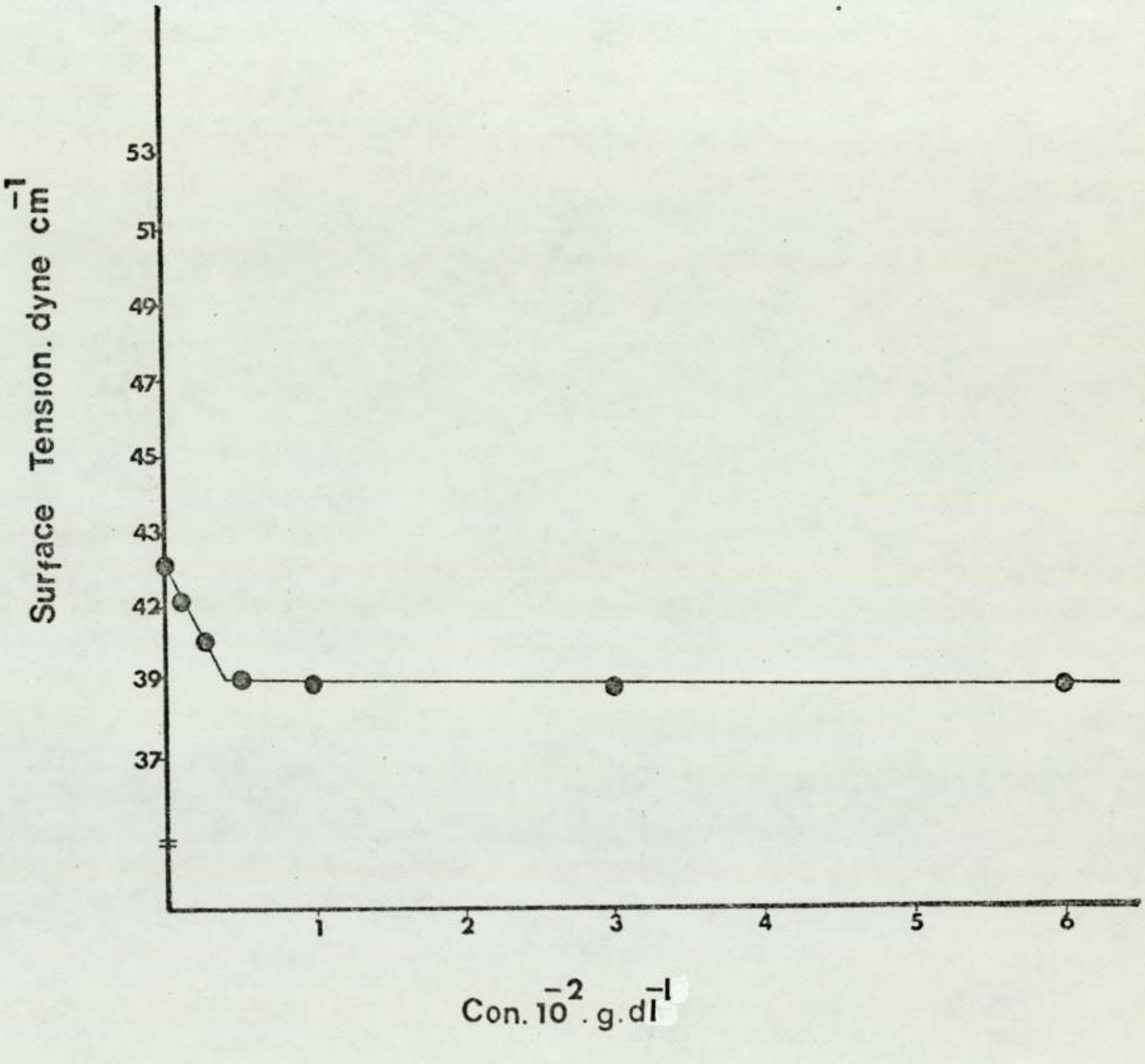


Fig.VII.7 Surface tension versus concentration Weight/Volume curve for the polyoxyethylene mono hexadecyl ether (A_{10}) in water at 25° C;

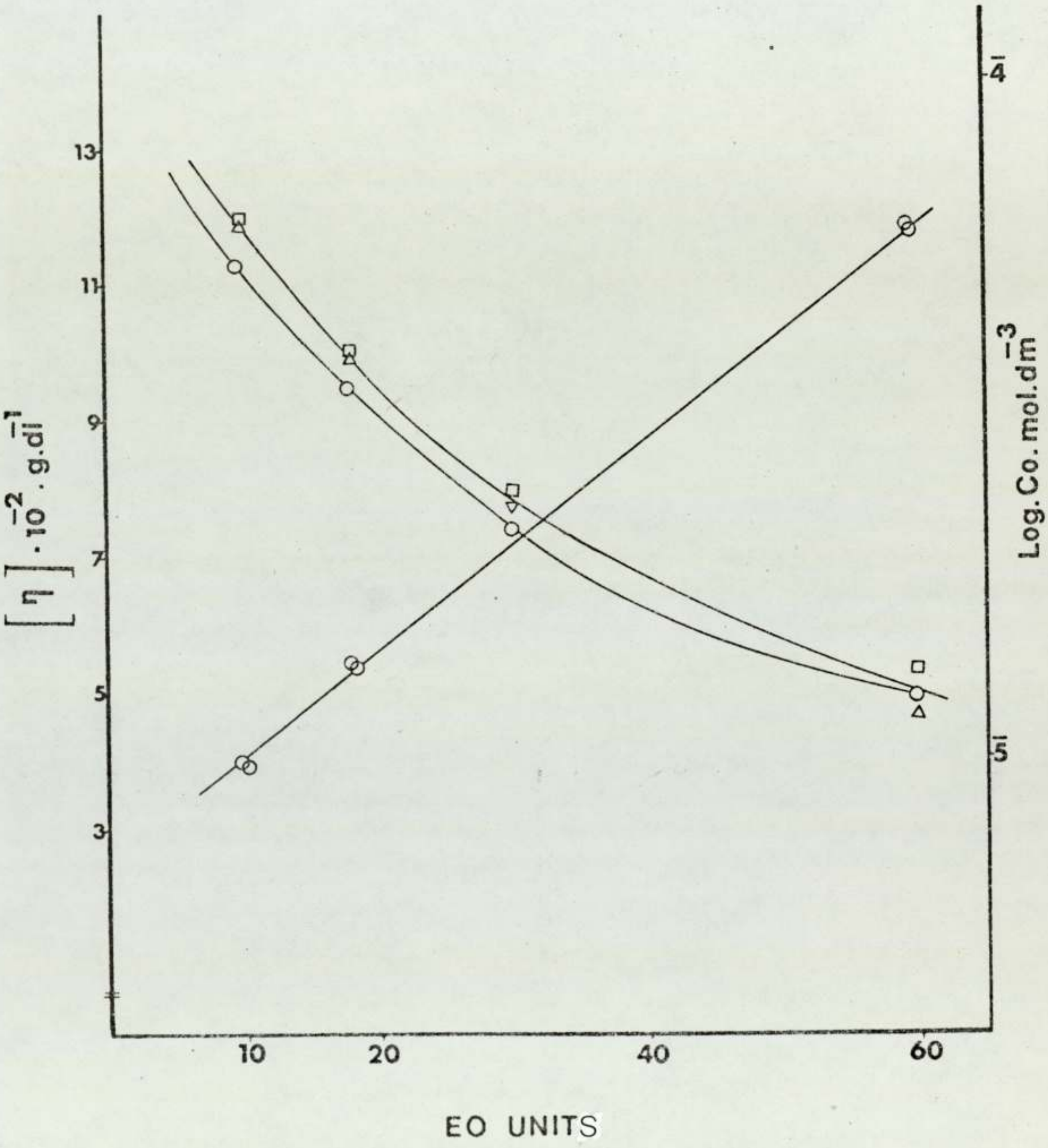


Fig.VII.8 Dependence of Co and intrinsic viscosity of the micelles of polyoxyethylene mono hexadecyl ethers on the ethylene oxide chain length in water at 25° C; □ Viscosity, ○ Surface Tension , △ Light Scattering (C_o) ; ○○ $[\eta]$

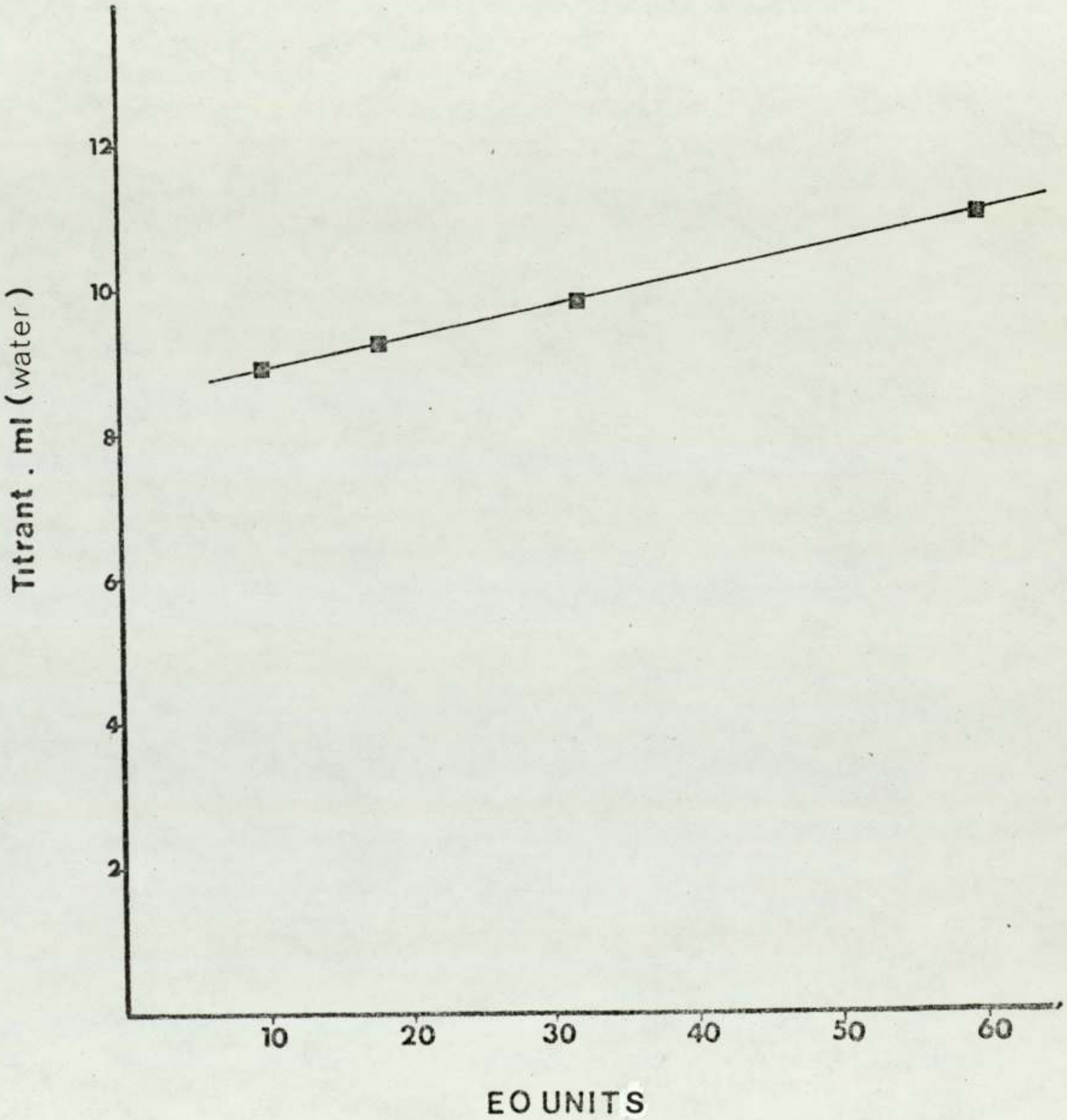


Fig.VII.9 Titrant versus ethylene oxide units curve for the polyoxyethylene mono hexadecyl ethers in 25 ml DMF and 5 ml Benzene at 25° C;

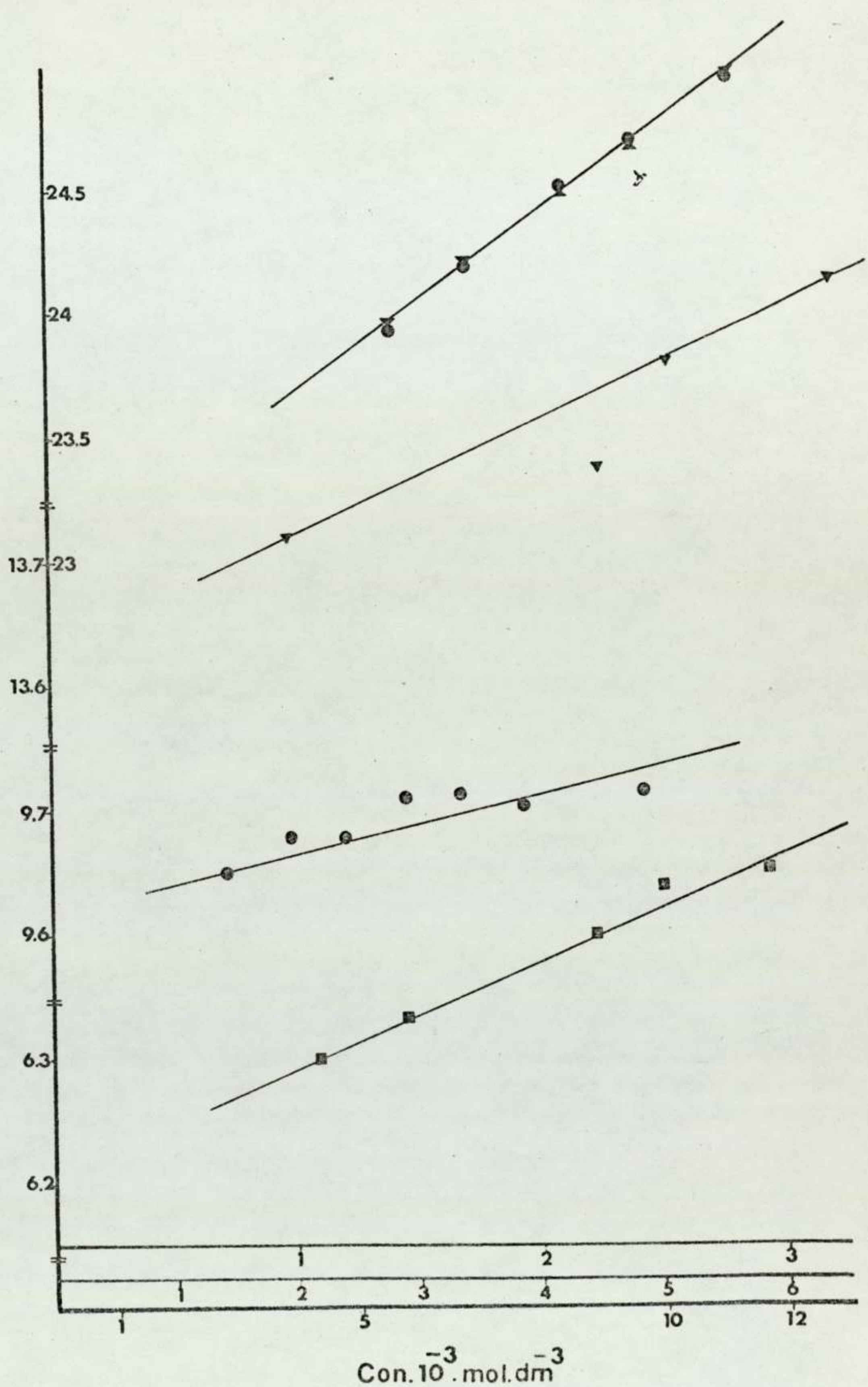


Fig.VII.10 Volumetric properties of the polyoxyethylene mono hexadecyl ethers below the Co at 25° C; ■ EO_{10}, ● EO_{18}, ▼ EO_{30}, and ⧗ EO_{60}

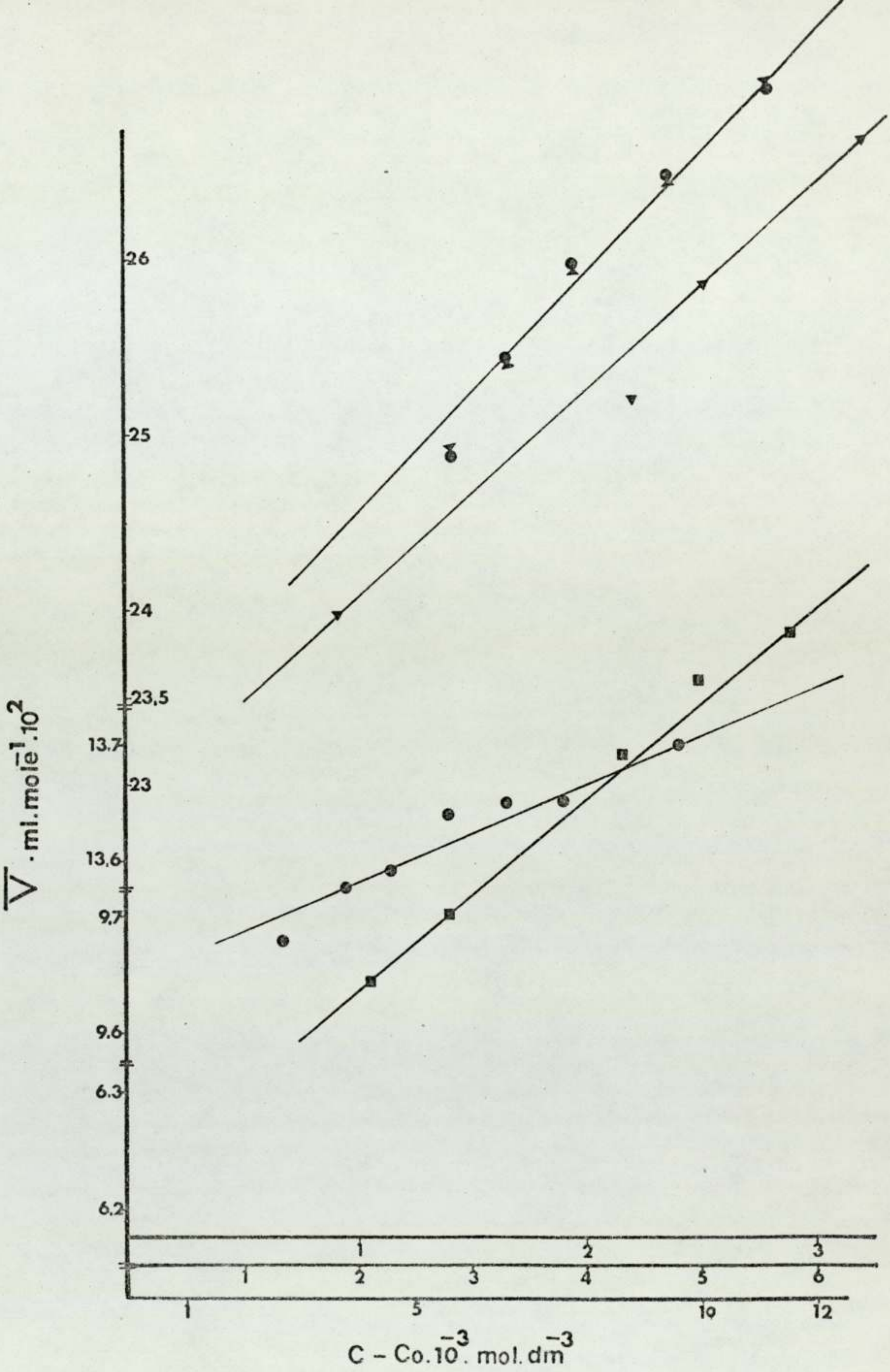


Fig.VII.11 Volumetric properties of the polyoxyethylene mono hexadecyl ethers above the Co at 25° C; ■ EO_{10}, ● EO_{18}, ▼ EO_{30}, and ⧗ EO_{60}

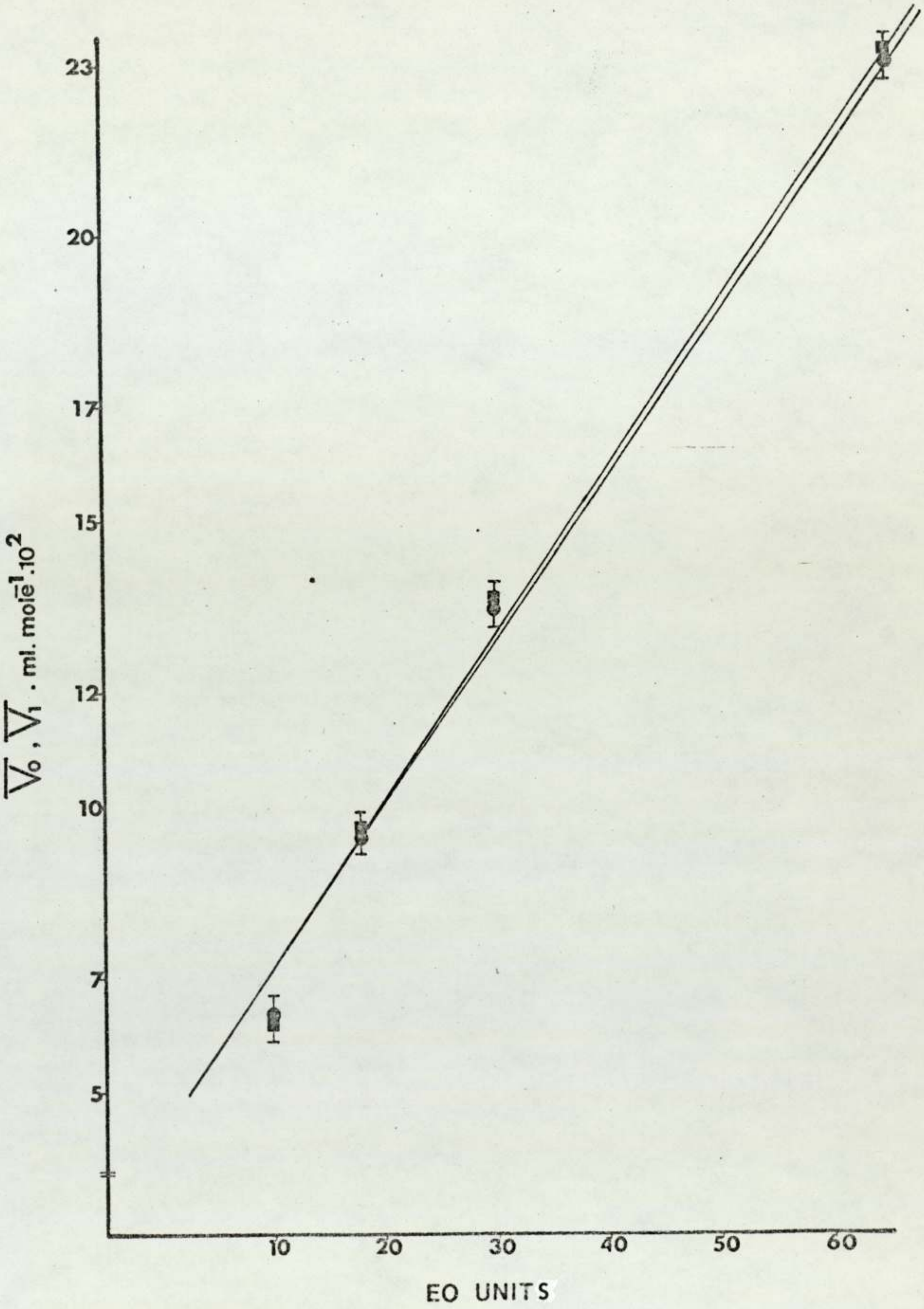


Fig.VII.12 Partial molal volumes of the polyoxyethylene mono hexadecyl ethers below the Co and above the Co as a function of the ethylene oxide chain length at 25° C; ▮ above the C_o, ● below the C_o

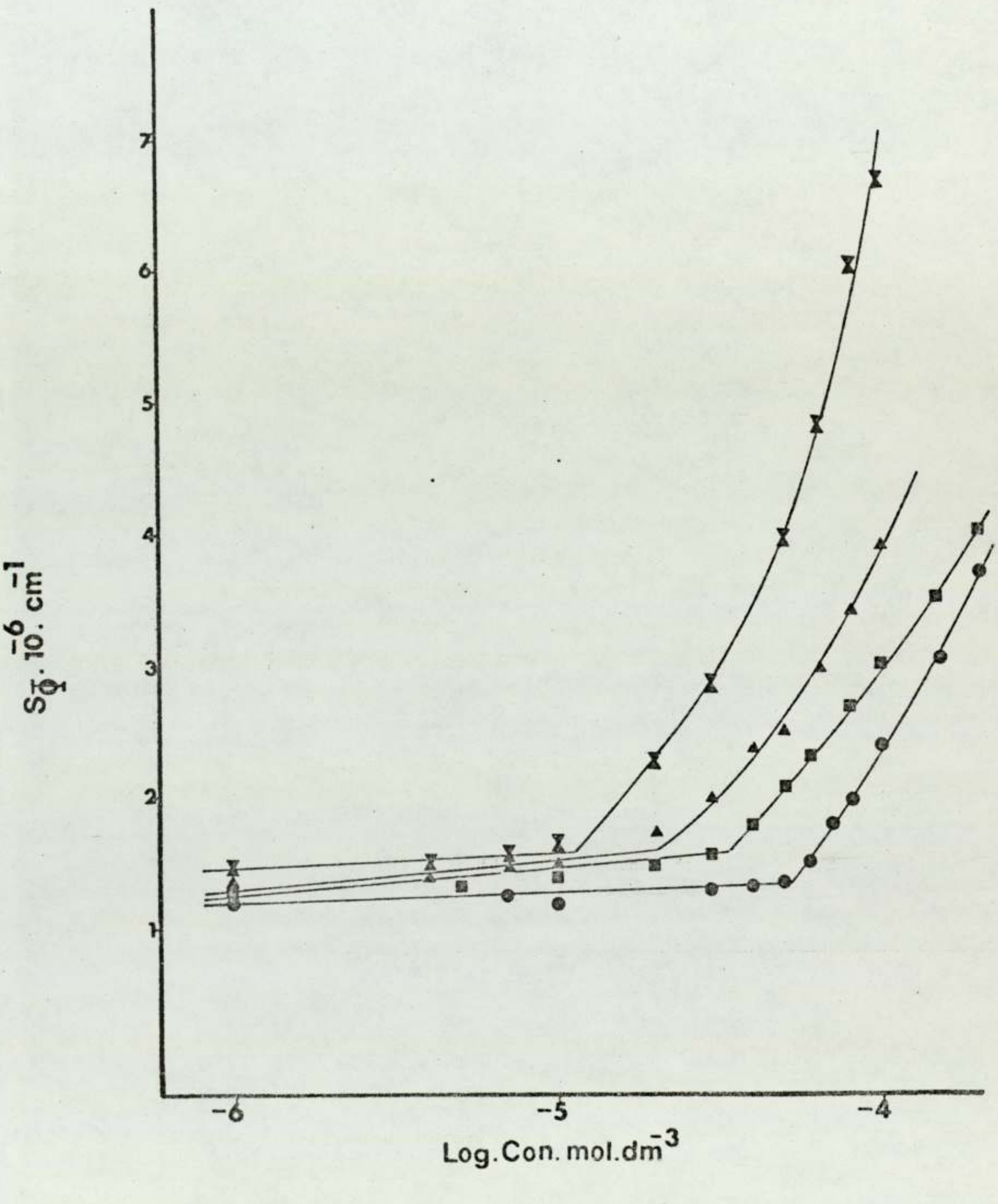


Fig.VII.13 Light scattering at 90° by polyoxyethylene mono hexadecyl ethers in water at 25° C; ● EO_{10}, ■ EO_{18}, ▲ EO_{30}, and Ⅹ EO_{60}

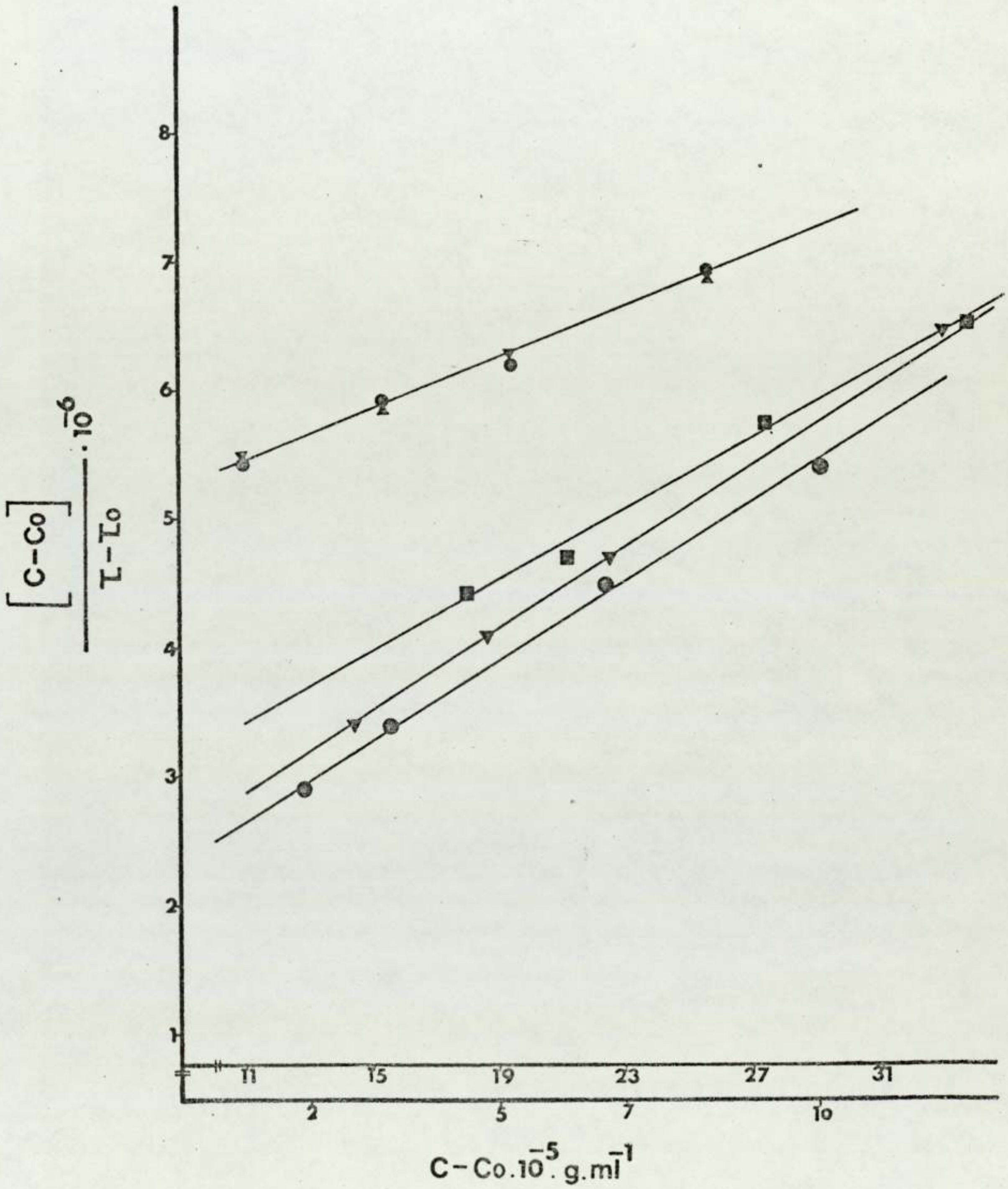


Fig.VII.14 Plot of H $(C-Co)/\tau-\tau o$ versus C-Co for the polyoxyethylene mono hexadecyl ether in water at 25° C; ● EO_{10} , ▲ EO_{18} , ■ . EO_{30} , and EO_{60}

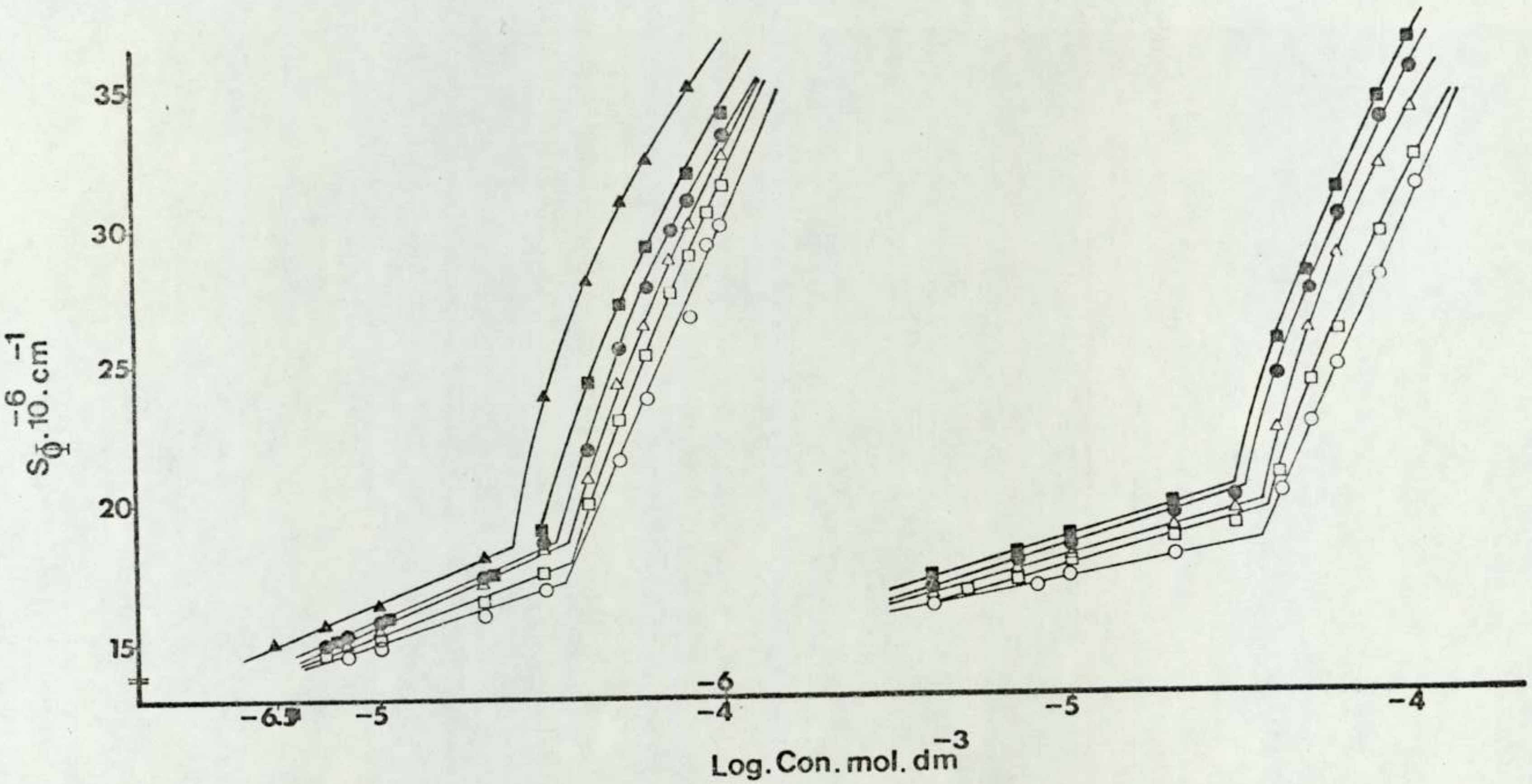


Fig. VII.15 Light scattering at 90° by polyoxyethylene mono hexadecyl ether (A $_{18}$) containing various concentration of the phenol and benzylalcohol in water at 25 °C; Phenol: ○ 0.01m, □ 0.02m, △ 0.03m, ● 0.04m, ■ 0.05m, and ▲ 0.08m, Benzylalcohol: ○ 0.01m, □ 0.02m, △ 0.03m, ● 0.04m, and ■ 0.05m

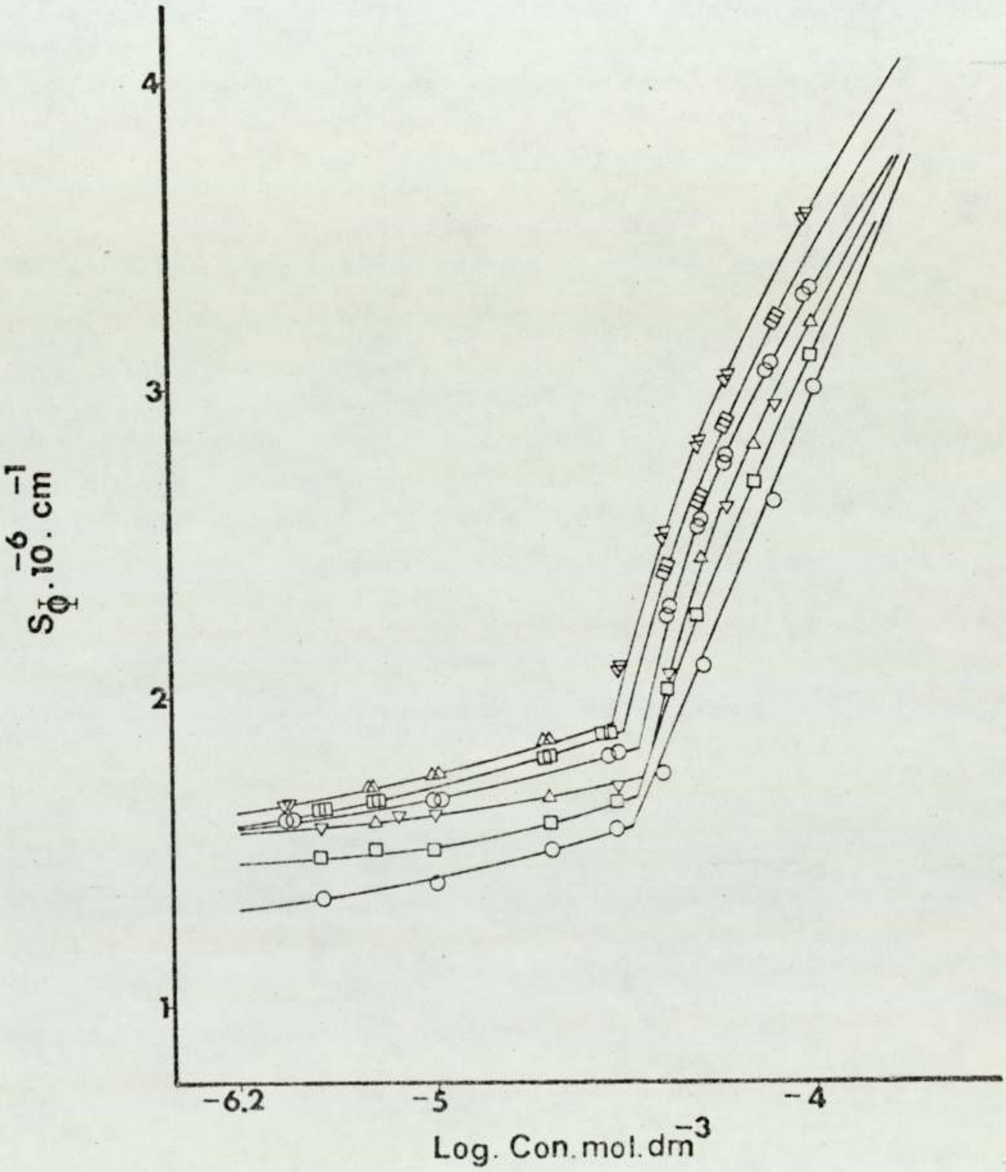


Fig.VII.15.A Light scattering at 90° by polyoxyethylene mono hexadecyl ether (A_{18}) containing various concentration of the phenylethanol in Water at 25° C ; ○ in Water, Phenylethanol: □ 0.01m, △ 0.02m, ◎ 0.03m, ▥ 0.04m, ⟁ 0.05m

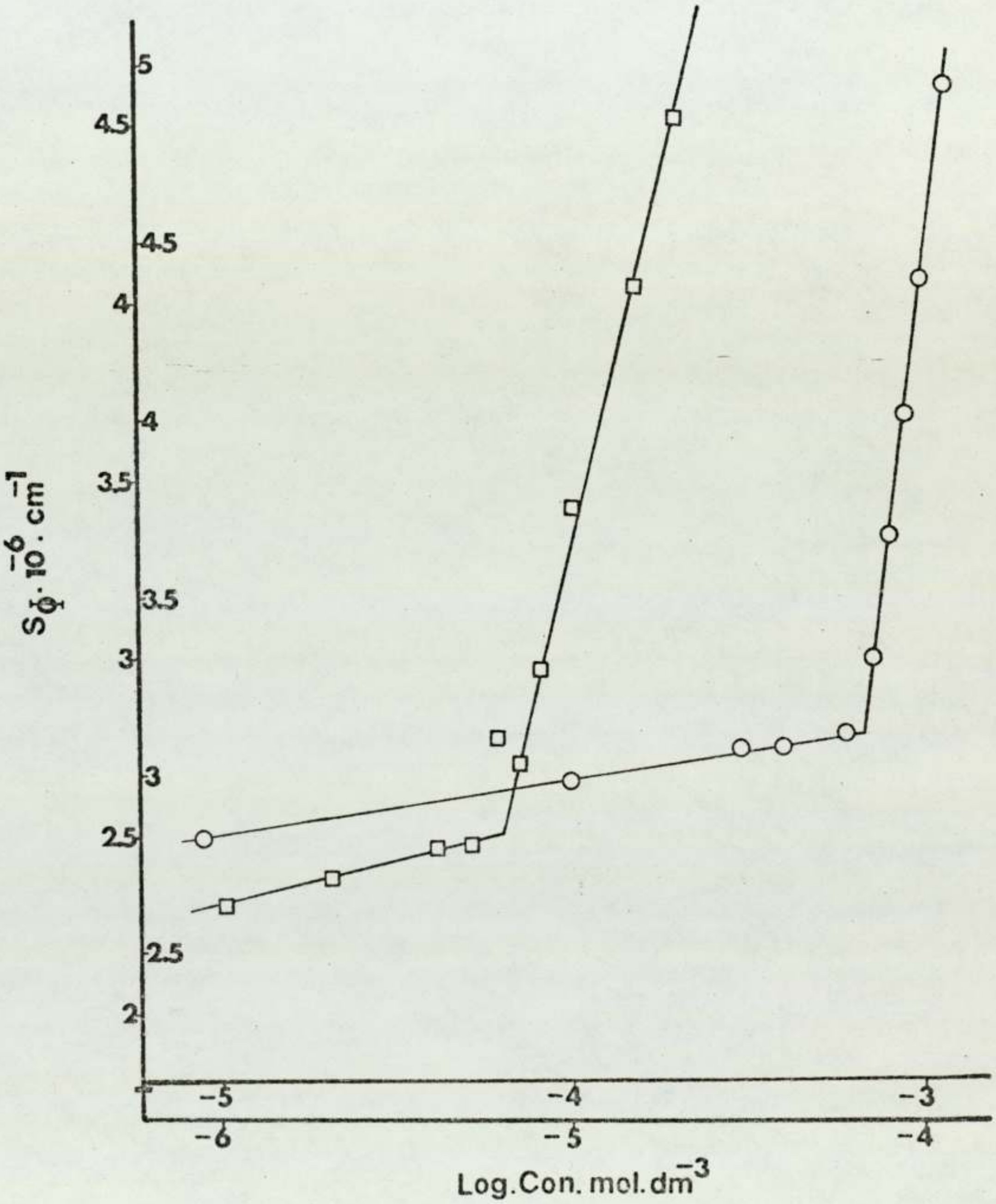


Fig.VII.16 Light scattering at 90° by polyoxyethylene mono hexadecyl ether (A_{18}) containing urea and urethane in water at 25° C; ○ 1M Urea, □ 0.7 M Urethane

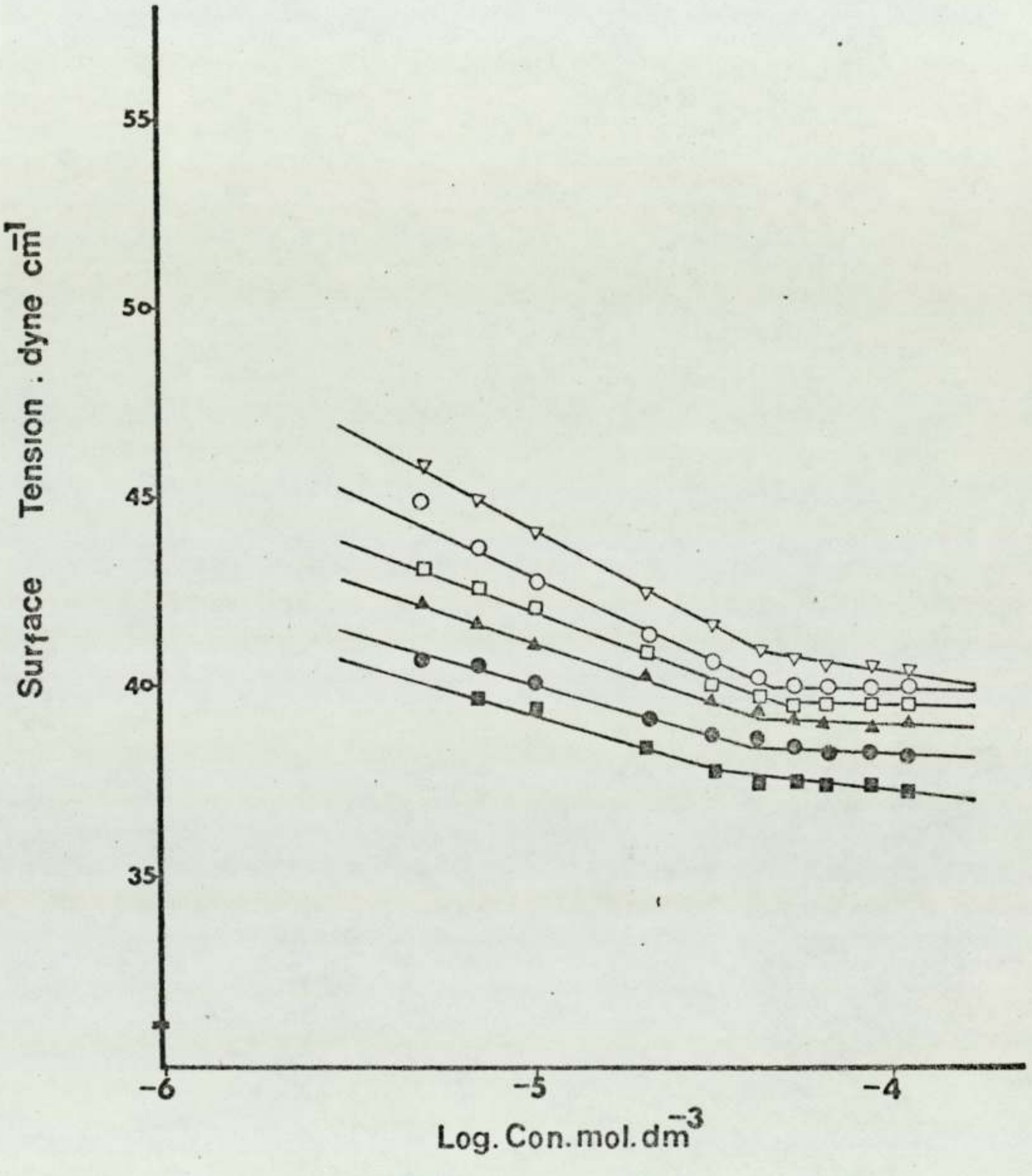


Fig.VII.17 Surface tension versus log. concentration for the polyoxyethylene mono hexadecyl ether (A_{18}) containing various concentration of phen in water at 25° C; ■ 0.01m, ● 0.02m, ▲ 0.03m, □ 0.04, ○ 0.05m, and ▽ 0.08m

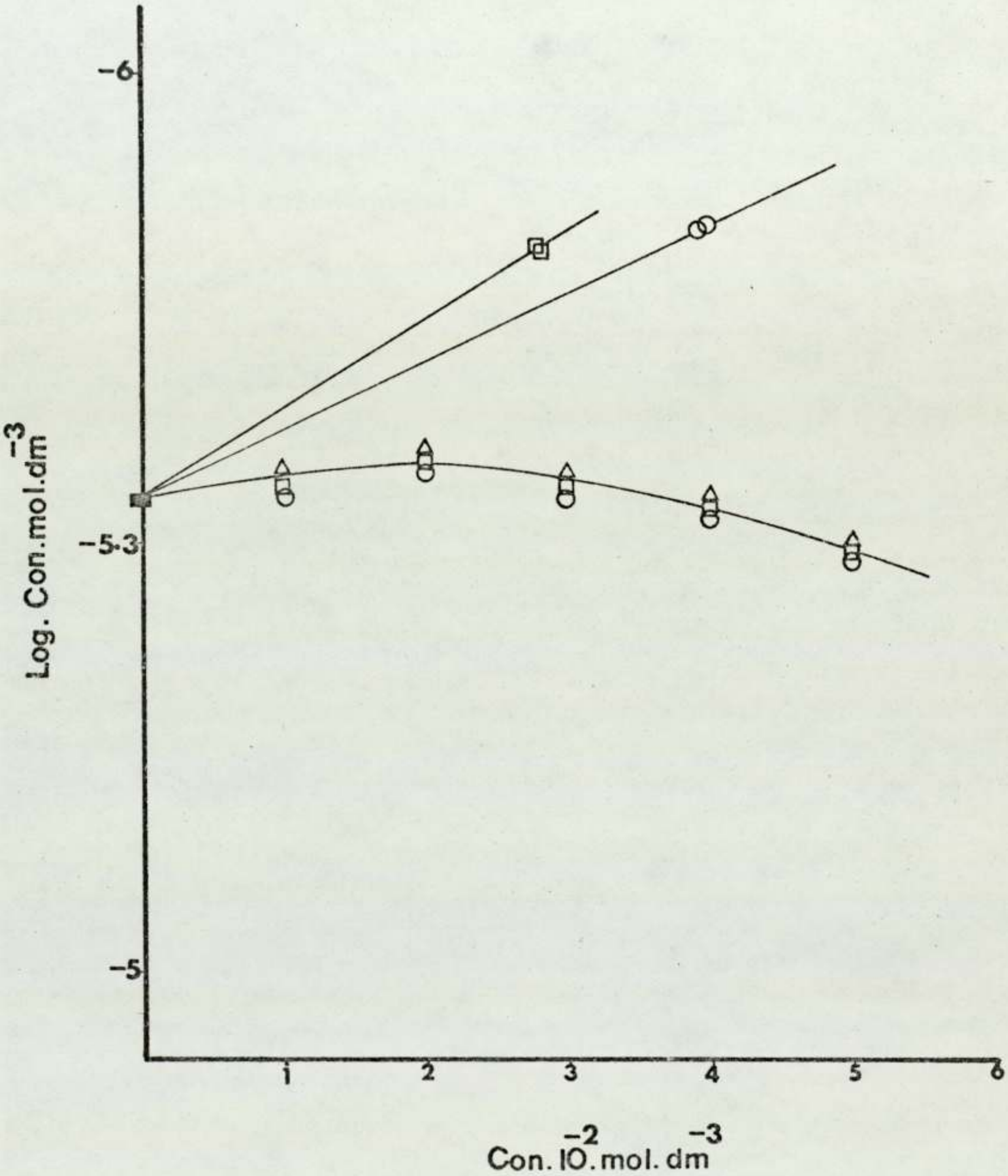


Fig. VII.18 The effect of the aromatic alcohols, urea and urethane on the Co of the polyoxyethylene mono hexadecyl ether (A 18) at 25° C; ⊞ Urethane, ⦾ Urea, ○ Phenol, □ Benzylalcohol, and △ Phenylethanol

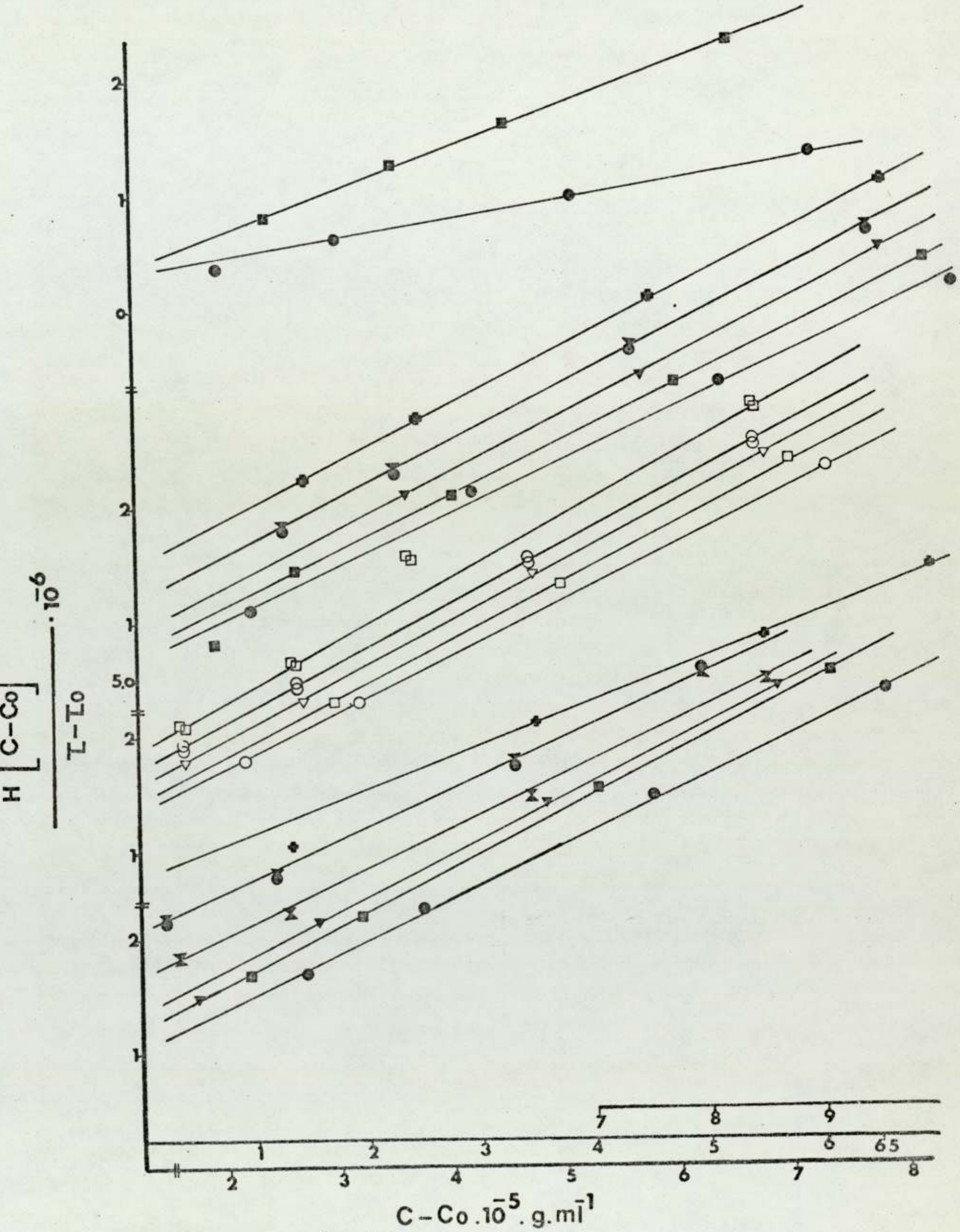


Fig.VII.19 H[C-Co]/τ-τo versus C-Co for the polyoxyethylene mono hexadecyl ether (A $_{18}$) containing various concentration of the aromatic alcohols, urea and urethane in water at 25° C;

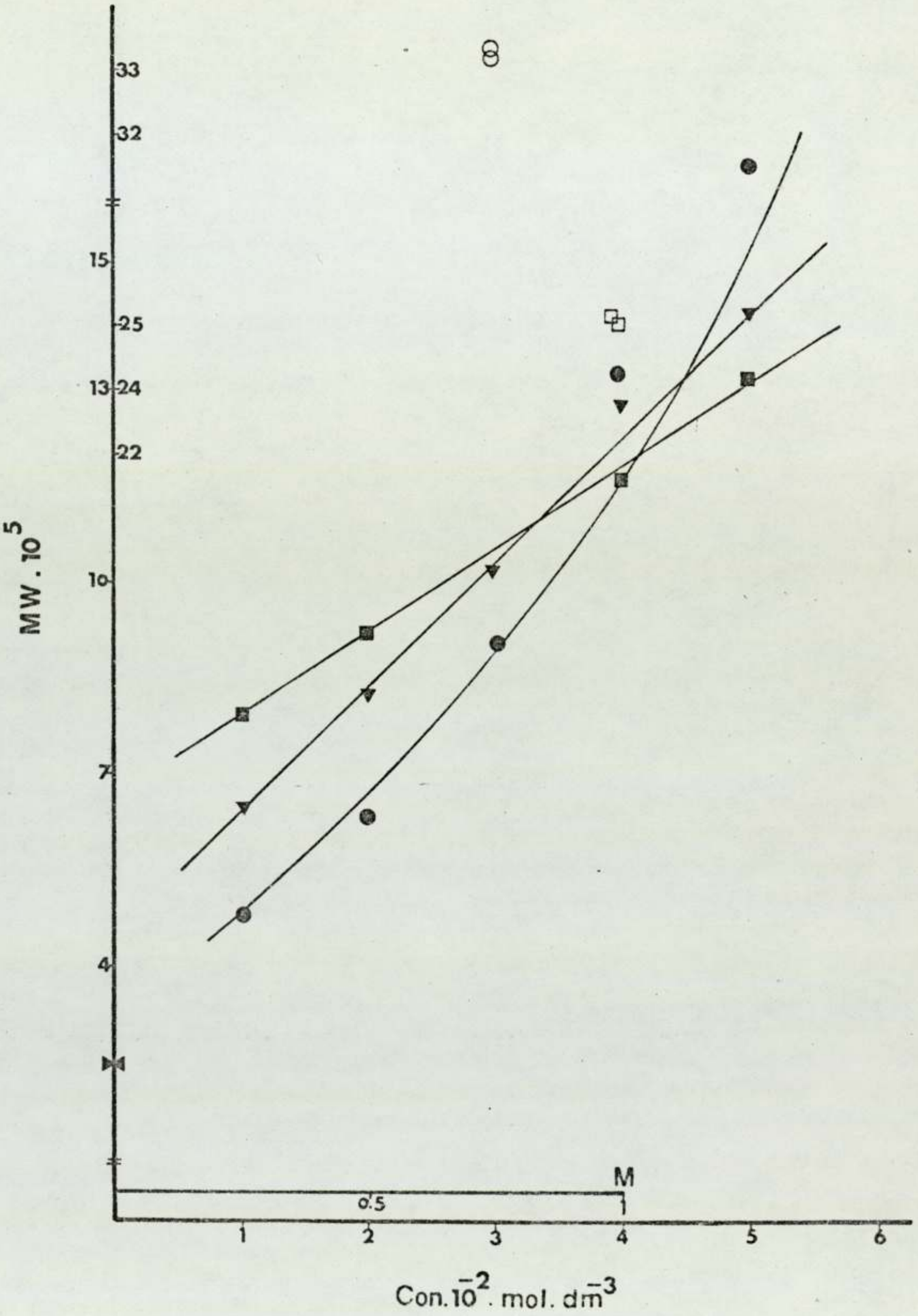


Fig.VII.20 The aromatic alcohols, urea and urethane concentration dependence of micellar molecular weight of the polyoxyethylene mono hexadecyl ether (A_{18}) in water at 25° C; ● Phenol, ■ Benzylalcohol, ▼ Benzylethanol, ⟐ Urea, and ⊖ Urethane

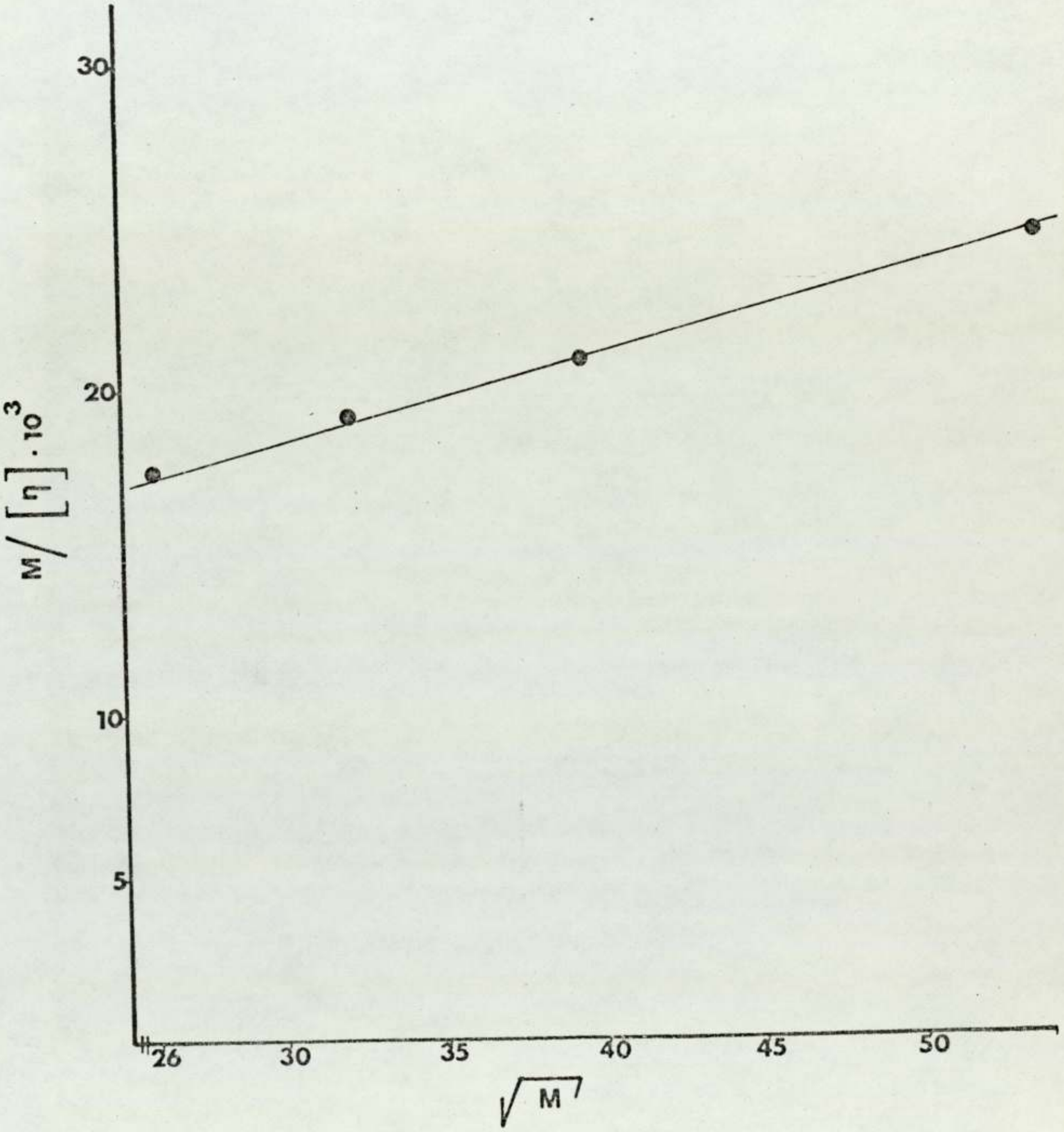


Fig.VII.21 $M/[\eta]$ versus $M^{1/2}$ for the polyoxyethylene mono hexadecyl ethers in water at 25° C;

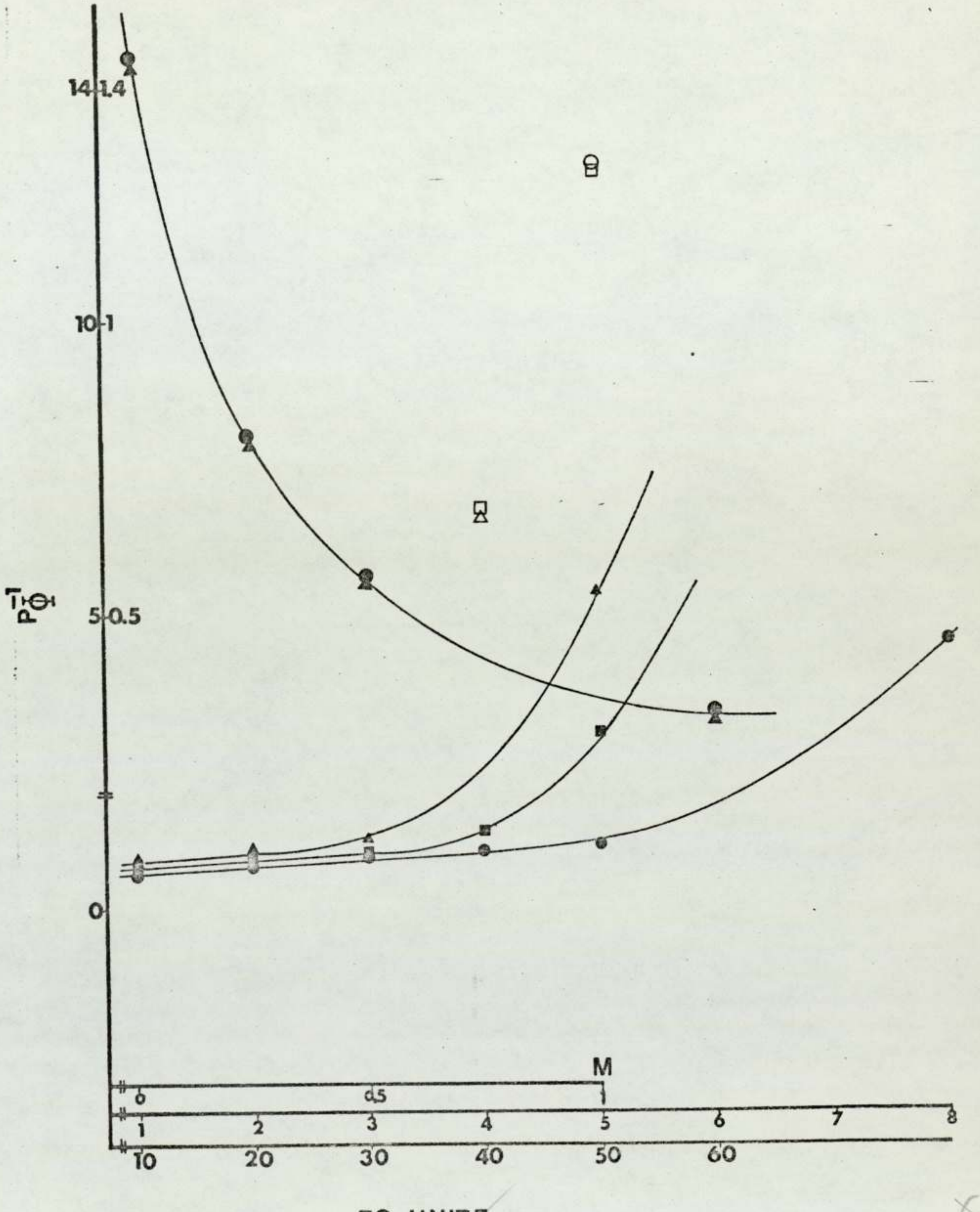


Fig.VII.22 Dependence of P^{-1}_{Φ} of the polyoxyethylene mono hexadecyl ether (A_{18}) on the concentration of the aromatic alcohols, urea and urethane at 25° C; EO$_n$, Urea, Urethane, ● Phenol, ■ Benzylalcohol, and ▲ Benzylethanol

VISCOSITY AND SURFACE TENSION DATA FOR THE AQUEOUS SOLUTIONS OF POLYOXYETHYLENE MONOHEXADEDECYL ETHERS AT 25° C

TABLE VII.I.1

Viscocity							Surface Tension		Correc. Surface Ten.	
C $mol.dm^{-3}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$\frac{\eta_{sp}}{C}$	C_o $mol.dm^{-3}$	C $mol.dm^{-3}$	γ $dyne.cm^{-1}$	γ $dyne.cm^{-1}$	C_o $mol.dm^{-3}$
$C_{16}EO_{10}$										
1×10^{-3}	0.99721	0.9002	1.0059	0.0059	11.46	5.6×10^{-5}	2×10^{-4}	39.21		6.0×10^{-5}
5×10^{-4}	0.99720	0.8996	1.0053	0.0053	6.44		1×10^{-4}	39.23	39.24	
2×10^{-4}	0.99718	0.8972	1.0025	0.0025	5.44		9×10^{-5}	39.31	39.25	
8×10^{-5}	0.99717	0.8961	1.0013	0.0013	4.20		8×10^{-5}	39.24	39.32	
6×10^{-5}	0.99715	0.8958	1.0011	0.0013	3.70		7×10^{-5}	39.22	39.21	
3×10^{-5}	0.99714	0.8955	1.0006	0.0006	3.03		6×10^{-5}	39.25	39.23	
1.5×10^{-5}	0.99713	0.8953	1.0004	0.0004	2.40		5×10^{-5}	39.62	39.60	
4×10^{-6}	0.99712	0.8952	1.0003	0.0003	1.70		4×10^{-5}	39.95	39.85	
							3×10^{-5}	40.65	40.55	
							1×10^{-5}	42.83	42.91	
							1×10^{-6}	47.60	47.72	
$C_{16}EO_{18}$										
5×10^{-4}	0.99723	0.9024	1.0083	0.0083	6.17	3.89×10^{-5}	4×10^{-4}	40.62		3.85×10^{-5}
2×10^{-4}	0.99722	0.8987	1.0043	0.0043	4.86		1×10^{-4}	40.63		
8×10^{-5}	0.99721	0.8968	1.0022	0.0022	3.76		8×10^{-5}	40.61		
5×10^{-5}	0.99721	0.8964	1.0017	0.0017	3.08		7×10^{-5}	40.62		
3×10^{-5}	0.99721	0.8962	1.0014	0.0014	2.15		6×10^{-5}	40.64		
1.5×10^{-5}	0.99721	0.8956	1.0008	0.0008	1.91		5×10^{-5}	40.62		
4×10^{-6}	0.99720	0.8953	1.0004	0.0004	0.89		4×10^{-5}	40.61		
1×10^{-6}	0.99720	0.8951	1.0003	0.0003	0.36		3×10^{-5}	41.62		

TABLE VII.I.1.A

-	-	-	-	-	-	-	2×10^{-5}	43.15	-
							1×10^{-5}	43.72	
							1×10^{-6}	54.56	
$C_{16}EO_{30}$									
1×10^{-3}	0.99732	0.9172	1.0249	0.0249	6.39	2.4×10^{-5}	3×10^{-4}	44.00	2.20×10^{-5}
5×10^{-4}	0.99728	0.9095	1.0163	0.0163	4.78		1×10^{-4}	44.10	
2×10^{-4}	0.99727	0.9018	1.0077	0.0077	4.04		5×10^{-5}	44.13	
7×10^{-5}	0.99725	0.8991	1.0046	0.0046	2.36		4×10^{-5}	44.14	
5×10^{-5}	0.99724	0.8984	1.0039	0.0039	1.98		3×10^{-5}	44.15	
3×10^{-5}	0.99723	0.8978	1.0033	0.0033	1.43		2×10^{-5}	44.12	
2×10^{-5}	0.99722	0.8973	1.0026	0.0026	1.19		1.5×10^{-5}	45.00	
5×10^{-6}	0.99721	0.8961	1.0013	0.0013	0.58		1×10^{-5}	46.72	
1×10^{-6}	0.99721	0.8956	1.0009	0.0009	0.18		8×10^{-6}	48.00	
							1×10^{-6}	55.65	
$C_{16}EO_{60}$									
1×10^{-3}	0.99750	0.9412	1.0517	0.0517	3.64	1.4×10^{-5}	5×10^{-5}	51.25	1.15×10^{-5}
5×10^{-4}	0.99746	0.9217	1.0299	0.0299	3.14		4×10^{-5}	51.23	
3×10^{-4}	0.99743	0.9152	1.0226	0.0226	2.49		3×10^{-5}	51.20	
6×10^{-5}	0.99739	0.9139	1.0212	0.0212	0.53		2×10^{-5}	51.24	
2×10^{-5}	0.99735	0.9133	1.0205	0.0205	0.18		1.5×10^{-5}	51.25	
9×10^{-6}	0.99730	0.9126	1.0197	0.0197	0.085		1×10^{-5}	51.40	
6×10^{-6}	0.99727	0.9114	1.0184	0.0184	0.062		8×10^{-6}	51.90	
3×10^{-6}	0.99724	0.9110	1.0180	0.0180	0.031		5×10^{-6}	53.05	
							3×10^{-6}	54.82	
							1×10^{-6}	58.00	

TABLE VII.I.1.B

C $g.dl^{-1}$	da $g.ml^{-1}$	η cp	η_r	η_{sp}	$\frac{\eta_r - 1}{C - C_o}$ $g.dl^{-1}$	$[\eta]$ $g.dl^{-1}$	C_p C°	H_k
EO_{10}								
1.0	0.99765	0.9366	1.0466	0.0466	0.0467			
0.8	0.99756	0.9283	1.0373	0.0373	0.0468			
0.7	0.99751	0.9225	1.0308	0.0308	0.0445			
0.6	0.99749	0.9182	1.0262	0.0262	0.0439	3.9×10^{-2}	50	5.84
0.4	0.99741	0.9106	1.0175	0.0175	0.0441			
0.3	0.99738	0.9065	1.0130	0.0130	0.0439			
0.2	0.99734	0.9037	1.0099	0.0099	0.0495			
EO_{18}								
1.0	0.99772	0.9556	1.0678	0.0678	0.0681			
0.8	0.99761	0.9424	1.0531	0.0531	0.0666			
0.7	0.99753	0.9349	1.0447	0.0447	0.0643			
0.6	0.99749	0.9282	1.0371	0.0371	0.0623	5.4×10^{-2}	68.80	4.98
0.5	0.99743	0.9225	1.0309	0.0309	0.0623			
0.4	0.99737	0.9164	1.0239	0.0239	0.0606			
0.3	0.99732	0.9110	1.0180	0.0180	0.0609			
0.2	0.99727	0.9052	1.0115	0.0115	0.0587			
EO_{30}								
1.0	0.99821	0.9812	1.0964	0.0964	0.0967			
0.8	0.99802	0.9617	1.0746	0.0746	0.0937			
0.7	0.99795	0.9519	1.0637	0.0637	0.0915			
0.6	0.99789	0.9426	1.0533	0.0533	0.0895	7.5×10^{-2}	72	3.95
0.5	0.99763	0.9344	1.0442	0.0442	0.0889			
0.4	0.99753	0.9251	1.0337	0.0337	0.0852			
0.3	0.99747	0.9174	1.0252	0.0252	0.0849			
0.2	0.99741	0.9096	1.0165	0.0165	0.0838			
EO_{60}								
1.0	0.99841	1.0522	1.1757	0.1757	0.1765			
0.8	0.99820	1.0140	1.1331	0.1331	0.1672			
0.7	0.99810	0.9957	1.1127	0.1127	0.1619			
0.6	0.99802	0.9775	1.0923	0.0923	0.1549	11.7×10^{-2}	79.60	4.63
0.5	0.99790	0.9605	1.0733	0.0733	0.1478			
0.4	0.99781	0.9456	1.0567	0.0567	0.1433			
0.3	0.9977	0.9314	1.0408	0.0408	0.1379			

PARTIAL MOLAL VOLUMES OF THE POLYOXYETHYLENE MONOHEXADECYL ETHERS IN WATER AT 25° C

TABLE VII.I.2

C mol.dm^{-3}	Ø ml.mole^{-1}	$\bar{V}$ ml.mole^{-1}	$\bar{V}_o$ ml.mole^{-1}	$\bar{V}_1$ ml.mole^{-1}	$\Delta\bar{V}_1$ ml.mole^{-1}	$\bar{V}^o_{1C}$ ml.mole^{-1}	$\bar{V}^o_{1D}$ ml.mole^{-1}	S_{pv} ml.g^{-1}
EO_{10}								
0.0146	646.72	677.68	620.05	624.0	3.95	28.70	29.0	0.91361
0.0117	645.14	669.95						
0.0102	644.29	665.93						
0.0088	640.16	658.83						
0.0058	633.48	645.78						
0.0044	629.98	639.31						
EO_{18}								
0.0097	973.13	984.62	961.50	964.5	3.0			0.91188
0.0077	970.91	980.03						
0.0067	973.05	980.98						
0.0058	972.19	979.06						
0.0048	968.56	973.68						
0.0039	968.04	972.66						
0.0029	964.89	968.32						
EO_{30}								
0.0064	1392.57	1422.22	1363	1365	2.0			0.87276
0.0051	1385.82	1409.45						
0.0045	1377.41	1398.26						
0.0038	1358.36	1375.96						
0.0025	1395.00	1406.58						
0.0019	1372.24	1381.00						
EO_{60}								
0.0035	2514.66	2777.86	2300	2316.6	16.6			0.80270
0.0028	2496.54	2707.10						
0.0024	2472.97	2653.45						
0.0021	2451.62	2609.54						
0.0017	2419.20	2547.04						
0.0014	2382.77	2487.28						

LIGHT SCATTERING BY POLYOXYETHYLENE MONO HEXADECYL ETHERS IN WATER AT 25° C

TABLE VII.I.3

C $mol.dm^{-3}$	$S_{\emptyset}$ $.10^{-5}.cm^{-1}$	τ $.10^{-5}.cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}.cm^{2}.g^{-2}$	C_o $mol.dm^{-3}$
			EO_{10}			
$2\ x10^{-4}$	0.3699	6.1945	1.05	0.145	2.31	$5.2x10^{-5}$
$1.5x10^{-4}$	0.3150	5.2752				
$1\ x10^{-4}$	0.2450	4.1030				
$8\ x10^{-5}$	0.1976	3.3091				
$6\ x10^{-5}$	0.1520	2.5455				
$5\ x10^{-5}$	0.1352	2.2641				
$4\ x10^{-5}$	0.1364	2.2842				
$3\ x10^{-5}$	0.1313	2.1988				
$1\ x10^{-5}$	0.1199	2.0079				
$7\ x10^{-6}$	0.1379	2.3093				
$1\ x10^{-6}$	0.1272	2.1301				
			EO_{18}			
$2\ x10^{-4}$	0.3995	6.6903	1.06	0.144	2.25	$3.4x10^{-5}$
$1.5x10^{-4}$	0.3499	5.859				
$1\ x10^{-4}$	0.3035	5.0826				
$8\ x10^{-5}$	0.2680	4.4881				
$5\ x10^{-5}$	0.2120	3.5502				
$4\ x10^{-5}$	0.1757	2.9423				
$3\ x10^{-5}$	0.1598	2.6761				
$2\ x10^{-5}$	0.1516	2.5387				
$1\ x10^{-5}$	0.1384	2.3177				
$5\ x10^{-6}$	0.1263	2.1151				
$1\ x10^{-6}$	0.1298	2.1737				

TABLE VII.I.3.A

C $mol.dm^{-3}$	S_0 $.10^{-5}.cm^{-1}$	τ $.10^{-5}.cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}.cm^{2}.g^{-2}$	C_0 $mol.dm^{-3}$
			EO_{30}			
1×10^{-4}	0.3848	6.4441	1.05	0.148	2.38	2.1×10^{-5}
8×10^{-5}	0.3392	5.6804				
6.5×10^{-5}	0.2966	4.9671				
5×10^{-5}	0.2492	4.1732				
4×10^{-5}	0.2469	4.1347				
3×10^{-5}	0.2141	3.5855				
2×10^{-5}	0.1845	3.0898				
1×10^{-5}	0.1483	2.4835				
7×10^{-6}	0.1544	2.5856				
4×10^{-6}	0.1423	2.3831				
1×10^{-6}	0.1313	2.1988				
			EO_{60}			
1×10^{-4}	0.6791	11.3730	1.05	0.149	2.45	1.15×10^{-5}
8×10^{-5}	0.6133	10.2710				
6.5×10^{-5}	0.4767	7.9831				
5×10^{-5}	0.3990	6.6819				
3×10^{-5}	0.2806	4.6991				
2×10^{-5}	0.2363	3.9572				
1×10^{-5}	0.1825	3.0563				
7×10^{-6}	0.1456	2.4383				
4×10^{-6}	0.1373	2.2993				
1×10^{-6}	0.1466	2.4560				

LIGHT SCATTERING AND SURFACE TENSION DATA FOR THE POLYOXYETHYLENE MONO HEXADECYL ETHER ($C_{16}\,E_{18}$) IN WATER CONTAINING AROMATIC ALCOHOLS AT 25° C

TABLE VII.I.4

Light Scattering							Surface Tension		
C $mol.dm^{-3}$	$S_{\emptyset}$ $.10^{-5}cm^{-1}$	τ $.10^{-5}cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}cm^{2}g^{-2}$	C_0 $mol.dm^{-3}$	C $mol.dm^{-3}$	γ $dyne.cm^{-1}$	C_0 $mol.dm^{-3}$
EO$_{18}$ 0.01 M Phenol									
2×10^{-4}	0.360	6.0288	1.05	0.1435	2.25	3.45×10^{-5}	1×10^{-4}	40.2	4.2×10^{-5}
1×10^{-4}	0.3056	5.1177					8×10^{-5}	40.64	
9×10^{-5}	0.2999	5.0223					6×10^{-5}	40.53	
8×10^{-5}	0.2750	4.6053					5×10^{-5}	40.98	
7×10^{-5}	0.2546	4.2637					4×10^{-5}	41.04	
6×10^{-5}	0.2399	4.0175					3×10^{-5}	41.82	
5×10^{-5}	0.2142	3.5871					2×10^{-5}	42.86	
4×10^{-5}	0.2013	3.3711					1×10^{-5}	44.09	
3×10^{-5}	0.1799	3.0127					7×10^{-6}	44.98	
2×10^{-5}	0.1601	2.6811							
1×10^{-5}	0.1510	2.5287							
8×10^{-6}	0.1482	2.4818							
0.02 M									
1×10^{-4}	0.3142	5.2618	1.06	0.1418	2.20	3.6×10^{-5}	1×10^{-4}	39.85	4.4×10^{-5}
9×10^{-5}	0.3022	5.0608					8×10^{-5}	40.09	
8×10^{-5}	0.2932	4.9101					6×10^{-5}	39.85	
7×10^{-5}	0.2781	4.6572					5×10^{-5}	39.55	
6×10^{-5}	0.2292	4.2285					4×10^{-5}	40.25	
5×10^{-5}	0.2292	3.8383					3×10^{-5}	40.70	
4×10^{-5}	0.2032	3.4029					2×10^{-5}	41.21	
3×10^{-5}	0.1753	2.9356					1×10^{-5}	42.74	
2×10^{-5}	0.1662	2.7833					7×10^{-6}	43.8	
1×10^{-5}	0.1499	2.5103					5×10^{-6}	44.99	
7×10^{-6}	0.1473	2.4667							
0.03 M									
1×10^{-4}	0.3223	5.3974	1.05	0.1417	2.2	3.4×10^{-5}	1×10^{-4}	39.62	4.5×10^{-5}
8×10^{-5}	0.3014	5.0474					8×10^{-5}	39.68	
7×10^{-5}	0.2901	4.8582					6×10^{-5}	39.64	
6×10^{-5}	0.2651	4.4395					5×10^{-5}	39.68	
5×10^{-5}	0.2444	4.0928					4×10^{-5}	39.79	
4×10^{-5}	0.2062	3.4532					3×10^{-5}	40.19	
3×10^{-5}	0.1799	3.0127					2×10^{-5}	40.87	
2×10^{-5}	0.1722	2.8837					1×10^{-5}	42.18	
1×10^{-5}	0.1523	2.5505					7×10^{-6}	42.58	
7×10^{-6}	0.1491	2.4969					5×10^{-6}	43.08	

TABLE VII.I.4.A

Light Scattering							Surface Tension		
C $mol.dm^{-3}$	$S_Ø$ $10^{-5}.cm^{-1}$	τ $.10^{-5}.cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}\ cm^{2}.g^{-2}$	C_0 $mol.dm^{-3}$	C $mol.dm^{-3}$	γ $dyne.cm^{-1}$	C_0 $mol.dm^{-3}$
0.04M									
1×10^{-4}	0.3303	5.5314	1.06	0.1417	2.19	3.3×10^{-5}	1×10^{-4}	39.05	4.0×10^{-5}
8×10^{-5}	0.3096	5.1847					8×10^{-5}	38.79	
7×10^{-5}	0.3021	5.0592					6×10^{-5}	39.09	
6×10^{-5}	0.2777	4.6505					5×10^{-5}	39.23	
5×10^{-5}	0.2563	4.2922					4×10^{-5}	39.55	
4×10^{-5}	0.2196	3.6775					3×10^{-5}	39.68	
3×10^{-5}	0.1846	3.0914					2×10^{-5}	40.35	
2×10^{-5}	0.1713	2.8687					1×10^{-5}	41.24	
1×10^{-5}	0.1542	2.5823					7×10^{-6}	41.77	
7×10^{-6}	0.1503	2.5170					5×10^{-6}	42.28	
0.05M									
1×10^{-4}	0.3401	5.6955	1.06	0.142	2.2	2.9×10^{-5}	1×10^{-4}	38.28	3.7×10^{-5}
8×10^{-5}	0.3186	5.3354					8×10^{-5}	38.48	
6×10^{-5}	0.2953	4.9452					6×10^{-5}	38.28	
5×10^{-5}	0.2721	4.5567					5×10^{-5}	38.48	
4×10^{-5}	0.2453	4.1079					4×10^{-5}	38.77	
3×10^{-5}	0.1902	3.1852					3×10^{-5}	38.80	
2×10^{-5}	0.1752	2.9340					2×10^{-5}	39.22	
1×10^{-5}	0.1632	2.7330					1×10^{-5}	40.12	
7×10^{-6}	0.1521	2.5471					7×10^{-6}	40.5	
5×10^{-6}	0.1435	2.4031							
0.08M									
1×10^{-4}	0.3663	6.1344	1.06	0.142	2.2	2.4×10^{-5}	1×10^{-4}	37.31	3.1×10^{-5}
8×10^{-5}	0.3486	5.8378					8×10^{-5}	37.55	
6×10^{-5}	0.3235	5.4175					6×10^{-5}	37.47	
5×10^{-5}	0.3102	5.1948					5×10^{-5}	37.72	
4×10^{-5}	0.2804	4.6957					4×10^{-5}	37.55	
3×10^{-5}	0.2461	4.1213					3×10^{-5}	37.98	
2×10^{-5}	0.1812	3.0345					2×10^{-5}	38.50	
1×10^{-5}	0.1635	2.7381					1×10^{-5}	39.50	
7×10^{-6}	0.1583	2.6509					7×10^{-6}	39.85	
5×10^{-6}	0.1502	2.5153					5×10^{-6}	40.70	

TABLE VII.I.4.B

C $mol.dm^{-3}$	$S_Ø$ $.10^{-5}\ cm^{-1}$	τ $.10^{-5}\ cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}\ cm^2.g^{-2}$	C_0 $mol.dm^{-3}$
0.01 M Benzyl alcohol						
1×10^{-4}	0.3078	5.1546	1.07	0.1475	2.38	3.45×10^{-5}
7×10^{-5}	0.2706	4.5316				
6×10^{-5}	0.2513	4.2084				
5×10^{-5}	0.2287	3.8299				
4×10^{-5}	0.2043	3.4213				
3×10^{-5}	0.1651	2.7648				
2×10^{-5}	0.1610	2.6962				
1×10^{-5}	0.1499	2.5103				
7×10^{-5}	0.1551	2.5974				
5×10^{-5}	0.1499	2.5103				
0.02 M						
1×10^{-4}	0.3210	5.3756	1.07	0.1470	2.35	3.65×10^{-5}
8×10^{-5}	0.2922	4.8933				
7×10^{-5}	0.2855	4.7811				
6×10^{-5}	0.2579	4.3193				
5×10^{-5}	0.2461	4.1213				
4×10^{-5}	0.2039	3.4146				
2×10^{-5}	0.1691	2.8318				
1×10^{-5}	0.1620	2.7129				
7×10^{-6}	0.1600	2.6794				
5×10^{-6}	0.1592	2.6661				
0.03M						
1×10^{-4}	0.327	5.4762	1.07	0.1475	2.39	3.4×10^{-5}
8×10^{-5}	0.304	5.0909				
6×10^{-5}	0.2771	4.6405				
5×10^{-5}	0.2540	4.2535				
4×10^{-5}	0.2342	3.9221				
3×10^{-5}	0.1830	3.0646				
1×10^{-5}	0.1670	2.7966				
8×10^{-6}	0.1624	2.7196				
4×10^{-6}	0.1660	2.7799				

TABLE VII.I.4.C

C $mol.dm^{-3}$	$S_ø$ $.10^{-5}\ cm^{-1}$	τ $.10^{-5}\ cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}\ cm^{2}.g^{-2}$	C_0 $mol.dm^{-3}$
0.04M						
1×10^{-4}	0.3389	5.6754	1.07	0.1467	2.35	3.18×10^{-5}
8×10^{-5}	0.3202	5.3622				
6×10^{-5}	0.2888	4.8364				
5×10^{-5}	0.260	4.3541				
4×10^{-5}	0.2410	4.0359				
2×10^{-5}	0.1820	3.0478				
1×10^{-5}	0.1720	2.8804				
7×10^{-6}	0.1692	2.8335				
5×10^{-6}	0.1601	2.6811				
0.05M						
1×10^{-4}	0.3564	5.9685	1.07	0.1465	2.35	2.9×10^{-5}
6×10^{-5}	0.2999	5.0223				
5×10^{-5}	0.2765	4.6304				
4×10^{-5}	0.2498	4.1833				
3×10^{-5}	0.2108	3.5348				
2×10^{-5}	0.1891	3.1667				
1×10^{-5}	0.1752	2.9340				
8×10^{-6}	0.171	2.8636				
4×10^{-6}	0.164	2.7464				

TABLE VII.I.4.D

C $mol.dm^{-3}$	S_ϕ $.10^{-5}.cm^{-1}$	τ $.10^{-5}.cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}.cm^2.g^{-2}$	C_0 $mol.dm^{-3}$
0.01 M Ph.ethanol						
1×10^{-4}	0.3107	5.2032	1.08	0.1485	2.41	3.58×10^{-5}
8×10^{-5}	0.2786	4.6656				
6×10^{-5}	0.2454	4.1096				
5×10^{-5}	0.2253	3.7730				
4×10^{-5}	0.2013	3.3711				
3×10^{-5}	0.1892	3.1684				
2×10^{-5}	0.1792	3.0010				
1×10^{-5}	0.1717	2.8754				
8×10^{-6}	0.1659	2.7783				
4×10^{-6}	0.1624	2.7196				
0.02M						
1×10^{-4}	0.3242	5.4292	1.08	0.1487	2.42	3.75×10^{-5}
8×10^{-5}	0.2966	4.9671				
6×10^{-5}	0.2570	4.3038				
5×10^{-5}	0.2427	4.0644				
4×10^{-5}	0.2081	3.4849				
3×10^{-5}	0.1923	3.2204				
2×10^{-5}	0.1821	3.0495				
1×10^{-5}	0.1752	2.9340				
7×10^{-6}	0.1681	2.8151				
5×10^{-6}	0.1642	2.749				
0.03M						
1×10^{-4}	0.3381	5.6620	1.08	0.1487	2.42	3.6×10^{-5}
8×10^{-5}	0.3193	5.3472				
6×10^{-5}	0.2856	4.7828				
5×10^{-5}	0.2570	4.3038				
4×10^{-5}	0.2204	3.6909				
3×10^{-5}	0.1942	3.2522				
2×10^{-5}	0.1914	3.2053				
1×10^{-5}	0.1754	2.9373				
8×10^{-6}	0.1740	2.9139				
4×10^{-6}	0.1633	2.7347				

TABLE VII.I.4.E

C $mol.dm^{-3}$	$S_ø$ $.10^{-5} cm^{-1}$	τ $.10^{-5} cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6} cm^{2}.g^{-2}$	C_0 $mol.dm^{-3}$
			0.04M			
$1x10^{-4}$	0.3528	5.9082	1.08	0.1481	2.4	$3.3x10^{-5}$
$8x10^{-5}$	0.3348	5.6067				
$6x10^{-5}$	0.2999	5.0223				
$5x10^{-5}$	0.2710	4.5383				
$4x10^{-5}$	0.2413	4.0409				
$3x10^{-5}$	0.2031	3.4012				
$2x10^{-5}$	0.1963	3.2873				
$1x10^{-5}$	0.1833	3.0696				
$7x10^{-6}$	0.1789	2.9959				
$5x10^{-6}$	0.1769	2.9624				
			0.05M			
$1x10^{-4}$	0.3812	6.3838	1.08	0.1481	2.4	$3 x10^{-5}$
$8x10^{-5}$	0.3422	5.7307				
$6x10^{-5}$	0.3067	5.1362				
$5x10^{-5}$	0.2832	4.7426				
$4x10^{-5}$	0.2529	4.2352				
$3x10^{-5}$	0.2024	3.3895				
$2x10^{-5}$	0.1974	3.3057				
$1x10^{-5}$	0.1862	3.1182				
$8x10^{-6}$	0.1821	3.0495				
$4x10^{-6}$	0.1712	2.8670				

LIGHT SCATTERING BY POLYOXYETHLYLENE MONO HEXADECYL ETHER (C_{16} E_{18})

IN WATER CONTAINING UREA AND URETHANE AT 25° C

TABLE VII.I.5

C $mol.dm^{-3}$	$S_ø$ $.10^{-5}.cm^{-1}$	τ $.10^{-5}.cm^{-1}$	D_R	ΔI $ml.g^{-1}$	H $.10^{-6}.cm^{2}.g^{-2}$	C_0 $mol.dm^{-3}$
0.7 M Urethane						
2×10^{-4}	0.4837	8.1004	1.05	0.1045	1.19	6.25×10^{-5}
1.5×10^{-4}	0.4360	7.3020				
1×10^{-4}	0.3739	6.2620				
9×10^{-5}	0.3349	5.610				
8×10^{-5}	0.3292	5.5130				
7×10^{-5}	0.3033	5.0790				
5×10^{-5}	0.2804	4.6960				
4×10^{-5}	0.2809	4.7041				
2×10^{-5}	0.2691	4.5065				
1×10^{-5}	0.2641	4.4227				
1M Urea						
1.2×10^{-4}	0.460	7.7035	1.05	0.151	2.48	6.8×10^{-5}
1×10^{-4}	0.4061	6.8008				
9×10^{-5}	0.3680	6.1627				
8×10^{-5}	0.3350	5.6101				
7×10^{-5}	0.310	5.1915				
6×10^{-5}	0.280	4.6891				
4×10^{-5}	0.276	4.6221				
3×10^{-5}	0.2786	4.6656				
1×10^{-5}	0.2658	4.4512				
8×10^{-6}	0.2386	3.9957				

MICELLAR DIMENSIONS OF POLYOXYETHYLENE MONO HEXADECYL ETHERS IN WATER

FROM LIGHT SCATTERING AND VISCOSITY DATA

TABLE. VII.I.6

Light Scattering							Viscosity					
S.A.A	A	B g.ml	MW	E_L A°	N_A	$P^{-1}\phi$	Vh $ml.10^{-18}$	$Wg.g.s^{-1}$	K	A_R	A_a A°	A_b A°
EO_{10}	$2.35x10^{-6}$	0.0313	$4.26x10^{5}$	60	624	1.456	0.642	0.648	4.3	3.7	130	35
EO_{18}	$2.6\ x10^{-6}$	0.032	$3.85x10^{5}$	74	372	0.798	0.594	1.231	5.8	5.0	153	30.50
EO_{30}	$3.25x10^{-6}$	0.023	$3.08x10^{5}$	91	197	0.557	0.444	2.133	8.6	7.0	175	25
EO_{60}	$4.5\ x10^{-6}$	0.002	$2.22x10^{5}$	120	77	0.337	0.295	3.886	14.57	10.4	198	19

MICELLAR DIMENSIONS OF THE POLYOXYETHYLENE MONO HEXADECYL ETHER (C_{16} E_{18}) IN WATER CONTAINING AROMATIC ALCOHOLS

TABLE VII.I.7

C $mol.dm^{-3}$	A	B g.ml	MW	N_A	$P^{-1}ø$	L/2 A°
			Phenol			
0.01	2.05×10^{-6}	0.0437	4.88×10^{5}	471	0.623	260
0.02	1.55×10^{-6}	0.0450	6.45×10^{5}	623	0.748	344
0.03	1.1×10^{-6}	0.0463	9.10×10^{5}	879	0.916	485
0.04	0.75×10^{-6}	0.0487	1.333×10^{6}	1287	1.068	710
0.05	0.6×10^{-6}	0.0500	1.667×10^{6}	1610	1.074	888
0.08	0.48×10^{-6}	0.0465	2.08×10^{6}	2009	1.459	1108
			Benzylalcohol			
0.01	1.25×10^{-6}	0.0533	8×10^{5}	773	0.644	426
0.02	1.08×10^{-6}	0.0514	9.26×10^{5}	895	0.938	493
0.03	0.98×10^{-6}	0.0587	1.02×10^{6}	985	0.533	543
0.04	0.85×10^{-6}	0.050	1.17×10^{6}	1136	1.137	627
0.05	0.75×10^{-6}	0.0484	1.333×10^{6}	1287	1.302	710
			Ph.ethanol			
0.01	1.5×10^{-6}	0.0487	6.67×10^{5}	644	0.685	355
0.02	1.2×10^{-6}	0.0512	8.33×10^{5}	804	1.002	444
0.03	0.95×10^{-6}	0.0527	1.05×10^{6}	1014	1.098	559
0.04	0.78×10^{-6}	0.0480	1.28×10^{6}	1236	1.577	682
0.05	0.7×10^{-6}	0.0487	1.43×10^{6}	1381	1.541	762
			Urea			
1.0	0.4×10^{-6}	0.0313	2.5×10^{6}	2415	12.770	1332
			Urethane			
0.7	0.3×10^{-6}	0.0169	3.33×10^{6}	3216	6.723	1774

NMR DATA FOR THE POLYOXYETHYLENE MONOHEXADECYL ETHERS IN CARBONTETRACHLORIDE AT 25 °C

TABLE VII.I.8

S.A.A	Protons	Chem. Shift of P.P.M (τ)	Proton per mol. cal. from Spect.	EO	$EO_{av.}$
IMPURE NON-IONICS					
A_{10}	C_2H_4	6.4 (2)	125	12.3	-
A_{18}	<	6.4 (8)	130	22.3	-
A_{30}	<	6.5	168	52	-
A_{60}	<	6.4 (9)	294	73	-
PURIFIED NON-IONICS					
Spect.s					
A_{10}	C_2H_4	6.5 6.4 (8)	97 100	9.65 8.6	9.6
A_{18}	<	6.4 (6) 6.5	107 116	18.1 17.5	17.8
A_{30}	<	6.4 (6) 6.4 (8)	174 170.5	30.6 30	30.3
A_{60}	<	6.5 6.4 (9)	150.5 133	60.8 60.1	60.45

CHAPTER VIII - Thermodynamics of Micellization

VIII.Ia - The theory of micelle formation

It is universally accepted that energy changes occur with micelle formation. However, details of the micellization process are not clearly known. The thermodynamics of micelle formation have been discussed from two stand points. Both approaches introduce familiar macroscopic treatments of micelles. The thermodynamic analysis of micellization is usually performed, in terms of a dynamic equilibrium between monomers and micelles.

In view of monomer - micellar equilibrium, the thermodynamic description of micellar solutions have been examined by means of mass action, and phase separation approaches as follows;

A_o Phase Separation Model

In this approach the micelles have been considered as constituting a distinct phase in a solution by Stainsby-Alexander(146), Matijevic-Pethica(294), and Hutchinson et al.(295,296). The phase change is assumed to occur at C_0.

The equilibrium between surfactant ions S_i^+, counter ions C_i^-, and micelles M can be written by the relation

$$NS_i^+ + NC_i^- \rightleftharpoons M \qquad \text{VIII.i.1}$$

treating the micelle, charged monomer, and equivalent number of counter ions bound to the micelle as a separate phase(297). The above expression takes the form for standard free energy of micellization (per mole of monomer)

$$\Delta G_{Mp} = - \frac{RT}{N} \ln \frac{F_M(M)}{F_{S_i}{}^N (S_i{}^+)^N (F_{C_i}{}^-)^N} \qquad \text{VIII-1}$$

The concentration of S_i^+ is equal to C_0 when the micellar phase is present. The expression (VIII.i.1) can be rewritten by the following expression, taking into account the standard state of S_i^+ in micellar phase, Fm and (M) which are equal to unity

$$\Delta G_{Mp} = RT \ln f_\pm^2 (C_o)(C_i) \qquad \text{VIII-2}$$

where $f_\pm$ is defined by $(F_{S_i}/F_{C_i})^{\frac{1}{2}}$. Since $f_\pm^2$ is close to unity in the absence of salt, the free energy of micellization can be given by the equation

$$\Delta G_{Mp} = 2RT \ln C_o \qquad \text{VIII-3}$$

when expression (VIII.i.1) is combined with the Gibbs-Helmholtz equation

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2} \qquad \text{VIII-4}$$

The standard enthalpy of micellization can be derived as follows,

$$\Delta H_{Mp} = -RT^2 \frac{d}{dt}\left[\ln f_\pm^2 (C_o)(C_i^-)\right] \qquad \text{VIII-5}$$

then the standard entropy of micellization can be obtained from

$$\Delta S_{Mp} = (\Delta H_{Mp} - \Delta G_{Mp})/T \qquad \text{VIII-6}$$

Since the free energy of micellization is zero under equilibrium condition, the entropy change is given by

$$\Delta S_{Mp} = \Delta H_M/T \qquad \text{VIII-7}$$

The basic assumption of this approach is that the monomer activity remains constant above C_o. This model has been modfied for ionic systems by Shinoda-Hutchinson(296), treating the micelles as a charged phase.

However the phase change has been treated as the separation of the colloidal electrolyte itself, in a dispersed form from the dispersion medium by Hutchinson et al.(295) and Stainsby-Alexander (146). Matijevic-Pethica (294) have considered that the micelles do not simply consist of the monomer alone; the micelles include also the components such as H_3O^+, and OH^- from water phase, and water molecules themselves. Their argument also allows the fact that the micellar phase will include the electrical double layer, since it is electrically neutral.

B_o Mass Action Model

This modal has considered micellization as the reversible formation of a large aggregate. The law of mass action has been applied by Jones-Bury(298), Hartley(143), Murray-Hartley(299), Vold(300) and Phillips(301) to the micellization in terms of considering the micelle as the reaction product. The equilibrium between the micelles and monomer can be written by the expression(297)

$$NS_i^+ + (N-z)C_i^- \rightleftharpoons M^{+z} \qquad \text{VIII.i.2}$$

The standard states of the various ionic species have been considered in a way that the mole fractions are unity. The thermodynamic equilibrium can be defined by the relation

$$K_m = \frac{F(M^{+z})}{(S_i^+)^N (C_i^-)^{N-z}} \qquad \text{VIII.8}$$

where $F = Fm/F_{S_i}^{\ N} \ F_{C_i}^{\ N-z}$.

If the value of F in the above equation is reasonably constant, K_m can be rewritten as follows

$$K_m = \frac{M^{+z}}{(S_i^+)(C_i^-)^{N-z}} \qquad \text{VIII-9}$$

The standard free energy per mole of monomeric surfactant ions (micellization) can be defined, in combination with expression (VIII.i.2) as follows(297),

$$\Delta G_{Mb} = -\frac{RT}{N} \ln K_m = -\frac{RT}{N} \ln \frac{F(M^{+z})}{(S_i^+)\ (C_i^-)^{N-z}} \qquad \text{VIII-10}$$

when N is larger, there is no added salt, and the value of C_o is used, the equation (VIII-10) takes the form with the approximations of

(S_i^+) and (C_i^-) by C_o and neglecting $(^1/N)\ln F(M^{+z})$

$$\Delta G_{Mb} = (2-z/N)RT \ln C_o \qquad \text{VIII-11}$$

when the micelles have zero charge (e.g. z is zero) the equation reduces to

$$\Delta G_{Mb} = 2RT \ln C_o \qquad \text{VIII-12}$$

In this approach the total number of moles at the C_o is equal to the sum of moles of micelles, free counter ions, water and surfactant ions. If no counter ions are bound to the micelle the equation becomes

$$\Delta G_{Mb} = RT \ln C_o \qquad \text{VIII-13}$$

Vold(300) has considered a series of equilibria between monomer and all possible micellar species, in terms of a series of equilibrium constants. This approach has an advantage because of N is fixed for each micellear species. Due to this fact, it can be also applied to multicomponent micelles.

Besides the described approaches Aranow(302), Hoeve-Benson(130) and Poland-Scheraga(145,303) have treated micelle formation within the framework of statistical mechanics. The application of this method to the micellization is more difficult because of the ionic solvation, and counter ion binding.

VIII.Ib - Standard free energy, enthalpy and entropy effects in micellization

Different views have been given by several authors(143,144,146,304) for micelle formation. However, the magnitude of standard free enegy change for micelle formation, can be evaluated by taking into account the monomer contributions to the micellization.

The hydrocarbon chain contribution can be derived by its arbitrary partition into hydrocarbon and electrical parts(297). Since electrical work is involved in micelle formation (Fel), which is positive, one can calculate the contribution of the hydrocarbon part Fch, subtracting the value of Fel from ΔG_M.

If the obtained value of Fch is compared with the free energies of transfer of hydrocarbons from aqueous to another region, it can provide the hydrocarbon chains role in the micelle formation.

Overbeek-Stigter(305) have observed Fel for a spherical micelle, taking into account its electrical double layer. They have also included the assumption that the charge of micelle is smeared out over its surface.

Emerson-Holtzer(306) have calculated that the contribution of dodecyl group (Fch) to micellization is of the order of -14.5 RT. On the other hand, Wishnia(307) has examined the solubility of hydrocarbons in surfactant solution, in terms of hydrophobic interactions. According to his investigation the hydrocarbon contribution to the free energy of micelle formation is in the range of -12.0 RT to -18.2 RT.

Mukerjee(308) has observed that the free energy change per $-CH_2-$ group (-1.15 RT = -0.68 K cal/mole), when a hydrocarbon chain is transferred from aqueous surroundings to the micelle, is close to the free energy change of transfer to the hydrocarbon solution (-1.39 RT = -0.825 K cal/mole).

In view of this fact he has concluded that the free energy change per $-CH_2-$ group, on transfer from aqueous to the nonpolar region (micelle) is due to the interaction of the organic chains between themselves. According to his view, the tendency of hydrocarbon chains of the monomers to associate with each other, reducing the extent of contact with water molecules causes the formation of micelles.

The free energy change per $-CH_2-$ group (1.08 RT) for short chain alcohols, has been examined by Shinoda in terms of the solubility of alcohols(178). In view of these observations one can assume that a "rule of four" appears better, on complete transfer from aqueous solution to the hydrocarbon environment than the "rule of three",(308).

On the other hand, the transfer free energy to a hydrocarbon-water interface(309,310), is 1.37 RT (0.810-0.82 K cal/mole). The effect of the hydrophilic nature of the polar head group, on the free energy of transfer of $-CH_2-$ group from an aqueous solution to nonpolar environment, has been examined by Adderson-Taylor(311). The energy change involved on transfer of $-CH_2-$ group ranges from -1.06 RT to -1.53 RT.

Since the enthalpy and entropy are related to the free energy by the expression,

$$G = H - TS$$

The evaluation of changes in these quantities, which occur during the micelle formation, provide important information about the role of participants in the process. A small negative enthalpy effect has been observed by Stainsby-Alexander(146), on examining heat effects involved in aggregation. They have assumed that the main factor involved in the aggregation of hydrocarbon chains in aqueous solution is the change in the hydrocarbon-water interface.

In their opinion(146), the hydrocarbon chains of surfactant ions surrounded by water molecules are curled up. Because of this fact the internal motions of monomers are considerably restricted, while the hydrocarbon chains of monomers are more flexible, and extended position in the micelle. The changes in enthalpy effects and entropy have been attributed to the internal motions of the monomers in the micelle formation.

The heats of micelle formation of several paraffin chain salts have been investigated by Goddard et al.(129). According to their observation the structural effects exist in water surrounding ions during the micellization process. The obtained small enthalpy of micelle formation, has been interpreted by the iceberg concept introduced by Frank-Evans(4).

However the decrement in structural order of water molecules, contributes a small positive contribution to the entropy change involved in the micelle formation. When the temperature is increased micellization becomes enthalpic in nature, due to the negative enthalpy, which arises from the loss of translational energy of monomer, and when hydrocarbon chains condense.

The change in sign of ehthalpy between 20°-40° for ionic surfactant, have been attributed to the structural melting of icebergs around the nonpolar parts of surfactant ions(128,312). On the other hand, micelle formation has been investigated in terms of hydrophobic interactions(145,179,308). In this approach the aggregation of hydrocarbon chains due to hydrophobic interactions with ordered water molecules, cause an increase in entropy. The decrement in the structural order of water molecules is one of the possible explanations for an entropy increase.

Aranow-Witten(89) have discussed the entropy effect of hydrocarbons, on transferring from a state of internal torsional oscillation, to the state of hindered internal rotation, neglecting the changes in water structure.

VIII.Ic - Thermodynamics of micellization of alkylammonium bromides in water.

The thermodyanmic properties of micelle formation in aqueous solution of alkylbromides, has been examined using micro calorimetry at 25°C as described in this chapter. The standard free energy change involved during the micellization, has been observed in terms of the following relation

$$\Delta G_M = RT \ln C_o$$

Since the standard free energy of micellization depends on the concentration unit used, and on the choice of standard state, the hypothetical standard state of unit mole fraction referred to the infinitly dilute solution has been adopted. As can be seen in Fig.VIII.1

and Table VIII.I.1 ΔG_M of micellization decreases as the chain length increases. (-4.0 K cal/mole and -4.8 K cal/mole for C_{10} and C_{12} respectively).

The standard free energy change involved due to the transfer of the hydrocarbon molecule from one state to another, has been attributed to the entropy effect rather than the potential energy by Aranow-Witten(89). However the decrement in ΔG_M has been discussed by Corkill et al.(304), in terms of the elimination of interfacial interaction between the monomers and water molecules, or decrement in hydrocarbon water interface.

Poland-Sheraga(145,157) introduced the idea that the free energy of the micellar system has three contributions such as, a, the external free energy of micelle, b, the free energy due to the hydrophobic interactions between structural water and monomer, and c, the energy due to the decrease in hydrophobic association during the micellization (internal free energy).

In addition to these factors Emerson-Holtzer(179) and Poland-Sheraga(157) have also considered the contribution of electrostatic free energy, and a free energy arising from the solvation of the charged head group. Since the aggregation is an energy effect, which results from the elimination of hydrocarbon-water interface in micelle formation, it is reasonable to introduce the idea that the major factor of change in the standard free energy during the micellization, is due to the release of energy because of the decrement in structural order of water molecules around the monomers, and transferring of the monomer to the nonpolar environment, which is thermodynamically favourable for nonpolar solutes.

In this critical state micelles occur at a certain concentration changing the collective properties of surfactant ions in solution. The change in standard free energy per $-CH_2-$ group on transferring from aqueous solution to micellar region has been found -0.5 K cal/mole, which is lower compared with the values given in literature(313,314) (-0.8 - 0.9 K cal/mole). In this observation, as it can be seen ΔH_M decreases (-0.65 K cal/mole and -1.4 K cal/mole for C_{10} and C_{12} respectively. Fig.VIII.2, Table VIII.I.1 as the ΔG_M decreases). The effect of increase in total hydrocarbon content to the ΔH_M, has been discussed by Corkill et al.(304), in view of exothermic process rather than endothermic. The enthalpic contribution to micellization has been discussed by Adderson-Taylor(313). in terms of three factors which are,

a_1 - the aggregation of charged head groups,
b_1 - decrement in structural order of water molecules, and
c_1 - the transfer from polar environment to nonpolar region (micelle).

Besides these factors, the increase in kinetic energy of the monomer, the release of heat when the hydrocarbon chains condense in micelle, and the loss of translational energy of surfactant ions can be introduced as possible reasons for the negative(297,314) ΔH_M.

Poland-Scheraga(157) have concluded that the reaction such as,

free charged monomer → charged monomer in a micelle is accompanied by a large negative enthalpy change due to the change in water structure around the charged head groups, when the above reaction occurs. They have also taken into account the effect of charge on water structure. The observed enthalpic contribution (-0.34 K cal/mole per methylene group) to the free energy change of micellar system is close to the value given by Benjamine(315) for aliphatic alcohols (0.590 K cal/mole).

The change in entropy during the micellization, compared with the free energy change per monomer is not significant (3.35 K cal/mole and 3.4 K cal/mole for C_{10} and C_{12} respectively), and is lower compared with the value given by Barry et al.(314) for impure alkylammonium bromides.

(9.1 K cal/mole and 7.4 K cal/mole for C_{12} phase separation and mass action models respectively).

The abnormal solubility of small nonpolar solutes (rare gases), and small hydrocarbons in aqueous solution has suggested the idea that these solutes increase the structuring of water molecules. The formation of these structural regions, has been interpreted by the term « icebergs », which leads to a loss of entropy.(11), The transfer of nonpolar solute from an aqueous region to nonpolar environment, decreases the ordered structure of water molecules, and consequently a positive entropy change occurs. The other entropy effect is due to the increase in flexibility of hydrocarbon chains in nonpolar region(89).

However the temperature variation of the C_o, and direct calorimetric measurements have shown that(129,315,318) the entropy change plays a unique role in micelle formation. The positive entropy changes that accompany micelle formation, can be attributed to the greater freedom of rotation of hydrocarbons in micelle than in polar medium, and the hydrophobic interactions between monomers and water molecules make a positive contribution to the entropy(129,318) of micellization. On the other hand, the loss of hydration(319) of monomer when it is transferred from an aqueous region to the micellar state, is also responsible for the positive ΔS_M of micellization.

VIII.Id - Experimental Procedure.

The calorimeter vessel consisted of a Dewar flask cemented to a flange to which the head of the Dewar flask could be bolted. An O-ring was used to produce a water tight seal between the head and flange. The calorimeter was immersed in a water bath, the temperature of which was controlled by a regulator to ± 0.01°C. Cold water passing through a copper cooling coil controlled by a needle valve was used to provide a constant leak for the water bath, which was housed in an air thermostat controlled to ± 1°C. The off balance current from the bridge was amplified using a Pye D.C. amplifier (Cat.No.11370), and displayed on a Sunvic d.c. recorder.

Current from a 2V accumulator bank was fed via a 100 ohm resistance through a standard 1 ohm resistance. The voltage across the standard resistance in the calorimeter circuit was measured with a Pye potentiometer, and it was used to check the resistance of the heating coil, and to calculate the current passed through the heating coil in the circuit. The calorimeter was capable of detecting heat changes of ~ 0.01 cal.

The calorimeter was calibrated in terms of the heating coil in series with standard 1 ohm resistance by measuring the heat of sodium chloride solution at 25°C. In order to measure the heat of 1M NaCl solution, 150 ml double distilled water was placed in the Dewar vessel, than the more concentrated NaCl solution in the mixing device, which was sealed at the bottom with silver foil and attached to the breaking mechanism by means of a screwed brass collar. Following this procedure the stirring motor was put into operation. Due to the stirring effect, at the beginning the recorded curve was not linear. After temperature equilibrium was reached (linear relation on the curve), the solution of NaCl (concentrated) was mixed with 150 ml water so that the concentration of final solution of NaCl is 1M. When the solution was mixed with the solvent the slope of curve on the recorder increased, then forming a small plateau, kept constant. Following this process (thermal equilibrium) the current was turned on to the heating coil. The slope of curve increased until the current was switched off. The time was recorded, and the potential drop across a standard resistance and heating coil was measured by potentiometer. After that with 15 minutes thermal equilibrium intervals the same procedure was repeated increasing the time of flow of the current in the circuit.

The work of stirring which is negative, and can be written in terms of the first law of thermodyanmics as follows

$$\Delta H = Q - \omega_s \qquad \text{VIII-14}$$

where Q is equal to the electrical energy dissipated in the resistor (heating coil) due to the current I for time t (in sec.). In this work, the heat of stirring, and the dilution of solution are assumed negligible, then the equation becomes

$$\Delta H = Q \qquad \text{VIII-15}$$

On the other hand it was considered that the resistance of the heating coil was constant throughout all the different heating periods of the solution. If the resistance of heating coil is constant and it is in series with the standard resistance, then with the measurement of potential drop across the two resistances, one can write the electrical work by the relation

$$\Delta H = \frac{R_H}{R_S^2} \int E_p^2 \, dt \qquad \text{VIII-16}$$

when the resistance is in ohms, potential in volts and time in seconds. The work given by the equation is in joules. It is converted to caloric by dividing by 4.184 joule. Since the heat input was dissipated in the system, the corresponding heat per molecule can then be calculated. The calculated heats of the solution at different time intervals were plotted against the time in sec. The slope of the curve, which was linear is the increment in heat of the solution per second, due to the heat input. The obtained curve was extrapolated to zero. The intercept on the ordinate gives the heat of the solution of 1M NaCl at 25°C (0.90 K cal/mole), which is in a good agreement with the value given in literature (320).

The same procedure was applied for the measurement of heat of the micellization of cationic and non-ionic surfactant when 20 ml of concentrated cationic solution was mixed with 150 ml double distilled water after 15 minutes thermal equilibrium (at 25°C). The slope of the curve on the recorder decreased, which is an indication of exothermic heat involved in the solution. After a certain time, the current was turned on, then the slope of curve reached its original slope (before mixing) then it increased until the current was switched off.

In the case of non-ionic surfactants the behaviour was different. When the same quantity (in ml) was mixed, after a certain equilibrium time, the slope of the curve on the recorder increased (endothermic) then making a small plateau kept unchanged until the current was turned on, the same procedure was applied to calculate the heat of micellization of both surfactants in aqueous solution at 25°C using equation (VIII-16), and plotting heat of the solutions, which were obtained in terms of the dissipation of heat, produced by known current at different time intervals, against the time in seconds. (Table VIII.I.1, Fig.VIII.1).

VIII.Ie - Application of small system thermodynamics to micellization of non-ionic surfactants.

Hill(231) has introduced an important new area of thermodynamics employing small systems. This approach is significant for analysis of micellization. The small system thermodyanmics considers the degree of association of the monomers in micellar state, and subdivision potential in a way that can be easily applied to micellization (322).

The advantage of using small system thermodyanmics to micelle formation over alternative approaches (such as mass-action and phase-separation) is that the actual intrinsic thermodyanmic functions of micelles can be discussed. In view of this approach the aggregation number as an thermodynamic variable, and the variations in the thermodynamic functions of micelle formation can be examined in terms of the degree of association of monomers, and the concentration of micelles.

The thermodynamic functions of micelle formation can be discussed as follows in view of the small system thermodynamics introduced by Hill. Consider a non-ionic monomer as single component (a), and the solvent (water) as component (b) at equilibrium

$$\mu_a^{s} = \mu_a^{m} = \mu_a \qquad \text{VIII-17}$$

and this relation takes the form for transition between equilibrium states

$$d\mu_a^{s} = d\mu_a^{m} \qquad \text{VIII-18}$$

The chemical potential of component (a) can be defined taking into account the standard chemical potential of component a and its activity coefficient by the relation

$$\mu_a^{s} = \mu_a^{os} + kT \ln x_a^{s}\, Ce_a^{s} \qquad \text{VIII-19}$$

then it takes the form in terms of temperature variation

$$d(\mu_a^{s}/T) = d(\mu_a^{os}/T) + kd \ln x_a^{s}\, Ce_a^{s} \qquad \text{VIII-20}$$

The above equation can be rewritten taking into account the temperature variation of the enthalpy and volume per monomer of component (a) at standard state such as,

$$d\left(\frac{\mu_a^{s}}{T}\right) = -\left(\frac{h_a^{os}}{T^2}\right) dT + \left(\frac{V_a^{os}}{T}\right) dp_1 + kd \ln x_a^{s}\, Ce_a^{s} \qquad \text{VIII-21}$$

on the other hand, at micellar state we have

$$d\left(\frac{\mu_a^{m}}{T}\right) = -\left(\frac{\mu_a^{m}}{T^2}\right) dT + \left(\frac{d\mu_a^{m}}{T}\right) \qquad \text{VIII-22}$$

The relation (VIII-22) can be defined in terms of T,p,$\bar{N}$ as follows

$$d\mu_a^{m} = - S_a^{m}\, dT + V_a^{m}\, dp + \left(\frac{\partial \mu_a^{m}}{\partial \bar{N}}\right)_{T,p} d\bar{N} \qquad \text{VIII-23}$$

where

$$S_a^{m} = \left(\frac{\partial \bar{S}}{\partial \bar{N}}\right)_{T,p} = -\left(\frac{\partial \mu_a^{m}}{\partial T}\right)_{\bar{N},p}$$

$$V_a^{m} = \left(\frac{\partial \bar{V}}{\partial \bar{N}}\right)_{T,p} = \left(\frac{\partial \mu_a^{m}}{\partial p}\right)_{T,\bar{N}}$$

The equation (VIII-23) can be rearranged taking into account the enthalpy per monomer of micelle, volume and average property of a small system (micelle)

$$d\left(\frac{\mu_a^{\,m}}{T}\right) = -\left(\frac{h_a^{\,m}}{T^2}\right) dT + \left(\frac{V_a^{\,m}}{T}\right) dp + \frac{1}{T}\left(\frac{\partial \mu_a^{\,m}}{\partial \bar{N}}\right)_{T,p} d\bar{N} \qquad \text{VIII-24}$$

where

$$h_a^{\,m} = \mu_a^{\,m} + TS_a^{\,m}$$

Substituting equation (VIII-21) into equation (VIII-24) it takes the form

$$-\left(\frac{h_a^{\,m} - h_a^{\,os}}{T^2}\right) dT + \left(\frac{V_a^{\,m} - V_a^{\,os}}{T}\right) dp + \frac{1}{T}\left(\frac{\partial \mu_a}{\partial \bar{N}}\right) d\bar{N} = kd \ln x_a^{\,s}\, Ce_a^{s} \qquad \text{VIII-25}$$

first term of equation (VIII-25) can be defined in terms of the temperature dependence of activity coefficient of monomer at pressure p, the variation of chemical potential of monomer depending on $\bar{N}$ at T,p and the temperature dependence of the average property of micelle at pressure p by means of the relation,

$$\left(\frac{h_a^{\,m} - h_a^{\,os}}{T^2}\right) = -k\left(\frac{\partial \ln x_a^{\,s}\, Ce_a^{s}}{\partial T}\right)_p + \frac{1}{T}\left(\frac{\partial \mu_a}{\partial \bar{N}}\right)_{T,p} \left(\frac{\partial \bar{N}}{\partial T}\right)_p \qquad \text{VIII-26}$$

on the other hand the second term of equation (VIII-25) can be introduced in the same way taking into account the pressure (p) dependence of above quantities mentioned in equation (VIII-26)

$$V_a^{\,m} - V_a^{\,os} = kT\left(\frac{\partial \ln x_a^{\,s}\, Ce_a^{s}}{\partial p}\right)_T - \left(\frac{\partial \mu_a}{\partial \bar{N}}\right)_{T,p} \left(\frac{\partial \bar{N}}{\partial p}\right)_T \qquad \text{VIII-27}$$

VIII-28

If an equation $\mu_a = \mu_a^{\,os} = kT \ln x_a^{\,s}\, Ce_a^{s}$ is substituted into equation (VIII-26) the following relation is obtained

$$S_a^{\,m} - S_a^{\,os} = - kT \left(\frac{\partial \ln x_a^{\,s}\, Ce_a^s}{\partial T}\right)_p + \left(\frac{\partial \mu_a}{\partial \overline{N}}\right)_{T,p} \left(\frac{\partial \overline{N}}{\partial T}\right)_p - k \ln x_a^{\,s}\, Ce_a^s \qquad \text{VIII-29}$$

Alternatively with the relation given for the small systems in a solvent,

$$0 = - \overline{S}\, dT + \overline{V}\, dp - \sum_{a=1}^{c} \overline{N}_a\, d\mu_a^{\,m} - d\varepsilon_m \qquad \text{VIII-30}$$

and with equation (VIII-29) the following relation can be given by an equation for a single component micelle

$$d\mu_a^{\,m} = - \left(\frac{\overline{S}}{\overline{N}}\right) dT + \left(\frac{\overline{V}}{\overline{N}}\right) dp - \frac{d\varepsilon_m}{\overline{N}} \qquad \text{VIII-31}$$

$$\frac{d\mu_a^{\,m}}{T} = - \frac{\mu_a^{\,m} dT}{T^2} - \frac{\overline{S}}{\overline{N}T}\, dT + \frac{\overline{V}}{\overline{N}T}\, dp - \frac{d\varepsilon_m}{\overline{N}T} \qquad \text{VIII-32}$$

The average enthalpy, entropy and free energy relation of the small system can be defined in terms of average properties of micelles and sub-division potential of micelles, such as

$$\overline{H} - T\overline{S} = \overline{F} = \overline{N}\mu_a^{\,m} + \varepsilon_m \qquad \text{VIII-33}$$

$$\frac{\overline{H}}{\overline{N}} - \frac{\varepsilon_m}{\overline{N}} = \mu_a^{\,m} + \frac{T\overline{S}}{\overline{N}} \qquad \text{VIII-34}$$

substituting this expression into equation (VIII-32) the following equation is obtained

$$d\left(\frac{\mu_a^{\,m}}{T}\right) = - \frac{\overline{H}}{\overline{N}T^2}\, dT + \frac{\overline{V}}{\overline{N}T}\, dp - \frac{1}{\overline{N}}\, d\left(\frac{\varepsilon_m}{T}\right) \qquad \text{VIII-35}$$

puting $\overline{H}/\overline{N} = h_a^{\,+}$, $\overline{S}/\overline{N} = S_a^{\,+}$, $\overline{V}/\overline{N} = V_a^{\,+}$ and $\overline{F}/\overline{N} = F_a^{\,+}$ and equation equation (VIII-35) with equation (VIII-21) the following relation is obtained

$$- \left(\frac{h_a^{\,+} - h_a^{\,os}}{T^2}\right) dT + \left(\frac{V_a^{\,+} - V_a^{\,os}}{T}\right) dp - \frac{1}{\overline{N}}\, d\left(\frac{\varepsilon_m}{T}\right) = k d\, x_a^{\,s}\, Ce_a^s \qquad \text{VIII-36}$$

and substituting $\varepsilon_m/T = - k \ln x_m$ into equation (VIII-36) it takes the form

$$-\Delta H_a = -\left(h_a^{+} - h_a^{os}\right) = kT^2 \left(\frac{\partial \ln x_a^{s}\, Ce_a^{s}}{\partial T}\right)_p - \frac{kT^2}{\bar{N}} \left(\frac{\partial \ln X_m}{\partial T}\right)_p \qquad \text{VIII-37}$$

$$\Delta V_a = \left(V_a^{+} - V_a^{os}\right) = kT \left(\frac{\partial \ln x_a^{s}\, Ce_a^{s}}{\partial p}\right)_T - \frac{kT}{\bar{N}} \left(\frac{\partial \ln x_m}{\partial p}\right) \qquad \text{VIII-38}$$

$$\bar{N} = \left(\frac{\partial \ln x_m}{\partial \ln x_a^{s} Ce_a^{s}}\right)_{T,p} \qquad \text{VIII-39}$$

and the entropy and free energy of micellization can be defined by an equations

$$\Delta F_a = \left(F_a^{+} - F_a^{os}\right) = kT \ln x_a^{s}\, Ce_a^{s} - \frac{1}{\bar{N}}\, kT \ln X_m \qquad \text{VIII-40}$$

$$\Delta S_a = \left(S_a^{+} - S_a^{os}\right) = -\, kT \left(\frac{\partial \ln x_a^{s} Ce_a^{s}}{\partial T}\right)_p + \frac{kT}{\bar{N}} \left(\frac{\partial \ln X_m}{\partial T}\right) \qquad \text{VIII-41}$$

$$-k \ln x_a^{s}\, Ce_a^{s} + (k/\bar{N}) \ln X_m$$

Since V_a^{os} and h_a^{os} are functions of T,p any changes in the left side of equations (VIII-37) and (VIII-38) at constant T,p can be defined by the corresponding changes in h_a^{+} and V_a^{+}. The variation of enthalpy and volume of micellization with mole fraction of micelles is defined by the relation

$$\left(\frac{\partial \Delta H_a}{\partial \ln X_m}\right)_{T,p} = \frac{k\, T^2}{\bar{N}^2} \left(\frac{\partial \bar{N}}{\partial T}\right)_{X_m,p} \qquad \text{VIII-42}$$

$$\left(\frac{\partial \Delta V_a}{\partial \ln X_m}\right)_{T,p} = \frac{kT^2}{\bar{N}^2} \left(\frac{\partial \bar{N}}{\partial p}\right)_{T,X_m} \qquad \text{VIII-43}$$

At constant T and p, at equilibrium from equation (VIII-30) the variation of chemical potential of monomer of component (a) with $\bar{N}$ can be defined in terms of the reciprocal relation of the average property of micelles and the variation of subdivision potential of micelles with $\bar{N}$ such as,

$$\left(\frac{\partial \mu_a}{\partial \bar{N}}\right)_{T,p} = - \frac{1}{\bar{N}} \left(\frac{\partial \varepsilon_m}{\partial \bar{N}}\right)_{T,p} \qquad \text{VIII-44}$$

and on the other hand the chemical potential of monomer can be given in terms of chemical potential of monomer at standard state and its mole fraction

$$\mu_a{}^s = \mu_a{}^{os} + kT \ln x_a{}^s \qquad \text{VIII-45}$$

and this relation (VIII-45) can be rewritten by means of

$$\left(\frac{\partial \bar{N}}{\partial \mu_a}\right)_{T,p} = \left(\frac{\bar{N}^2 - \bar{N}^2}{kT}\right) \qquad \text{VIII-46}$$

an equation is obtained

$$\left(\frac{\partial \bar{N}}{\partial \mu_a{}^s}\right)_{T,p} = \frac{\bar{N}^2 - \bar{N}^2}{x_a{}^s} \qquad \text{VIII-47}$$

and it takes the following form with equation (VIII-23)

$$\left(\frac{\partial x_a}{\partial x_a{}^s}\right)_{T,p} = \frac{x_m \bar{N}}{x_a{}^s}$$

If $xt = (x_a{}^s + \bar{N}_{x_m})$ is total concentration of surfactant then the fraction of total surfactant (fa) goes into monomeric form can be defined by

$$fa = \left(\frac{\partial x_a^s}{\partial x_t}\right) ; \quad 1\text{-}fa = \left(\frac{\partial \bar{N} x_m}{\partial x_t}\right)_{T,p} \qquad \text{VIII-48}$$

If above expressions are combined, the following relation is obtained

$$\frac{1\text{-}fa}{fa} = \left(\frac{\partial x_m \bar{N}}{\partial x_a{}^s}\right)_{T,p} \qquad \text{VIII-49}$$

The approach mentioned in this section on small systems in a solvent, concerns solutions which are so dilute that they do not interact. But in view of this observation a question arises as to how a small system can be defined. In fact it is purely a matter of convenience whether the aggregate formation can be considered explicitly. As has been discussed above, the non-ionic surfactant system can be treated as a two component solution consisting of non-ionic surfactant plus water in terms of activity coefficients.

In view of this treatment, the change in the thermodynamic properties of micelles can be discussed with aggregation number, and the concentration of monomer.

VIII.If - Thermodynamics of micellization of polyoxyethylene mono hexadecyl ethers in waters.

Benjamine(315) has measured the partial molal enthalpy values of a series of dimethyl-n-alkylamine oxides in water. He has found that the partial molal free energy decreases with increasing chain length, and the partial molal enthalpy of the micellization is positive, and it decreases with chain length studied. The positive values ofenthalpy have been interpreted in terms of hydrophobic bonding present during the micellization. The positive entropy increase has been introduced with the concept of releasing of order of water molecules associated with the monomer during the micellization process. The enthalpy and entropy contributions to the micelle formation has been estimated as -140 cal/mole of $-CH_2-$ group + 2.9 e.u.

Hermann(323) has studied the heat of micellization of n-dimethyl-dodecylamine oxide from the temperature variation of C_o determined by light scattering. He has observed that the heat and entropy of micellization are positive, and remain positive over the temperature range 1-50°. The positive entropy change has also been discussed with the change in solution. The value for enthalpy of micellization (1.9 K cal/mole) is lower than found by Benjamine (2.6 K cal/mole).

Corkill et al.(319) have investigated the thermodynamics of micellization of the alkylsulphinylakanols. They have shown that the additional methylene group away from the head group contributes a decrement in enthalpy as the additional methylene group in the head group gives an increase in enthalpy. The increment in entropy has been interpreted by the solvation of head group causing the losses of ordered water molecules. They have also observed that the extent of the hydration of the head group decreased as the temperature increased.

Corkill et al.(304) have shown,that the free energy, and enthalpy of the micellization of alkyltrimethyl ammonium alkyl sulphates are linear functions of the total alkyl chain length. The increment in enthalpy per -CH_2- group has been discussed in terms of the major contribution to the free energy increment. According to their view, the process of micellization is promoted due to the cohesive forces between water molecules, which extrude the hydrocarbon chain, and the heat and entropy changes are due to solvent reorientation.

The increment in free energy of micellization per -CH_2- group has been interpreted(304) by means of the elimination of a fraction of the monomers hydrocarbon-water interface which causes the minimization of interfacial free energy. Although the electrical contribution to the free energy of micellization is a second order effect, the minimization in interfacial energy has been discussed as the driving force for micellization.

Corkill et al.(319) have also examined the thermodynamics of a homologous series of polyoxyethylene surfactants. They have shown that the positive heat of micellization increases with increasing ehtylene oxide chain length, and the micellization is governed by the gain in positive entropy associated with the transfer of the monomer from an aqueous environment to the micelle.

Schick(324) has investigated the thermodynamics of micellization of non-ionic surfactants (ethylene oxide condensates of n-dodecanol and n-hexadecanol) in aqueous solution. The partial molal entropy change which occurs on micelle formation has been attributed to the desolvation, or increment in the configurational entropy of surfactant moonomers. The enthalpy contribution to the free energy increment in the micellization of n-alkylhexaoxyethylene glycol monoethers has been discussed in terms of the change in cohesional energy of the hydrocarbon chain on micellization, and the release of energy associated with the reformation of hydrogen bonds in solvent molecules.

Elworthy-McDonald(325) have shown that the positive differential entropy is due to a mixing process of water molecules around the polyoxyethylene chains. They have also concluded that the mixing process is considerable at higher temperatures.

Moroi et al.(326) have investigated the contributions of hydrophobic, and hydrophilic groups to the enthalpy of micellization of sodium alkyl sulphates with the chain length from C_8 to C_{14}, and polyoxyethylene oxide surfactant containing different numbers of ethylene oxide units. They have shown that although the hydrophilic group has a major contribution at low temperature, it gives a minor contribution at higher temperature. The hydrophilic part of enthalpy is positive and it shows a minimum at 35°C, while the hydrophilic part of enthalpy is negative. It decreases with increasing temperature. They have also discussed that the water molecules around the hydrophilic group have a great effect on C_0. In the case of non-ionic surfactants, the hydrophilic part of enthalpy makes a major contribution to the enthalpy of micellication resulting in a positive enthalpy change. The positive partial molal enthalpy and entropy have also been discussed(129) as being concerned with water structure surrounding the monomer hydrocarbon chains.

The thermodynamics of micellization of polyoxyethylene hexadecyl mono ethers were studied using micro calorimetry at 25°C as described in the previous section. The free energy of micellization decreases with increasing exthylene oxide units (-8.2 K cal/mole, -9.0 K cal/mole for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively Table VIII.I.1,

Fig.VIII.3). The free energy change involved in the micelle formation has an entropy origin rather than the potential energy, and it also has a contribution from the enthalpy of micellization.

The enthalpy of micellication increases with decreasing free energy (7.2 K cal/mole and 8.85 K cal/mole for $C_{16}E_{10}$ and $C_{16}E_{60}$ respectively). The enthalpy contribution to free energy change 34 cal/mole Table VIII.I.1 while the entropy contribution is 50 cal/mole the decrement in free energy per (CH_2-CH_2-O) group is -20 cal/mole which is smaller in magnitude compared with-0.5 K cal/mole per CH_2 group. This is due to the opposing effects of the alkyl and ether units in the head group. On the other hand the hydrocarbon free energy was derived from the extra polation of the enthalpy - EO unit curve to zero, which is-6.86 K cal/mole Fig.VIII.3.

The increase in entropy which occurs on micellization can be discussed in terms of water molecules surrounding a hydrocarbon chain, and aggregation of the monomers. The structure of water molecules increases near nonpolar groups. In this stage water molecules are more highly hydrogen bonded than in bulk water having a state of lower entropy. The aggregation of nonpolar groups causes the melting of water clusters, consequently the entropy of the system increases. This process is typical hydrophibic interactions because it is an entropy derived process. The release of energy due to reorientation of water molecules, the decrement in solvation because of minimization of water hydrocarbon interface contributes an increase in entropy. At this state, the removal of aggregated monomers to a nonpolar environment micelles are formed. Enthalpy and entropy of micelle formation are positive, showing that the micellization is governed by the gain in entropy.

VIII.Ig - Conclusions.

Thermodynamic properties of micelle formation in aqueous solution of alkylammonium bromides and polyoxyethylene monohexadecyl ethers were examined at 25°C using a microcalorimeter. In this work it has been observed that ΔG_M decreases with a decrease in enthalpy. The decrement in ΔG_M has been discussed in terms of hydrophobic interactions between monomers, and water icebergs. The reduction in structural order of water molecules due to a minimization of hydrocarbon water interface, and transferring of monomer from aqueous region to nonpolar environment reduce the free energy of system.

However, according to this observation a decrement in ΔH_M accompanied with the standard free energy change, has been attributed to the change in translational energy of monomer, water molecules, and the effect of charged hydrated head groups. Micelle formation appears to be an exothermic process due to a high enthalpic contribution.

The change in entropy during micelle formation is not significant. It is believed that the entropic contribution to the micellization, is due to the increment in flexibility of monomer in nonpolar region, the decrement in hydration of monomer when it enters in to the micelle, and the interactions between hydrocarbon chains and structured water molecules.

In the case of non-ionic surfactants the free energy of micellization decreases with increasing ethylene oxide chain length. The enthalpy of micellization is positive, and it increases with decreasing free energy. On the other hand the entropy of micelle formation increases. The increment in entropy is due to the release of water molecules around the nonpolar groups, the decrement in solvation because of the minimization of water-hydrocarbon interface, and the removal of aggregated monomers to a nonpolar environment. The positive entropy of micellization indicates that the micelle formation is an entropy derived process, which is governed by the presence of hydrophobic interactions during the micellization.

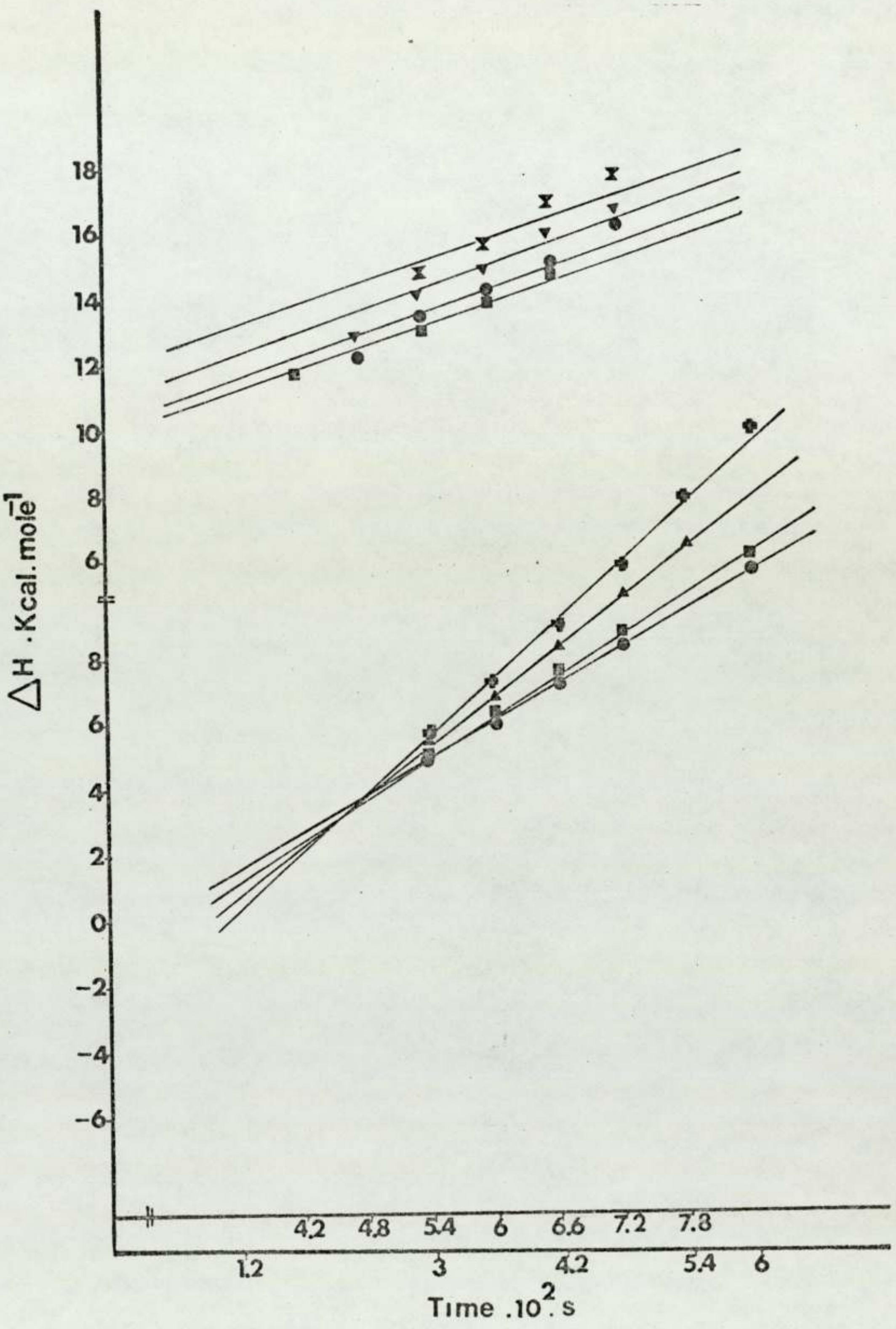


Fig.VIII.1 Heat of solution variation with time in seconds for the alkyltrimethyl ammonium bromides and the polyoxyethylene mono hexadecyl ethers; ● C_{10}, ■ C_{12}, ▲ C_{14}, and ✚ C_{16}: ■ EO_{10}, ● EO_{18}, ▲ EO_{30} and ⧗ EO_{60}

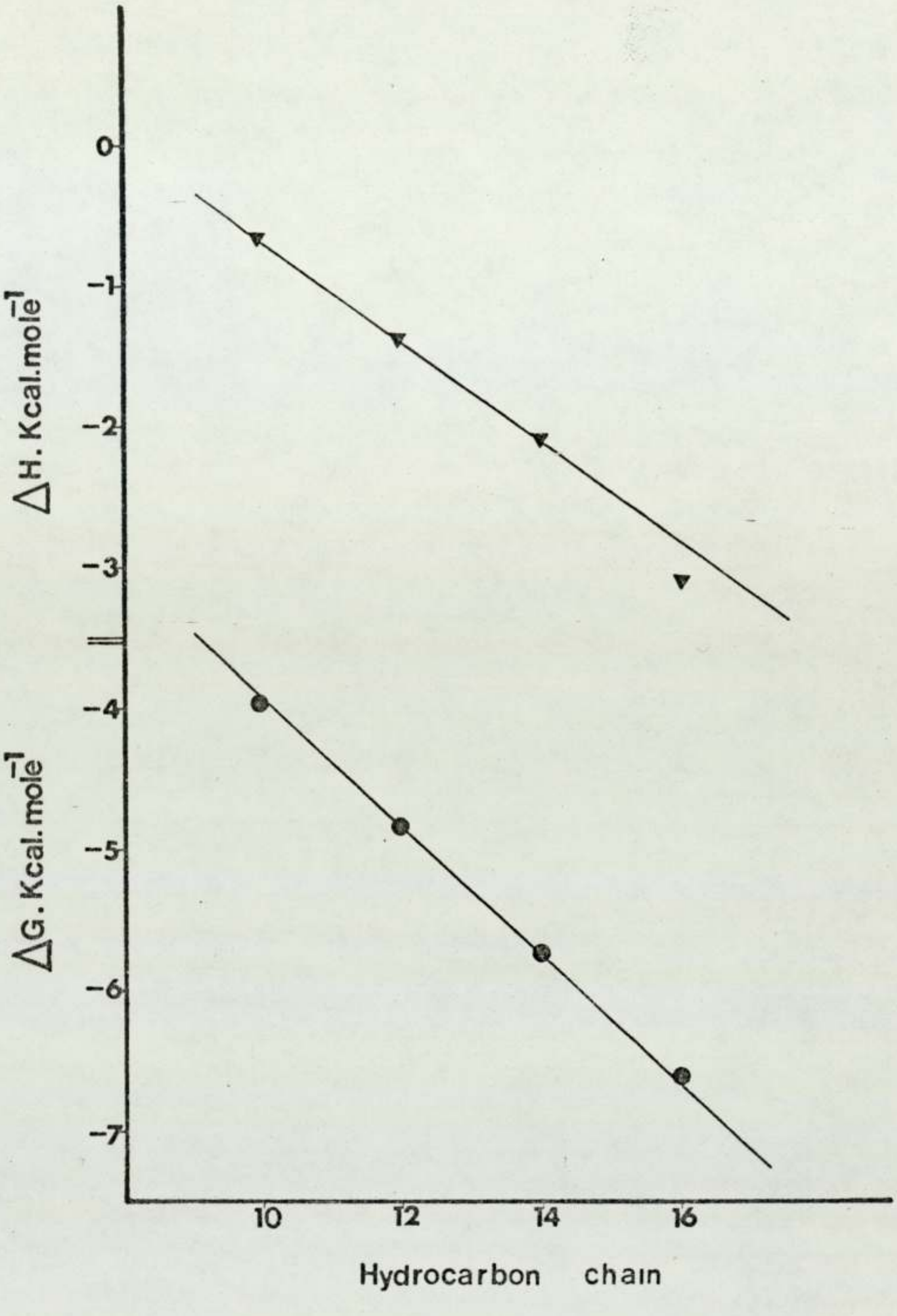


Fig.VIII.2 Heat of micellization of the alkyltrimethyl ammonium bromides as a function of hydrocarbon chain length; Relation ship between free energy of micelle formation for the alkyltrimethyl ammonium bromides and the alkyl chain length at 25° C;

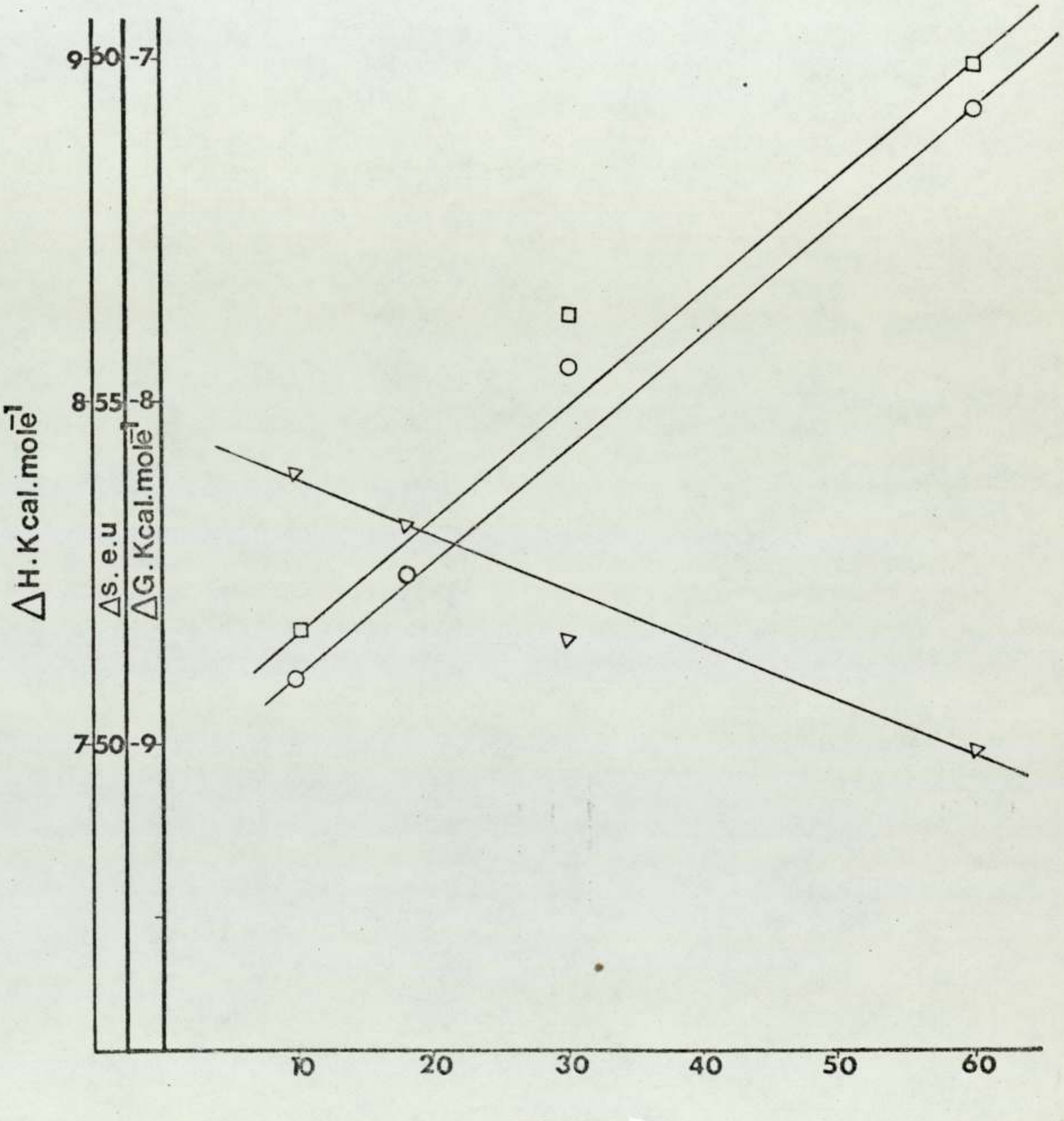


Fig.VIII.3 Thermodynamic parameters of micellization of the polyoxyethylene mono hexadecyl ethers in water as a function of the alkyl chain length at 25° C;

THERMODAYNAMIC DATA FOR THE MICELLIZATION OF .ALKYAMMONIUM BROMIDES

AND POLYOXYETHEYLENE ETHERS IN WATER AT 25° C

TABLE VIII.I.1

S.A.A	ΔG Kcal.mole^{-1}	ΔH Kcal.mole^{-1}	TΔS Kcal.mole^{-1}	ΔS Cal.mol.deg^{-1}	C_0 mol.dm^{-3}	ΔG change per CH_2	ΔH Contr. to ΔG
				CATIONICS			
C_{10}	-4.0	-0.65	3.35	11.23	6.5 x10^{-2}	-0.5 Kcal.mol.$^{-1}$	-0.34 Kcal.mol^{-1}
C_{12}	-4.8	-1.4	3.4	11.40	1.68x10^{-2}		
C_{14}	-5.7	-2.1	3.6	12.07	3.7 x10^{-3}		
C_{16}	-6.6	-3.2	3.4	11.40	8.0 x10^{-4}		
				NON-IONICS			
EO_{10}	-8.2	7.2	15.4	51.65	5.6 x10^{-5}	ΔG per $-CH_2-CH_2-O-$	ΔH Contr. to ΔG
EO_{18}	-8.4	7.5	15.9	53.32	3.89x10^{-5}	-20 cal. mole^{-1}	34 Cal.mol.$^{-1}$
EO_{30}	-8.7	8.1	16.8	56.34	2.4 x10^{-5}	Hydrocarbon Cont. to Micellization −6.86 Kcal.mole^{-1}	
EO_{60}	-9.0	8.85	17.85	59.87	1.4 x10^{-5}		

<

C_{10}	ΔH Kcal.mole^{-1}	C_{12}	ΔH Kcal.mole^{-1}	C_{14}	ΔH Kcal.mole^{-1}	C_{16}	ΔH Kcal.mole^{-1}
t s.		t s.		t s.		t s.	
300	5.3	300	5.2	300	5.4	300	5.5
360	6.24	360	6.3	360	6.9	360	7.2
420	7.3	420	7.4	420	8.4	420	9.1
480	8.4	480	8.5	480	10.5	480	10.9
600	10.7	600	11.1	540	11.67		

<

Eo_{10}	ΔH Kcal.mole^{-1}	Eo_{18}	ΔH Kcal.mole^{-1}	Eo_{30}	ΔH Kcal.mole^{-1}	Eo_{60}	ΔH Kcal.mole^{-1}
420	10.6	480	12.0	480	12.6	540	17.4
540	12.8	540	13.7	540	13.4	600	15.5
600	14.1	600	14.2	600	14.9	660	17.1
660	15.4	660	15.5	660	16.4	720	17.9
		720	17.0	720	17.3		

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SYMBOLS.

$\breve{A}$ = A parameter which depends on the properties of the solvent, Anstrom.

$A_{N+2}(R_1,R_2)$ = The quantity which is in effect a function of the distance $R_{12} = [R_1-R_2]$

AHl (R_1,R_2) = Hydrophobic interaction between two solute particles at fixed positions (R_1,R_2)

A = The intercept (light scattering), constant
$A_{a,b}$ = Equatiorial radius, Semi-axis of revolution
A_o, E_L = Effective length
A_R = Axial ratio
a = The radius of the micelle = $\sqrt[3]{3M/4\,Nod}$

a_o = Hydrodynamics radius

a_i = Coefficient of friction of ions

$\bar{a}_2$ = The partial molal expansibility of infinite dilution

$\Delta\bar{V}^o_{1A}$ = Increment in $\bar{V}_1$ per $-CH_2-$ group of alkyl chain length

B = Constant for the particular homog series and temperature (158) second virial coefficient

B_1, B_2 = Experimental constants

b = κa

be = Effictive bond length

b_i = The functions of the properties of the double layer

$\bar{V}^o_{1B}$ = Increment in $\bar{V}_o$ per $-CH_2-$ group of alkyl chain length

C_A = Concentration of the alcohol

C^o_A = Concentration of alcohol equilibrium with the imaginary alcohol micelle at a given temperature and pressure

C_a = Initial concentration of the electrolyte in the syringe
Λ_c = Conductance
C_i^- = Counter ion

(C_i^-) = Respective equilibrium concentration of C_i

C_i, c_i = Concentration of ion (i), molarity of ion (i) at C_o

Ceq = Unit equivalent concentration

C_o = Critical micelle concentration

Ce^s_a = Activity coefficient of component (a)

$\bar{C}p^o$ = Vapour heat capacity

C_s = Concentration of the surfactant

C_s° = Concentration of the monomer equilibrium with the micelle at a given temperature and pressure

Csp = Chart speed

C_t = The concentration of the electrolyte in the titration vessel at time t

$\bar{V}_c$ = Crystal molar volume of the surfactant

$\bar{V}_{1C}^{\circ}$ = Increment in $\bar{V}_0$ per $(-CH_2-CH_2-O)$ group

ΔCp = The heat capacity

ΔCp° = Heat capacity of the hydration

D = Dielectric constant of the solvent

D_i = Diffusion coefficient of ion (i)

D_L = The density of the reference liquid
D_R = Dissymmetry
D_s = The density of the solid (surfactant)

d = Density of the micelle

da = The density of the solution

dw = Density of the solvent

ΔD = Chart distance from t_0-t_1

$\bar{V}_{1D}^{\circ}$ = Increment in $\bar{V}_1$ per $(-CH_2-CH_2-O)$

E = Electric intensity, a correction term for electro viscous effect
Λeq = Equivalent conductance
e = Electronic charge, electrical charge

F = Faraday constant, the intensity of a homogeneous electric field

Fa = Free energy of micellization

$\bar{F}$ = Average free energy

fa = The fraction of total surfactant goes into monomeric form

$f_{\pm}$ = The mean ionic activity coefficient

F_m, F_{S_i}, F_{C_i} = Activity coefficients of S_i, micelle, and C_i

ΔF = Rate of flow

ΔG = Free energy

ΔG_H^θ = Hydration free energy

ΔG_{iel}^θ = Electrostatic contribution to the hydration free energy

ΔG_{inel} = Non electrostatic i to the hydration free energy

ΔG_{Mp} = Free energy of micellization (phase separation model)

ΔG_{Mb} = " " " " (mass-action model)

ΔG_{soln} = Free energy of the solution

H = The magnetic intensity, optical constant

Ha = Enthalpy of micellization

h_a = Mean entropy value of component (a)

h_a^{os} = Enthalpy per monomer component (a) at standard state

ΔH = Enthalpy

ΔH_h = Enthalpy of the hydration

$\Delta H_{Mp}, \Delta H_{Mb}$ = Enthalpy of micellization (phase-separation and mass-action models)

ΔH_{soln} = Enthalpy of the solution

ΔH_t = Enthalpy of the aqueous binary mixture

I = The intensity of light
ΔI = Refranctive indiex increment of the solution
i = The various ion species present in solution at C_o including unassociated detergent

Λi = Initial conductivity in the titration vessel

K = Shape factor of the particle depending on the axial ratio

k = Boltzmann constant

L = Length of the conductor

M = The micelles (phase-separation model)

M = The number of the moles of the solvent per 1000g of solvent, molecular weight of the surfactant, corrected micellar molecular weight

M = Equilibrium concentration of the micelles

M' = The apparent micellar molecular weight

M_1 = The molecular weight of the monomer

M_0 = Molecular weight of water molecule, molecular weight of the statistical element

M_2 = The additive molecular weight

M^{+z} = The micelles (mass-action model)

m = Dipole, molarity and mass

N = Aggregation number, number of molecules

NA = The uncorrected degree of association of micelles, number of particles (solvent)

$N_A/(N_s+N_a)$ = The molecular fraction of the alcohol

No = Avagadro number

$\bar{N}$ = Average property of a small system or micelle

$\bar{N}^2$ = As in $\bar{N}$ refers to an average property of a small system or micelle

Nc = The corrected degree of association of micelles

N^{-z} = The number of bound counter ions

(N+1) = Number of particles in a system

$N_S/(N_S+N_A)$ = The molecular fraction of the surfactant

n = Number of the particles, molar number of alkylammonium bromides, number of the components in the system, number of the volent molecules in the cosphere

n_1, n_2 = Number of the moles of components 1 and 2 respectively

n_0 = Number of moles of water

n^{-2}, n_s = Refractive index of the solution

$\bar{n}_0, n_0$ = Refractive index of the solvent

O = Oxygen

P = Pressure

p = The effective charge (corrected) pressure, axial ratio

p' = The apparent ratio (uncorrected)

p_1 = Density of the solution

p_1H_2O = Density of water

pt = Dilution factor at time t

Q = Space charge

q = Conductivity coefficient

R = Gas constant, resistance of the conductor

R_1, R_2 = The fixed positions of the simple two solute particles

r = Distance

r_i = Radius of ion (i)

r_1, r_2 = Location of ρ_1, ρ_2 ...

2R in M = Cratic term (cratic portion of the conventional partial molal entropy of the solution)

S = Cross-section of the conductor

Sa = Entropy of the micellization

Sa^m = Entropy of component (a) at micellar state

S_a^{os} = Entropy of " (a) at standard state

S_a = The electrostatic contribution to the stress

S_b = The stress between the solvent molecules.

S_i = Ionic space

$\bar{S}$ = Average entropy

$Spv, \bar{\nu}$ = Specific volume of the monomer at C_0

ΔS = Entropy

$\overline{\Delta S}$ = The partial entropy of the solution

ΔS_h = Entropy of hydration

$\Delta S_{Mp}, \Delta S_{Mb}$ = Entropy of micellization (phase-separation and mass-action models)

Λsp = Specific conductance

ΔS_{soln} = Entropy of the solution

ΔS_t = Entropy of the aqueous binary mixture

$\Delta S_{unitary}$ = Unitary entropy

Λ_{sp} = Specific conductivity

T = Temperature

t = time

ta = Flow time of the solution at 25°C

Λt = Recorded conductivity at time t

U_i = Mobility of ion (i)

$U_{12}(R_1, R_2)$ = The interation potential for the pair solute particles at R_1 and R_2 positions

U_{N+1} = Potential of the interaction of the N+1 particles in the specified configuration

U_+, U_- = Mobility of positive and negative ion

$U^{\circ}_{+,-}$ = Limiting ion conductivity

V = Molar volume of the polar liquid, volume

v = The angle of solution containing (n) particles in 1 cm^3

$\overline{V}$ = Average volume

Va = Anhydrous volume of the micelle, volume of the micelle

Va_m^+ = Mean volume quantity of component a

Va^m = Volume of component (a) at micellar state

Va^{os} = Volume of single component (a) at standard state

Vh = Hydrated volume of the micelle

V_i = Initial volume in the titration vessel

Vp = The volume of the pycnometer

V_t = The volume delivered by the syringe at time t

$\overline{V}$ = Partial molal volume of the particular concentration

$\overline{V}_o$ = Partial molal volume at infinite concentration

$\overline{V}_1$ = Partial molal volume of the micelles in aqueous solution partial molal volume of the component 1.

$\overline{V}_2$ = Partial molal volume of the component 2, partial molal volume of the surfactant in mixed systems

$\overline{V}_2^{\circ}$ = Partial molal volume of the mixed micelle

$\Delta\overline{V}_1 = \overline{V}_1 - \overline{V}_o$

$\Delta\overline{V}_2 = \overline{V}_2^{\circ} - \overline{V}_1$

$\overline{V}^{op}_1$ = Excess limiting partial molal volume

$\overline{V}_2(x_2)$ = Partial molal volume - molfraction curve

$\partial\overline{V}_2/\partial T$ = " " " - temperature slope

$\partial\overline{V}_2/\partial X_2$ = " " " - molfraction "

$\partial\overline{V}_2^E(X_2)$ = Concentration dependence of partial molal volume

$\frac{\partial V_X}{\partial y}$ = The relative rate of deformation

Y = An extensive property of a given system

Y_1, Y_2 = Partial moal quantities

Z = Degree of polymerization, a function of b evaluated by Booth(43,44)

z_i = Valency

Z_{ie} = Charge of ion (i)

Wd = The weight of the dry pycnometer

Ww = The weight of the pycnometer filled with water

W_S = The weight of the solid

W_T = The weight of the pycnometer filled with the liquid and solid

W = Weight of water hydrating one gram substance

x = Electrolytic conductivity, the mole fraction of the alcohol in the micelle

X_m = Mole fraction of micelle

X^z = An ion where z is positive or negative charge

X_a^s = Mole fraction of component a

X_1, X_2 = Number of moles of component 1 and 2

X Fo(X) = Hydrodynamic-draining parameter

X-X' = m'w = cohesive energy change per one alcohol molecule

Xt = Total concentration of surfactant

ϵ = The dielectric constant of the solution electronic charge, average dielectric constant of the medium

ϵ = The dielectric constant of the solvent

ϵ' = The dielectric constant of the region exhibiting the fluctuation

ε_m = Subdivision potential of micelle

α = Degree of dissociation, polarizibility of the particle

β = The viscosity increment

βs = The adiabatic compressibility

δB = The zeta potential of the micelles from their size and electrophoretic mobility in terms of an equation proposed by Booth(43,44)

δ = $6\pi n\mu/D$

$(\delta a')^2$ = The mean square of the excesspolarizability

$(\delta d)^2$ = " " " " " fluctuation in density

$\overline{(\delta\varepsilon)^2}$ = The mean square of the dielectric constant of the medium

$\overline{(\delta m)^2}$ = " " " " " concentration fluctuations

δV = The volume element

η_o = The absolute visoosity of the solvent

η_1 = " " " of water at 25°C

η_2 = " " " of 20% sucrose solution at 25°C

η_k = Kinematic viscosity of water at 25°C

μ = Electrophoretic mobility of the micelles extrapolated to the C_o

μ_a^s = Chemical potential of component (a)

μ_1 = Electrophoretic mobility of the micelles estimated from conductivity data

μ_a^m = Chemical potential of component (a) at micellar state

μ_a^{os} = Standard chemical potential of component (a)

μ_o = Dipole moment of the molecule

$\overline{\mu_o}$ = Average dipole moment per molecule

v_1 = The velocity of light in a vacuum

p = The polarization or dipole moment per unit volume of a continuous material

ρ_1, ρ_2 = Each set of moment a

τd = The turbidity due to density fluctuations

τE = " " " " concentration "

ϕ = Volume fraction, apparent molal volume

λ_o = The wave length in vacuo

λ^o = Limiting ion conductivity

$\lambda_i^{\,o}$ = " conductivity of ion i

ω = The frequency of light vibrations

σ = The specific conductivity of the solution at C_o

R_H = Resistance of heating coil

Rs = Resistance of standard coil

E_p = Potential difference between resistances when current is turned on to the heating coil in solution.