DIELECTRIC STUDIES OF MOLECULAR INTERACTION AND GROUP REORIENTATION

A thesis submitted to
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Summary

Molecules in liquids are constantly reorienting owing to the Brownian Motion. A measure of the time taken for reorientation of a dipolar molecule is the dielectric relaxation time (τ). If a molecule is non-rigid its relaxation time is shorter than expected but if it interacts it is longer than expected.

An apparatus for the measurement of the dielectric constant and loss of solutions at microwave frequencies and procedures for analysing the data into one or two relaxation times using a computer are described. The main body of the thesis discusses the relaxation processes of hydroxylic compounds in solution. If the OH group is not prevented from interacting, its relaxation time is dependent upon the electron donor capacity of the solvent. Phenols with intramolecular hydrogen bonds of weak or medium strength are found to undergo OH group relaxation but those with a strong hydrogen bond are rigid. The data are explained in terms of an asymmetric energy barrier. In molecules having a para nitro substituent mesomeric effects are found to account for the long group relaxation time. Phenols with intramolecular hydrogen bonds should not readily form intermolecular hydrogen bonds. o-Nitrophenol and 8-hydroxyquinoline seem to interact with p-dioxan, and dinitrophenols also with p-xylene but these interactions do not directly involve the OH group.

Phenols with weak or medium intramolecular hydrogen bonds interact strongly with a strong electron donor, 1,4-diazabicyclo-(2,2,2)-octane (DBO). A strong interaction is even found for 2,4,6-trichlorophenol which is intramolecularly hydrogen bonded in both preferred OH configurations.

Finally some systems of chloroform with various electron donor molecules were examined with a view to finding formation constants and dipole moments of the complexes. The method is shown to be potentially valuable. In an appendix, relationships between the mean relaxation time and distribution parameter and the contributing relaxation times and weight factors are considered.

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CHAPTER I

THEORY AND EXPERIMENTAL

group moment being greater than the OCH_3 group moment and both being inclined at the same angle from their respective C-O links (23), it follows that the OH relaxation time must be similar to the observed value in this molecule and is therefore rather higher than the normal OH relaxation time. This conclusion is borne out by the analysis of the catechol data, giving an OH relaxation time of 6×10^{-12} sec. Catechol is structurally similar to guaiacol but the analysed group relaxation time is not composite.

In each of these phenols the OH re-orientation may be regarded as a jumping of the hydrogen atom from the potential well to another (62). When the wells are of equal depth as in phenol and 2,6-dihalophenols, one relaxation time characterises the process, but when the wells are of unequal depths as in o-substituted phenols two relaxation times may be expected (32), τ_T corresponding to a trans→cis re-orientation and τ_c corresponding to a cis→trans re-orientation. τ_c should be significantly longer than τ_T owing to the energy of the hydrogen bond. The model is illustrated in Fig. (11). In fact, only one relaxation time emerges (63,64) and is given by:

$$\tau_2 = \frac{2\tau_T\tau_C}{\tau_T + \tau_C} \qquad \text{............(61)}$$

where τ_2 is the observed relaxation time of group rotation. From equation (61) it follows that when $\tau_c = {}_T$(i.e the

Introduction.

Most of the published work on the dielectric behaviour of chemically interesting systems at microwave frequencies has been obtained by impedence (1,2) or resonance methods (3,4). Transmission methods, despite their obvious relationships with conventional spectroscopy, have been neglected by chemists interested in dielectric absorption. Westphal (5) has reviewed the techniques available for dielectric constant and loss measurement and includes transmission methods. Buchanan has described a type of waveguide bridge apparatus which he, Grant and Cook have subsequently used in several papers (6,7) concerned with water and aqueous solutions. The bridge method seems not to have been used for the study of dilute solutions of polar molecules in non-polar solvents

In this chapter a waveguide bridge, sufficiently accurate for dilute solution work, is described together with the minimum of theory consistent with the understanding of the method. An account is given of the experimental procedure and the precautions necessary for accurate measurement. The apparatus used to determine the static dielectric constant is also described. Finally certain subsidiary measurements are mentioned and methods used for purification of the materials are given.

Theory.

(a) Dielectric Constant and Loss Factor.² When an alternating voltage (V) is applied to the plates of a condenser in a vacuum the resulting current (I) leads the voltage by $\pi/2$ radians. Consequently the field loses no power in heating the sample because:

$$\text{Joule Heat} = IV \cos 90 = 0$$

In general on placing a dielectric material between the plates the current no longer leads the voltage by $\pi/2$ radians the angle being reduced by δ radians. Thus a component of the current ($I\sin\delta$) is in phase with the voltage and Joule heating occurs:

$$\text{Joule Heat} = IV\sin\delta$$

Energy is lost by the applied field and so δ is termed the loss angle and the current ($I\sin\delta$) the loss current. Since the loss current is a property of the dielectric it is best dealt with by introducing a complex dielectric constant

$$\epsilon^* = \epsilon' - i\epsilon'' \qquad \ldots\ldots\ldots\ldots (1)$$

so that the condenser current has a real component,

ϵ' (the dielectric constant) having the properties of the dielectric constant of a loss free material while ϵ'', being a measure of the loss current, is called the loss factor.

(b) Attenuation and Phase Shift.- Consider a periodic electric field in a medium. The time dependence of the field at any initial point is given by:

$$E_1 = E_1^o e^{i\omega t} \quad \ldots\ldots\ldots\ldots(2)$$

Where ω is the angular frequency ($2\pi\nu$) and E^o is the maximum value of the field strength, considered for simplicity to occur at $t = 0$.

At a further point at a distance z along the direction of propagation of the wave the field intensity has altered to:

$$E_2 = E_1 e^{-\gamma z} \quad \ldots\ldots\ldots\ldots(3)$$

where γ is the propagation constant of the material. In general γ is a complex quantity

$$\gamma = \alpha + i\beta \quad \ldots\ldots\ldots\ldots(4)$$

so that the field intensity at the second point is given by:

$$E_2 = E_1^o e^{-\alpha z} . e^{i(\omega t - \beta z)}$$

$$= E_2^o e^{i(\omega t - \beta z)} \quad \ldots\ldots\ldots\ldots(5)$$

from which it is clear that the intensity at the second point is reduced by a factor $e^{-\alpha z}$ and the phase is altered by β z radians. Thus α is the attenuation coefficient and β the phase constant of the material. The units of α are nepers cm^{-1} and those of β are radians cm^{-1}.

For a guided wave α and β are related to the dielectric constant (ϵ') and loss factor (ϵ'') of the medium by the equation:

$$\alpha + i\beta = \frac{2\pi}{\lambda_0}\left[\frac{\lambda_0^2}{(2a)^2} - (\epsilon' - i\epsilon'')\right]^{\frac{1}{2}} \quad \ldots(6)$$

where λ_o is the wavelength in cm of the radiation in a vacuum and 'a' is the broader dimension of the cross section of the waveguide. Separation into real and imaginary parts gives:

$$\epsilon' = \frac{\lambda_o^2}{4\pi^2} (\beta^2 - \alpha^2) + \frac{\lambda_o^2}{(2a)^2} \quad \ldots\ldots\ldots\ldots (7)$$

$$\epsilon'' = \frac{\lambda_o^2}{4\pi^2} . 2\alpha\beta \quad \ldots\ldots\ldots\ldots (8)$$

from which ϵ' and ϵ'' can be obtained by measuring α , β and λo.

The Bridge Method.

(a) The Principle.- The principle of the method is that the output of a signal generator divides into the two arms of a waveguide bridge. One arm contains the dielectric cell while the other contains a rotary calibrated attenuater and phase shifter. The outputs of the two arms are recombined and their vector sum passes on to a crystal detector and thence to a sensitive amplifier and voltmeter. Amplitude and phase balance of the signals in the arms can be achieved so that the detected signal is minimal. From the attenuation and phase values for different sample lengths in the specimen cell the propagation constant and therefore the complex dielectric constant can be calculated. The bridge method is consequently a null method and has the advantage that the response characteristic of the crystal is unimportant since, ideally, no power is detected at the balance point.

Unlike most fields of spectroscopy no single apparatus can be used to determine the dielectric absorption at all microwave frequencies. Each apparatus is limited to only a small variation in frequency for the following reasons:

(i) the microwave radiation generators are tunable only over a small range of frequencies;

(ii) the dimensions of the waveguide permit transmission of the H_{01} mode for only a limited frequency range;

(iii) even within the limitations imposed by (ii) some of the components are designed to function at or near to a particular frequency.

The range of frequencies which may be propagated along a waveguide of given cross section is summarised in Table (1) for the wavebands employed in this work. The letter used to designate the band and the actual working frequency are also given.

Table (1) Internal dimensions ofthe waveguide, frequency range of propagation, identification letter of the frequency band and actual working frequency for the apparatus used in this research.

Waveguide internal dimensions (ins.)	Frequency range (Gc/s)	Working frequency (Gc/s)	Identifi'ion letter
0.122 x 0.061	60.0 - 90.0	70.00	O
0.280 x 0.140	26.5 - 40.0	34.86	Q
0.420 x 0.170	18.0 - 26.5	23.98	K
0.622 x 0.311	12.4 - 18.0	16.20	P
0.900 x 0.400	8.2 - 12.4	9.313	X

(b) The Apparatus (8).- A block diagram of the apparatus is shown in Fig.(1). The components of the circuit and the letters used to identify them in Fig.(1) are:

(i) A stabilised power supply (A);

(ii) A reflex Klystron (B);

(iii) Anisolator or, on some wavebands, an attenuator (C);

(iv) A wavemeter (D);

(v) Magic 'T's (E,K);

(vi) The dielectric cell (H);

(vii) The calibrated rotary attenuator (I);

(viii) The calibrated rotary phase shifter (J);

(ix) The crystal detector (L);

(x) The amplifier and galvanometer (M);

(xi) Matched loads (G);

(xii) Attenuators, or in some cases isolators (F).

The components are joined by rectangular waveguide indicated in Fig.(1) by the black lines. Components (A) and (M), however, are joined to B and L respectively by co-axial cable and so are shown at an angle from the main circuit.

Each component can now be briefly discussed.

(i) Reflex klystrons require carefully stabilised power supplies since fluctuations in the klystron resonator and reflector voltages are translated into frequency and power fluctuations in the output signal. The power supply also

Fig 1. Block Diagram of the Bridge Apparatus.

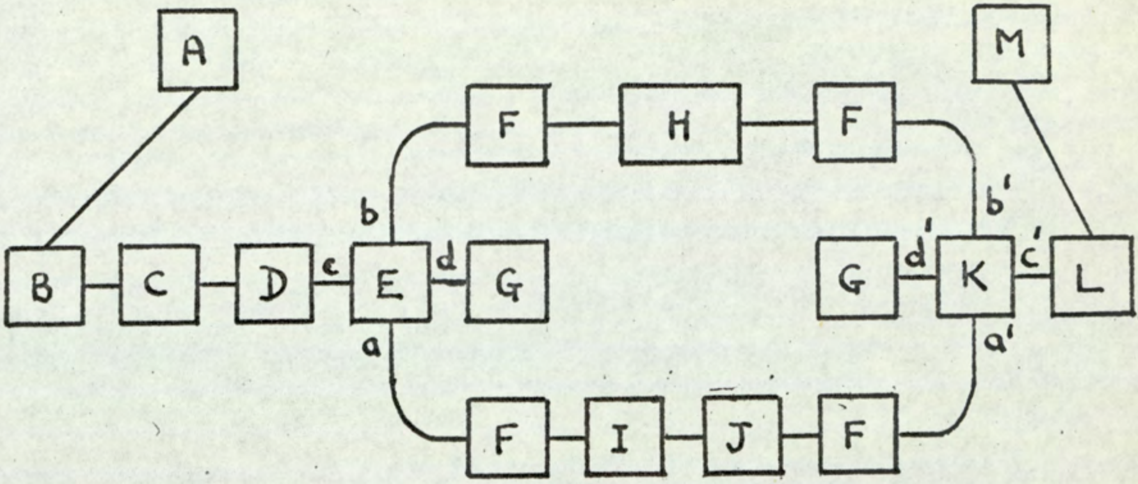
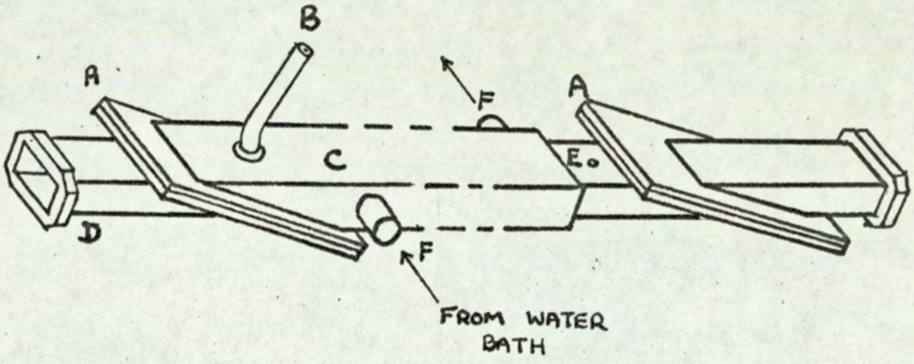


Fig 2. Diagram of the Dielectric Cell.



provides a saw-tooth or square wave modulation of the reflector voltage at 1 kc/s or 3 kc/s. The resultant amplitude modulation of the microwave signal aids amplification of the output from the crystal detector.

(ii) A reflex klystron is the source of microwave radiation which is virtually monochromatic, fluctuations normally being less than 1 Mc/s. Most klystrons need cooling so a draught of air is directed on to them from a fan. The frequency can be adjusted when necessary in two ways; by mechanical tuning or by electrical tuning. Mechanical tuning involves a change of the shape of the resonator cavity by pressure from a screw. Since the oscillater's frequency depends primarily on the size of the cavity, a variation in frequency of about 15% can be achieved and so mechanical tuning is used when large adjustments are needed. Electrical tuning involves alteration of the reflector voltage. The reflector voltage cannot be greatly altered, however, because power is rapidly lost and eventually oscillation may cease. Electrical tuning is therefore used for fine adjustments of 10 or 20 Mc/s. When mechanical tuning has to be used the reflector voltage usually requires adjustment also.

(iii) An isolator is a magnetic device which is transparent to microwave radiation in one direction only. The one at C (Fig.1) is used to prevent reflections from re-entering the klystron and thus altering its frequency.

(iv) The frequency is one of the measured quantities and a wavemeter is provided so that the predetermined frequency can be checked. The wavemeter consists of a cylindrical resonant cavity with one wall movable and attached to a micrometer head or a calibrated drum. As the end wall is moved, the distance between two resonance peaks can be measured because, at resonance, the detected power drops sharply. From this distance the frequency can be found. The Hewlett-Packard frequency meters used on most bands permitted direct reading of the frequency from observation of a single resonance.

(v) The magic 'T' marked E splits the radiation into two equal signals which pass along arms bb', through the dielectric cell, and aa', through the rotary attenuator and phase shifter. The magic 'T' marked K recombines the waves vectorially. The difference arm (d and d') of each magic 'T' is connected to a matched load. 3 db directional couplers were used in the P band apparatus instead of magic 'T's.

(vi) The dielectric cell is discussed in detail in the following section.

(vii) The amplitude of the signal in arm aa' can be varied by known amounts using the calibrated rotary attenuator. At the balance point the amplitude of the signal at a' is equal to that at b'.

(viii) Similarly the phase of the signal in arm aa' can be adjusted in a known manner until the phase of the signal at a' differs from that at b' by 180°. Since the amplitudes of the signals arriving at K, at the balance point, are equal and since the signals are in antiphase, the power output from the sum arm c' is at a minimum.

(ix) The detector consists of a fine wire (catswhisker) in contact with a crystal of a semiconducting material, usually silicon. This arrangement has a greater resistance in one direction than in the other so it acts as a rectifier of the power incident upon the crystal.

(x) The high gain, low noise amplifier and galvanometer permits observation of the balance point since the galvanometer deflection is least at this point.

(xi) Matched loads are attached to the difference arm of the magic 'T's to absorb the power which passes into this arm when the apparatus is not balanced. At the balance point no power enters arm c'.

(xii) The apparatus is fairly sensitive to standing wave patterns set up by reflections from the various components of the apparatus. If reflections are present, unwanted variations of power occur as the amount of liquid in the dielectric cell is varied. The 3 db attenuators F help to reduce standing waves because reflected waves pass the attenuator twice in passing up and down the waveguide and so their intensity is reduced. Isolators replace some of the attenuators in the K and X band apparatus. These have the advantage of cutting out reflections without appreciably reducing forward power.

The whole apparatus is mounted on a board inclined at about 15° from the horizontal with the klystron at the lower end. The purpose of this is twofold: firstly, each increment of liquid volume results in an increment of liquid length through which the wave must pass, secondly, reflections at the upper surface of the liquid are reduced if the electric field vector of the wave leaves the medium gradually. This is discussed more fully in connection with mica windows in the next section.

The Dielectric Cell.

A diagram of a typical cell is given in Fig.(2).

(a) Features.- Basically the cell consists of a length of waveguide separated from the remainder of the apparatus by mica windows. These are glued between the flanges (A) which are then bolted firmly together so that the cell waveguide has no discontinuities which might cause reflections. The filler tube (B) of internal diameter 0.03 to 0.06 cm passes through the water jacket (C) to connect with the waveguide and fit flush with the inner edge of the cell wall. The cell is connected into the apparatus by the flanges (D). A small hole (E) permits the escape of air when filling the cell. Temperature controlled water enters and leaves the water jacket through the inlet and outlet tubes (F).

(b) Windows.- The flanges (A) and hence the mica windows are inclined at an angle of about 15° from the direction of propagation of thewave. Thus for the H_{10} mode, in which the electric field is perpendicular to the broad side of the waveguide, the electric component of the wave is introduced gradually into the liquid and reflections are minimised. The optimum angle differs for each waveband and can be calculated from theory. Since the whole apparatus is inclined at $\sim 15^{\circ}$ the shape of the liquid within the cell is a parallelogram, or if the containing window is inclined in the other direction, as in the X band cell, a trapezium. In either case reflections are minimised at both the entry and exit of the microwave from the medium.

Attention has to be paid to the thickness of the mica windows since, if the windows are too thin, bowing is apt to occur and cause reflections. The optimum thickness was thought to be 0.0015 cm for O, Q and K bands and 0.0025 cm for P and X bands.

(c) Filling.- Different methods of filling are used at different bands. At O, Q and K bands the liquid is measured into the cell from a 0.5 ml capacity 'Agla' micrometer syringe, calibrated in steps of 0.0002 ml. The filler tube (B) is used at Q and K bands but cannot be used at O because the volume of the filler tube is comparable with the volume of the same length of waveguide; an error would therefore arise since all of the added liquid would not be increasing the sample length in the waveguide. To overcome this difficulty the O-band cell is inverted and (B) used only for draining the cell after a run, while during the run it is securely soldered. Filling can then be affected through a hole near (E) but on the opposite wall of the waveguide and entering the cell diagonally by passing through the flange (A). The 'Agla' needle is pushed into the hole and penetrates deep into the cell so that little or no drainage within the cell is required. The hole (E) is absent at O band.

50 ml grade A burettes are used to fill P and X bands. Entry into the cell is made at (B) for P band but not for X band owing to the greater quantity of liquid required for the latter. At X band a small funnel is soldered on to the cell at (E) and the liquid run into the cell through the funnel. This method, at the higher frequencies, is inferior to the use of the filler tube because droplets of fluid adhere to the cell walls, affecting attenuation and especially phase readings, but the large volume of liquid used at X band renders this inaccuracy negligible.

The dimensions of the cell, in fact set the limits of frequency within which a waveguide bridge is applicable. Above about 70 Gc/s the volume of liquid inserted into the cell is inconveniently small while below about 7 Gc/s it is formidably large.

(d) Temperature Control.- The burettes used at P and X bands are water jacketted as are the 'Agla' syringes. For O, Q and K bands the liquids are preheated in a jacketted stoppered tube, the stopper only being removed when refilling the syringe. The jackets are all supplied with water pumped from thermostat baths controlled to ± 0.01 °C.

Experimental.

(a) Preparation of Solutions.- The solutions were made up in flasks which had been cleaned with a strong detergent, washed several times with distilled water then absolute alcohol, dried in an oven at 120°C especially kept for the purpose and finally cooled in a desiccator. The flasks were fitted with ground glass stoppers which could be held firmly in position with springs when the solution was not in use and solutions and solutes not in use were kept in a desiccator. Runs were carried out as quickly as possible, with the higher frequency runs first, since the dielectric absorption of water is strongest at these frequencies and so there is less risk of absorbed water affecting the results.

(b) Procedure.- Before any measurements were taken the klystron was allowed to stabilise for at least an hour and then the frequency was checked and adjusted if necessary. Sufficient solution was added to the dielectric cell to cover the mica window. The rotary variable attenuator (I) was altered until the power output indicated by the galvanometer (M) was minimised. The phase shifter (J) was then altered until a new, lower, minimum was found. The attenuator and phase shifter were altered alternately until the balance point was found. At this point any movement of the phase or attenuation resulted in a greater galvanometer deflection. The readings of attenuation and phase shift were noted.

Enough liquid was added to the cell to cause a phase shift of approximately 360° and the new balance point found. This was repeated, usually about eight or ten times or until sensitivity was lacking, the readings of liquid volume increment, attenuation and phase being noted each time. Finally the frequency was rechecked. The purpose of the 360° phase shift was to reduce variation of attenuation due to the phase shifter setting. By keeping the setting virtually the same for each reading, phase shifter attenuation was eliminated since it remains constant.

After each run the cell was washed out with a suitable solvent, then cyclohexane and finally blown dry using a reciprocating air pump. For a successful run, plots of attenuation and phase reading against the volume of added liquid are linear.

Additional Measurements.

(a) Static Dielectric Constant.- The dielectric constant was also measured at 1 or 2 Mc/s. Some measurements were carried out on a heterodyne beat apparatus based on a circuit described in Physical Methods of Organic Chemistry (9), but employing a cathode ray oscilloscope to detect the balance point. The fixed oscillator was a quartz crystal which resonated at 1 Mc/s. Balance was achieved by using a Sullivan precision air condenser.

Later measurements were made using a 'Dipolmeter', type DM 01 manufactured by Wissenshaftlich-Technique Werkstatten and operating at 2 Mc/s. The instrument is thermostated for maximum stability. Dielectric cells used in conjunction with both instruments are of robust metal construction and gold plated inside. The cells are jacketted and supplied with water from a thermostat both maintained to 0.01°C.

The instruments were calibrated with purified cyclohexane and p-xylene of dielectric constants 2.015 and 2.262 at 25°C respectively and the sample dielectric constant was found by extrapolation.

(b) Other Measurements.- Refractive indices were measured with a Pulfrich refractometer capable of an accuracy of $\pm$ 0.00001. The prism was temperature controlled. Densities were measured using a pyknometer and viscosities were measured using an Ubbelohde viscometer, calibrated with the solvent used to make up the solutions. A spirit level was used to ensure that the viscometer was vertical. Temperature control was maintained to $\pm$ 0.01°C.

Purification of materials.

Because water absorbs strongly at microwave frequencies and is omnipresent, its removal is of paramount importance and so drying is the major step in most of the purifications.

Solvents.- Cyclohexane, p-xylene, dioxan and n-heptane were dried over sodium then distilled from sodium through a 20 plate column. A middle fraction was retained and stored in dark, well stoppered bottles over sodium. Carbon tetrachloride was treated in a similar fashion with the exception that phosphorus pentoxide was substituted for sodium as the drying agent. Gas chromatograms of the solvents were periodically taken to check on impurities. All were "G.C. pure" except for carbon tetrachloride which sometimes had traces of impurities but insufficient to give any detectable dielectric loss.

Solutes.- 2,4-Dinitrophenol and 2,6-dinitrophenol were supplied, stabilised with 20% water which was removed by refluxing in a Dean and Stark apparatus for three hours with benzene as the solvent. The water was run off at intervals until none remained. The nitrophenol was precipitated with petroleum spirit (b.p 60° - 80°C) and recrystallised from a p-xylene / 60-80 petroleum spirit mixture. o-Nitrophenol and p-nitrophenol were recrystallised from p-xylene. 8-Hydroxyquinoline was recrystallised from 60-80 petroleum spirit. 2,4,6-Trichlorophenol and 2,4,6-tribromophenol were recrystallised from a mixture of p-xylene and 60-80 petroleum spirit. 2,4-Dichlorophenol was recrystallised from n-heptane. Chloroform was passed through an alumina column, distilled through a spinning band column with a small reflux ratio (1 : 50) and stored over phosphorus pentoxide. Acetone was dried with anhydrous calcium sulphate, distilled through a spinning band column and stored over anhydrous~~e~~ calcium sulphate. Ether was dried over sodium, distilled and stored over sodium. Triethylamine was dried over caustic soda and distilled. p-Chlorophenol and p-cresol were also distilled through a spinning band column although they are solids at room temperature. The purified materials were metastable as liquids at room temperature until seeded with a small crystal.

Solids not mentioned specifically above were used unpurified other than by drying in a phosphorus pentoxide. dry vacuum desiccator for several days. Other liquids were dried as were the solids and distilled from the spinning band column. In each case purity was checked by gas chromatography or infrared spectroscopy as well as melting or boiling point.

CHAPTER II

INTERPRETATION OF DATA AND ASSESSMENT OF THE METHOD

Introduction.

In order to evaluate the microscopic behaviour of molecules from dielectric data it is necessary to analyse the data into parameters characteristic of the decay of polarisation of the material and relate these to model systems devised to simulate the behaviour of the individual molecules. A model, successful in many cases is that of Debye (10) in which one relaxation time characterises the system (11). In other systems the decay of polarisation may be described by a distribution of relaxation times about a most probable value (mode) (12). Two parameters are needed, the mode and a quantity representing the spread of relaxation times. Interest has been directed at systems involving two discrete relaxation mechanisms of the Debye type. Budo has given the theory of such systems (13), three parameters being required. A number of methods for obtaining these parameters have been used (14-16) but have not been critically appraised. In this chapter, the method of obtaining relaxation parameters using a computer is described, the limitations and sources of error are considered and the accuracy of the determined parameters are estimated (17).

Calculation of Results.

The attenuation coefficient (α) and the phase constant (β) are obtained from the slopes of attenuation reading and phase reading respectively, against length of added liquid. If the measured attenuation is α' decibels and the length of liquid is ℓ cm then the slope of the attenuation graph is $\Delta\alpha'/\Delta\ell$ where Δ signifies a difference, and the attenuation coefficient is given by:

$$\alpha = \frac{1}{8.634} \cdot \frac{\Delta\alpha'}{\Delta\ell} \text{ nepers cm}^{-1} \quad \ldots\ldots\ldots(9)$$

similarly if the measured phase value is β' degrees then the slope of the phase graph is $\Delta\beta'/\Delta\ell$ and the phase constant is given by:

$$\beta = \frac{1}{57.29} \cdot \frac{\Delta\beta'}{\Delta\ell} + \frac{2\pi}{\lambda g} \text{ radians cm}^{-1} \ldots(10)$$

Here λg is the wavelength of the radiation in the wave-guide, the term $2\pi/\lambda g$ being necessary to allow for the phase shift incurred by a wave travelling in air. Since $\Delta\ell$ is found from the volume of liquid added and the cross sectional area of the waveguide both of which differ for different frequencies, it is convenient to measure the slopes of attenuation reading and phase reading against volume of liquid added and multiply these slopes by factors which take into account the waveguide dimensions as well as the numerical factors in equations (9) and (10).

In the case of phase shift the term $2\pi/\lambda g$ also changes with frequency. The general equations for α and β, therefore, become equations (11) and (12) where ΔV is the volume increment in mls.

$$\alpha = a_1 \frac{\Delta\alpha'}{\Delta V} \quad \ldots\ldots\ldots\ldots(11)$$

$$\beta = a_2 \frac{\Delta\beta'}{\Delta V} + a_3 \quad \ldots\ldots\ldots\ldots(12)$$

The values of a_1, a_2 and a_3 are listed in Table (2).

Table (2) Values of the constants in the attenuation and phase shift equations (11) and (12) for the different frequencies.

Waveband	Frequency (Gc/s)	a_1	a_2	a_3
O	70.00	0.0055332	0.00083872	10.6077
Q	34.86	0.029123	0.0044144	5.8205
K	23.98	0.053040	0.008040	4.0752
P	16.20	0.14374	0.021784	2.7537
X	9.313	0.26750	0.040548	1.3834

Having determined α and β, equations (7) and (8) are used to evaluate ϵ' and ϵ''. The terms $\lambda_o^2/4\pi^2$ and $\lambda_o^2/4a^2$ are constant at each frequency and so the equations can be simplified to the forms:

$$\epsilon'' = b_1 \alpha \beta \quad \ldots\ldots\ldots\ldots(13)$$

$$\epsilon' = b_2 (\beta^2 - \alpha^2) + b_3 \quad \ldots\ldots\ldots\ldots(14)$$

The factors b_1, b_2 and b_3 at each frequency are given in Table (3). The slopes $\Delta\alpha'/\Delta V$ and $\Delta\beta'/\Delta V$ are found by the method of least squares. The lines can be described by the equation:

$$y = mx + c \quad \ldots\ldots\ldots\ldots(15)$$

Where y is the attenuation reading or the phase shift reading, x is the volume reading, m is the required slope and c is the trivial constant depending upon the amount of solution put into the cell to cover the mica window. Assuming negligible error in x the slope is then given by:

$$m = \frac{\sum xy - \bar{y}\sum x}{\sum x^2 - \bar{x}\sum x} \qquad \ldots\ldots\ldots\ldots(16)$$

Here $\sum$ has its usual meaning of the sum over the N readings of the term which it precedes and $\bar{x}$ and $\bar{y}$ represent the mean values of x and y i.e.

$$\bar{x} = \frac{\sum x}{N} \qquad \bar{y} = \frac{\sum y}{N} \qquad \ldots\ldots\ldots\ldots(17)$$

The results were calculated using an Elliott 803 computer.

Table (3) Values of the constants in the dielectric constant and loss equations (13) and (14) for the different frequencies.

Waveband	Frequency (Gc/s)	b_1	b_2	b_3
O	70.00	0.009286	0.0046431	0.4770
Q	34.86	0.03746	0.018729	0.3655
K	23.98	0.07914	0.039568	0.3413
P	16.20	0.1735	0.086726	0.3432
X	9.313	0.5252	0.26263	0.4958

Errors.

(a) Statistical Error.- When computing the root mean square slopes and ϵ' and ϵ'', the computer also calculates the standard deviations (s_m) of the slopes. The 95% confidence limits are then computed from s_m and these are treated as the statistical errors in the slopes and hence $\Delta\epsilon'$ and $\Delta\epsilon''$ can be computed. according to the theory of transmission of errors. $\Delta\epsilon'$ and $\Delta\epsilon''$ represent the errors in ϵ' and ϵ'' respectively. The values obtained are expected themselves to vary, especially since the number of points on the graphs is only small. Mean values obtained from about 80 separate runs on dilute solutions are given in Table 4.

Table (4) Errors in ϵ' and ϵ'' due to random variations in the phase shift and attenuation graphs, from 80 runs on dilute solutions.

Waveband	Error in ϵ'	Error in ϵ''
O	0.0015	0.0017
Q	0.0011	0.0015
K	0.0012	0.0014
P	0.0017	0.0024
X	0.0015	0.0017

(b) Error in λ_o.- Precautions to ensure accuracy of frequency measurement have been mentioned (Chapter I) but accuracy is limited by the tolerance (better than 0.1%) on the wavemeters. The resulting errors are also random. Small deviations in λ_o affect λ_g and β via the quantity a_3 in equation (12) and also ϵ' via the term $\lambda_o^2/(2a)^2$. From the theory of propagation of errors, making approximations applicable for dilute solutions, the following expressions are obtained.

$$\frac{\Delta\epsilon'}{\epsilon'} = 2.5\,\frac{\Delta\lambda_o}{\lambda_o} \qquad \text{............(18)}$$

$$\frac{\Delta\epsilon''}{\epsilon''} = 2.3\,\frac{\Delta\lambda_o}{\lambda_o} \qquad \text{............(19)}$$

Values of $\Delta\epsilon'$ and $\Delta\epsilon''$ arising from $\Delta\lambda_o$ are shown in Table (5) for $\epsilon' = 2.4$ and $\epsilon'' = 0.06$.

(c) Errors in 'a'.- The maker's tolerances in the dimensions of the waveguides are ± 0.0008 ins. for O, Q and K bands and ± 0.001 ins. for P and X bands. The waveguide dimensions are very important since they affect the factors a_1, a_2 and a_3 in equations (11) and (12) and the factor b_3 in equation (14). The inaccuracy in 'a' is constant at each band since the waveguide dimensions are fixed so that the error in ϵ' and ϵ'' due to the waveguide tolerance is a systematic error. An estimate of the errors in ϵ' and ϵ'' from this source is given by:

$$\frac{\Delta\epsilon'}{\epsilon'} = 2.8\,\frac{\Delta a}{a} \qquad \ldots\ldots\ldots\ldots(20)$$

$$\frac{\Delta\epsilon''}{\epsilon''} = 3.4\,\frac{\Delta a}{a} \qquad \ldots\ldots\ldots\ldots(21)$$

values of $\Delta\epsilon'$ and $\Delta\epsilon''$ arising from Δa are shown in Table (5) for $\epsilon' = 2.4$ and $\epsilon'' = 0.06$.

Of course Table (5) gives extreme errors which will rarely occur in practice. From Tables (4) and (5) the most important error in ϵ'' is that due to the error in determining the slope of the attenuation plot. The error in ϵ' due to the wavemeter is probably of comparable magnitude to that due to the phase graph, the former being a limiting value, whereas the latter is a most likely value.

The systematic error, due to the waveguide dimensions, seems negligible in ϵ'' except at O band but may be very serious in ϵ' at higher frequencies. If such an error is found it is desirable to find its size in order to correct it empirically.

Table (5) Errors in ϵ' and ϵ'' due to the tolerance in frequency measurement and in the waveguide dimensions computed for typical dilute solution values of $\epsilon' = 2.4$ and $\epsilon'' = 0.06$.

Waveband	Maximum Errors due to the wavemeter.		Maximum Errors due to the waveguide.	
	$\Delta\epsilon'$	$\Delta\epsilon''$	$\Delta\epsilon'$	$\Delta\epsilon''$
O	0.006	0.00014	0.044	0.0013
Q	0.006	0.00014	0.019	0.0006
K	0.006	0.00014	0.013	0.0004
P	0.006	0.00014	0.011	0.0003
X	0.006	0.00014	0.007	0.0002

(d) Reproducibility.- So far we have considered those errors which can be treated quantitatively but other errors might also be present. Thus at Q, K and P bands the finite volume of the filler tube, at X band droplets adhering to the cell walls and for all the apparatus, but especially O band the possibility of minute air bubbles trapped within the liquid might lead to additional errors. The practical test of the apparatus, is the reproducibility and this was assessed in two ways: (i) cyclohexane ($\epsilon' = 2.015$) was measured five times independently on each apparatus; (ii) seven solutions of o-nitrophenol in cyclohexane at different concentrations were measured and the graphs of ϵ' and ϵ'' against concentration drawn.

(i) The runs on cyclohexane indicate the size of the errors in ϵ'. The results are shown in Table (6).

Table (6) Dielectric constant (literature value, 2.015) of cyclohexane from five independent runs at each frequency. O band was not in use when these tests were carried out, but see (ii) below.

Waveband	Range of ϵ'	Mean value	$\epsilon'_{(obs)} - \epsilon'_{(lit)}$
Q	1.9903 - 1.9984	1.9942	0.021
K	2.0045 - 2.0076	2.0057	0.009
P	2.0106 - 2.0234	2.0161	0.001
X	2.0143 - 2.0154	2.0146	0.000

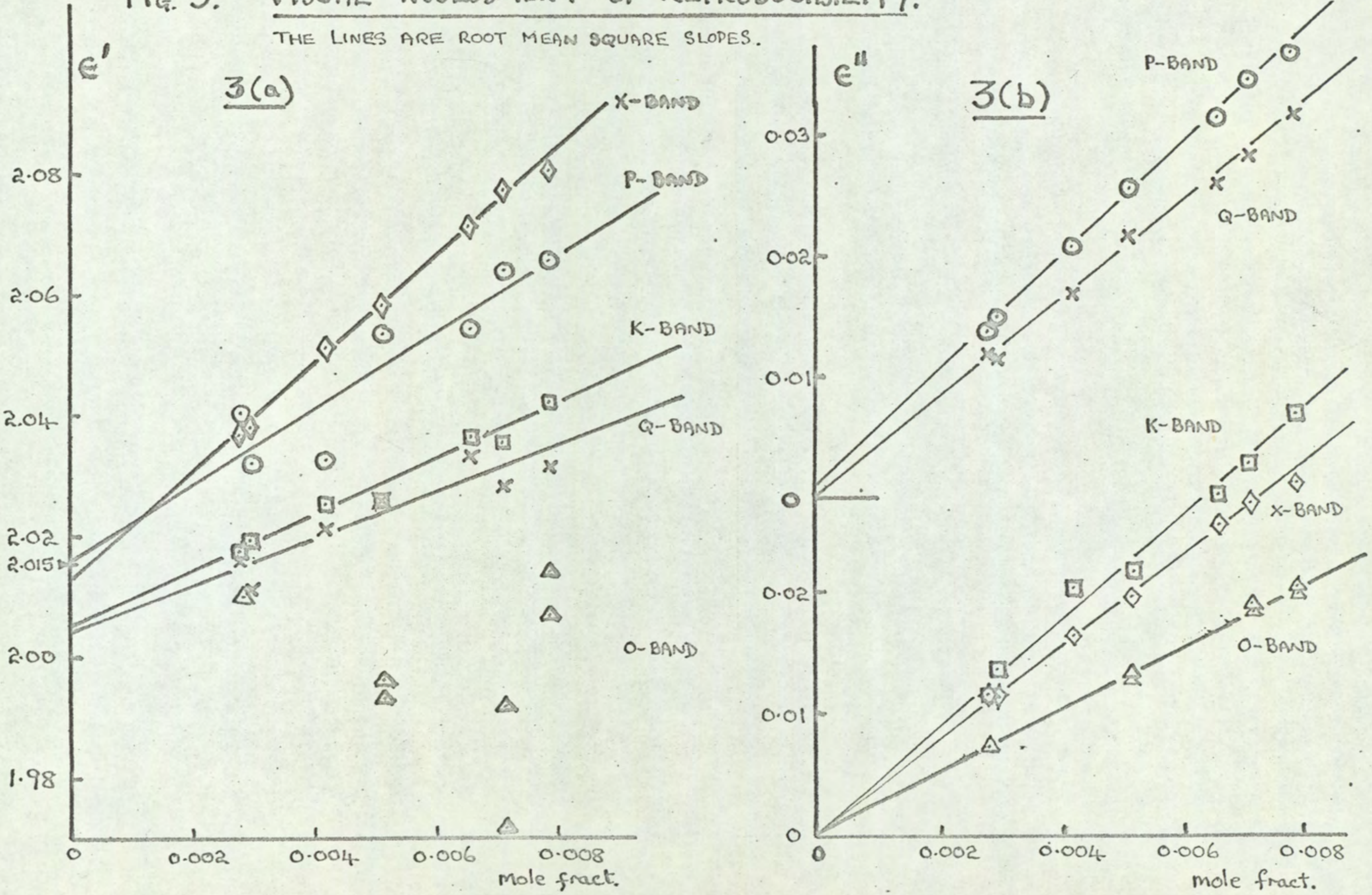
(ii) The graphs of ϵ' and ϵ'' against mole fraction of o-nitrophenol for the system o-nitrophenol cyclohexane are shown in Fig (3). Cyclohexane is chosen because, unlike p-xylene and dioxan, it has no loss of its own which might be confused with the systematic errors.

The ϵ'' values in Fig (3(b)) do not deviate by more than 0.002 from the least squares slope for any point at any band. This is in agreement with the value of ϵ'' calculated in the preceding sections.

As expected, reproducibility of ϵ' is not as good. From Table (6), X band seems to have only slight random error, the range of ϵ' being small, and little systematic error. The ϵ' graph in Fig (3(a)) confirms these conclusions.

FIG. 3. VISUAL ASSESSMENT OF REPRODUCIBILITY.

THE LINES ARE ROOT MEAN SQUARE SLOPES.



Both Table (6) and Fig. (3(a)) indicate a broader scatter in P band values of ϵ', deviations being up to 0.01, although systematic error again seems negligible. The apparatus at P band is of course slightly different from that at the other frequencies since directional couplers and flexible waveguide are used instead of magic 'T's.

Q and K bands show deviations in ϵ' smaller than 0.01 but more important are their low intercepts in Fig. (3(a)) (2.004 and 2.005 respectively) and the low values in Table (6). These confirm the presence of systematic errors.

From Fig (3(a)) it appears that O band has both a large systematic and a large random error. The systematic error has been accounted for, but the random error is greater than expected. One possible source of scatter is the presence of small bubbles trapped in the narrow waveguide. These might be expected to affect the phase shift in an uncertain manner, but not seriously alter the attenuation. Furthermore since ϵ' is proportional to β^2 and β is largest at O band the errors in β caused by the bubbles need only be quite small to cause the variability observed. At any rate ϵ' at O band seems of little diagnostic value for dilute solution work.

(e) Conclusions.- The empirical correction factors finally decided upon are 0.021 and 0.012 for Q and K bands respectively. These are probably somewhat high but ϵ' is, therefore, less likely to be misleading, for example by suggesting spurious distribution coefficients (see following sections) owing to an estimated ϵ_∞ which is low.

ϵ'' can be obtained to an accuracy of ± 0.002, or better, for most of the solutions used. ϵ' can be obtained to about ± 0.01 after correction for systematic errors although at X band the inaccuracy is probably less. Other methods seem to be less accurate; for example the errors quoted for a method extensively used by Smyth (18) and others over a number of years, are ± 2% in ϵ' and ± 5% in ϵ'' in the most favourable case. For dilute solutions ($\epsilon' = 2.4$, $\epsilon'' = 0.06$) these correspond to $\Delta\epsilon' = 0.048$ and $\Delta\epsilon'' = 0.003$.

Frequency Dependence of Dielectric Constant and Loss.

(a) The Debye Equations.- Debye (10) assumed that the decay of polarisation of a dielectric material was characterised by an exponential decay function and obtained simple expressions for the frequency dependence of the dielectric constant and loss:

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega\tau} \qquad \ldots\ldots\ldots\ldots(22)$$

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau^2} \qquad \ldots\ldots\ldots\ldots(23)$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \qquad \ldots\ldots\ldots\ldots(24)$$

where ϵ_0 is the dielectric constant at zero frequency or at frequencies very small compared with $1/2\pi\tau$, ϵ_∞ is the dielectric constant at frequencies much greater than $1/2\pi\tau$ but not so great as to encompass absorption due to atomic polarisation, τ is the relaxation time, which is characteristic of the rate of decay of polarisation, and ω is the angular frequency ($2\pi\nu$).

The relaxation time in these equations is that of the macroscopic material. The origin of dielectric relaxation lies in the rate of reorientation of molecular dipoles as the field alternates. The relaxation time for molecular dipoles is not necessarily that of the macroscopic material. Debye gives the relationship as:

$$\tau^* = \tau.\frac{(\epsilon_\infty + 2)}{(\epsilon_0 + 2)} \qquad \ldots\ldots\ldots\ldots(25)$$

where τ^* is the microscopic (molecular) relaxation time. However, since ϵ_0 and ϵ_∞ are almost equal for dilute solutions, τ and τ^* can be taken as the same.

At frequencies such that the dielectric constant is ϵ_∞ the molecular dipoles are unable to follow the alternations of the field whereas at low frequencies ($\nu \ll 1/2\pi\tau$) the dipoles respond immediately to variations in the field. At intermediate frequencies there is a time lag between the field and the response of the dipoles. For dilute solutions of small polar molecules the time lag occurs at microwave frequencies.

(b) Cole-Cole behaviour.- The Debye equations are obeyed by many systems but in many more, notably polymers, another theory is necessary. Cole and Cole (19) assumed a continuous distribution of relaxation times about a most probable value τ_0. The expressions obtained are:

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau_0)^{1-\alpha}} \qquad \ldots\ldots\ldots\ldots(26)$$

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)\left[1 + \omega\tau_0^{(1-\alpha)} \sin (1-\alpha)\pi/2\right]}{1 + 2\omega\tau_0^{(1-\alpha)} \sin (1-\alpha)\pi/2 + \omega\tau_0^{2\,(1-\alpha)}} \qquad \ldots(27)$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\, \omega\tau_0^{(1-\alpha)} \cos (1-\alpha)\pi/2}{1 + 2\omega\tau_0^{(1-\alpha)} \sin (1-\alpha)\pi/2 + \omega\tau_0^{2\,(1-\alpha)}} \qquad \ldots(28)$$

α is an empirical constant which measures the width of the distribution of relaxation times. When $\alpha = 0$ the Debye equations are obtained.

(c) Multiple discrete relaxation times.- Budo (13) has shown that the dielectric constant and loss can be obtained as the sum of Debye terms when the decay of polarisation is characterised by n independent relaxation times:

$$\epsilon^* = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \sum_{k=1}^{n} \frac{C_k}{1 + i\omega\tau_k} \qquad \ldots\ldots\ldots\ldots(29)$$

$$\epsilon' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \sum_{k=1}^{n} \frac{C_k}{1 + \omega^2\tau_k^2} \qquad \ldots\ldots\ldots\ldots(30)$$

$$\epsilon'' = (\epsilon_o - \epsilon_\infty) \sum_{k=1}^{n} \frac{C_k \, \omega \tau_k}{1 + \omega^2 \tau_k^2} \quad \ldots\ldots\ldots\ldots\ldots (31)$$

τ_k is the relaxation time characteristic of the k th mode of relaxation and C_k is a factor representing the proportion by which the k th mode contributes to the total dispension:

$$\sum_{k=1}^{n} C_k = 1 \quad \ldots\ldots\ldots\ldots\ldots (32)$$

This thesis is concerned mainly with the case of $k = 2$ so that:

$$\epsilon' = \epsilon_\infty + (\epsilon_o - \epsilon_\infty)\left[\frac{C_1}{1 + \omega^2 \tau_1^2} + \frac{C_2}{1 + \omega^2 \tau_2^2}\right] \quad \ldots\ldots\ldots (33)$$

$$\epsilon'' = (\epsilon_o - \epsilon_\infty)\left[\frac{C_1 \, \omega \tau_1}{1 + \omega^2 \tau_1^2} + \frac{C_2 \, \omega \tau_2}{1 + \omega^2 \tau_2^2}\right] \quad \ldots\ldots\ldots (34)$$

$$C_1 + C_2 = 1 \quad \ldots\ldots\ldots\ldots (35)$$

(d) Representation of Data.- The frequency dependence of dielectric constant and loss can be shown as plots against log ω. A useful representation, however, has been given by Cole and Cole (19). The complex dielectric constant is plotted as an Argand diagram. According to the Debye theory this should be a semi-circle: elimination of $(\omega\tau)$ between equations (23) and (24) yields the equation of a circle of centre on the ϵ' axis at $(\epsilon_o + \epsilon_\infty)/2$ and radius $(\epsilon_o - \epsilon_\infty)/2$ but ϵ'' cannot be negative so the result is a semi-circle.

The value of the Cole-Cole plot is that deviations from Debye behaviour result in points lying within this semi-circle. For a Cole-Cole distribution the semi-circle has its centre below the ϵ' axis, the angle subtended by the centre at $(\epsilon_0, 0)$ being $\alpha\pi/2$ radians, where α is the Cole-Cole distribution parameter (see equations (26)-(28).

For two discrete relaxation mechanisms, the shape of the plot depends upon the parameters but can often be approximated by a sector of a circle, as for a Cole-Cole distribution.

Parameter Determination.

(a) Conventional Methods.- The object of measuring dielectric constant and loss at different frequencies is to obtain τ , τ_0 and α , or τ_1, τ_2, and C_1, according as to which theory is applicable. A number of methods are in common use. In most cases ϵ_∞ must be known.

(i) Debye Behaviour.- The Debye equations yield (11):

$$\epsilon' = \epsilon_0 - \tau(\epsilon''\omega) \quad \text{............(36)}$$

$$\epsilon' = \epsilon_\infty + \frac{1}{\tau}\left(\frac{\epsilon''}{\omega}\right) \quad \text{............(37)}$$

τ can be obtained from the slope of a plot of ϵ' against $\epsilon''\omega$ or ϵ''/ω. Equation (36) is the more useful because the additional point $(\epsilon_0, 0)$ is known, an important consideration in view of the scarcity of microwave data points, and ϵ_∞ is not required.

(ii) Cole-Cole distribution.- τ_0 may be calculated from (19):

$$\frac{v}{u} = (\omega\tau_0)^{1-\alpha} \qquad \text{.............(38)}$$

where v is the distance on the Cole-Cole plot from ϵ_0 to the experimental point and u is the distance from the point to ϵ_∞. v and u can, of course, be obtained by Pythagoras' Theorem. Taking logs:

$$\log (v/u) = (1 - \alpha) \log\omega + (1 - \alpha) \log \tau_0 \qquad \text{.........(39)}$$

so that a plot of log (v/u) against logω yields - log τ_0 as the intercept on the logω axis and $(1-\alpha)$ as the slope. Unfortunately log-log plots are insensitive to small variations so the method is not very accurate especially for α and when the measuring frequencies are not close to $(1/2\pi\tau_0)$.

If α is small, equation (36) is useful for estimating τ_0.

(iii) Two discrete relaxation times.- Simple linear relationships have not been obtained and therefore graphical methods have been devised (14,15). Such methods are inaccurate and tedious, however, and it is usually necessary to verify the determined parameters by trial and error. It is probably more convenient to use trial and error from the start but this is time consuming and prone to bias. It is quicker, more accurate and more objective to use a computer (17).

(b) Assignment of ϵ_∞.- The Budo equations (33)-(35) contain four unknown quantities; τ_1, τ_2, C_1 and ϵ_∞. There are insufficient microwave data to allow a direct data fit involving all the parameters so ϵ_∞ must either be assigned by some suitable approximation or be determined independently. The second alternative is the most desirable but necessitates accurate measurement of the refractive index in the infrared, a technically difficult process.

Approximations for ϵ_∞ can be found in several ways:

(i) If it is assumed that the data can be represented by a Cole-Cole arc plot the best semi-circle can be fitted and ϵ_∞ found by extrapolation to the high frequency region. The approximation is not great for systems with two relaxation times fairly close together or in which one mechanism has a large weight factor. Practical verification of these statements is given in a subsequent section.

Error does arise if there is a frequency region of relaxation absorption much greater than the highest measuring frequencies. ϵ_∞ would then be too high.

(ii) For very dilute solutions ϵ_∞ can be identified with the solvent dielectric constant (ϵ_1). This method is equivalent to Higasi's approximate method of finding dipole moments. In microwave absorption work it is only useful for strongly polar solutes (dipole moment preferably greater than 3D) since only these molecules are sufficiently absorptive for measurement at the concentrations applicable (mf < 0.005). For less polar molecules at higher concentrations ϵ_1 can only serve as a guide.

(iii) The refractive index (n_D^2) of the solution can be found at the sodium D line and used as the lower limit of ϵ_∞. A better approximation is to use ($\epsilon_1 + n_D^2 - n_1^2$), where n_1 is the solvent refractive index, since this takes into account atomic and orientational polarisation of the solvent. It still neglects at least part of the atomic polarisation of the solute and so is likely to be low and lead to apparent non-Debye behaviour.

(iv) In a method related to method (iii) the dipole moment from the literature is compared with that obtained from the Debye equation for dilute solutions using the assigned ϵ_∞ value. If the microwave dipole moment does not agree with the accepted value, the discrepancy must be capable of explanation by a high atomic polarisation contribution caused, for example, by libration of a group, or the assigned ϵ_∞ must be reconsidered.

Method (i) has been preferred but the others, especially (ii) and (iv) have been used to aid the assignments whenever appropriate.

There are three practical means of finding ϵ_∞ by method (i); simple trial and error using compasses and graph paper; using a least squares criterion to compute the best fitting circle; using a least squares criterion to fit equations (27) and (28). The latter was eventually employed since ϵ_∞ is given as well as τ_0 and α.

(c) Computer Analysis.-

(i) Process Used.- An Elliot 803 computer was used to carry out the program which was written in Elliott Autocode. The minimisation process was an Elliott 803 Application Program, reference number L03. The program will minimise any well behaved, non-linear function of any number of independent variables each of which is restrained between upper and lower limits.

The user must provide a subroutine which, given a set of values X_1, X_2, --- X_n, will evaluate the function as the floating point variable A. The user must also provide initial estimates for the values of each variable at the minimum, an upper and lower limit for each variable and an initial step size (DI) for each variable. The function is evaluated at the given starting point, and with the first variable (X_1) augmented by the given step size (D_1). If the function has not decreased, the sign of D_1 is changed, X_1 augmented by the new D_1 and the function re-evaluated. Further steps are taken providing that the function continues to decrease. The step size is adjusted automatically at each value of X_1 by calculating the curvature of the function. When A no longer decreases, the current step size is divided by four and attention is turned to the second variable X_2.

The process is repeated for this and the other variables until each has shown improvement. The program then takes a series of composite steps during which all the variables are augmented before A is calculated. As soon as A ceases to decrease, the routine reverts to simple steps and resumes the iteration.

When two complete cycles through the variables, with step sizes divided by 4 each time fails to improve A, a minimum is indicated. The title MINIMUM REACHED is then printed followed by the best values of X_1, the current step sizes, the final function value and the number of evaluations of A performed during the program.

(ii) Function used:- The parameters were fitted to the data using a least squares criterion. The function A is accordingly given by:

$$A = \sum (\epsilon''_{obs} - \epsilon''_{calc}) + \sum \left(\frac{\epsilon'_{obs} - \epsilon'_{calc}}{4} \right)^2 \quad ....(40)$$

the sum being taken over the number of frequencies employed. The subscripts obs refers to the observed values and calc to the calculated values. The second term contains the scaling factor 1/4 which is chosen to reduce the errors in ϵ' to about the same magnitude as those in ϵ''. If the factor is less than 1/4 at P band it is greater at X band, but its exact value is not critical providing that it is sufficiently great to prevent the term in ϵ' from dominating the function value.

(iii) Cole-Cole.- ϵ'calc and ϵ''calc were obtained from equations (27) and (28). X_1 was τ_o, X_2 was α and X_3 was ϵ_∞. The data required were: the observed values of ϵ' and ϵ'', and the angular frequencies in radians per sec; guesses for τ_o, α and ϵ_∞; ϵ_o; ϵ_1; the lower bound for τ_o; the upper bound for τ_o. ϵ_1 is the lower bound for ϵ_∞ and ϵ_o the upper bound. α has bounds at 0 and 1 but is slightly constrained to assume a low value.

(iv) Budo.- ϵ'calc and ϵ''calc were obtained from equations (33)-(35). X_1 was τ_1, X_2 was τ_2 and X_3 was C_1. The data required were: ϵ'obs, ϵ''obs and the angular frequencies; guesses for τ_1, τ_2 and C_1; ϵ_o; ϵ_∞; the lower and upper bounds for τ_1 and τ_2. The lower and upper bounds for C_1 are set at 0 and 1 within the program.

In both programs the initial step size (DI) is computed as a fifth of the initial guesses for the variables (XI). Upon completion of the minimisation, the calculated values of ϵ' and ϵ'' are printed, for visual comparison with the observed values.

The time required depends upon the total number of function evaluations necessary but is normally about five minutes.

(d) Determination of Dipole Moment.- Knowing ϵ_∞, the dipole moment can be found using Debye's equation (10) for dilute solutions:

$$\mu^2 = \frac{9\,kT}{4\pi N} \; \frac{(\epsilon_0 - \epsilon_\infty)}{(\epsilon_1 + 2)^2} \; .c \qquad \ldots\ldots\ldots\ldots(41)$$

where k is Boltzmann's constant, N is Avogadro's number and c is the concentration in moles per litre. This can be written, since the solution is dilute:

$$\mu = 0.01281 \left[3T \; \frac{(\epsilon_0 - \epsilon_\infty)}{(\epsilon_1 + 2)^2 d_1} \; . \; \frac{M_1}{f_2} \right]^{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots(42)$$

where f_2 is the mole fraction of the solute and M_1 is the molecular weight of the solvent.

The most serious error in μ arises from the uncertainty about ϵ_∞. The error in ϵ_∞ generally would be less than that in ϵ' at Q and K bands and so should be no greater than about 0.01. The percentage error in μ is then:

$$\frac{\Delta\mu}{\mu} = \frac{0.5}{(\epsilon_0 - \epsilon_\infty)} \qquad \ldots\ldots\ldots\ldots(43)$$

thus, for a dispersion of 0.5 the error in μ would be 1%. Smaller values of the dispersion will lead to greater errors. In the following chapters dipole moments will, therefore, be quoted to three significant figures, the third of which usually has statistical significance.

Tests on Synthetic Data.

(a) Validity of the Cole-Cole Approximation.- It has been mentioned in the section on computer analysis that, in certain cases of Budo behaviour, the Cole-Cole plot is closely approximated by a Cole-Cole distribution of relaxation times. Since the determination of ϵ_∞ depends upon this assumption it perhaps deserves some justification. To do this the dielectric constant and loss were calculated at the five practical frequencies for systems with various relaxation times and C_1 values, and with an ϵ_∞ of 2.200 and an ϵ_0 of 2.350. The data were rounded off to the same number of figures as are significant in real measurements and then used in the Cole-Cole program to determine ϵ_∞.

The results are given in full in Appendix (I). It is found that ϵ_∞ is lower than the correct value if α is greater than zero; but that α can be fairly large and the ϵ_∞ value not be depressed, within the significance of three decimal places, so that no direct relationship between α and the depression of ϵ_∞ can be formulated. There does, however, seem to be a linear relationship between the maximum possible depression of ϵ_∞ and α. Hence:

$$\epsilon_\infty \geqslant \epsilon_\infty(\text{Cole-Cole}) \qquad \ldots\ldots.(44)$$

$$\epsilon_\infty \leqslant \epsilon_\infty(\text{Cole-Cole}) + 0.042\alpha(\epsilon_0 - \epsilon_\infty(\text{Cole-Cole}))$$

ϵ_∞(Cole-Cole) is the value given by the Cole-Cole approximation and α is measured in units of $\pi/2$ radians. It is therefore justifiable to use in the analysis, values of ϵ_∞ within the quoted limits. For most dilute solution work α is less than 0.08 so the difference is probably within the experimental error in determining ϵ_∞, but the apparent depression of ϵ_∞ does become a significant factor in systems involving specific interactions. It must be remembered that this relationship is only true within the limitations imposed by the assumptions, the frequencies used and the method of data fitting; its absolute value is dubitable.

(b) Budo: effect of ϵ_∞ .-Data were composed for systems with $\tau_1 = 16 \times 10^{-12}$ sec, $\tau_2 = 4 \times 10^{-12}$ sec and C_1 of 0.2, 0.5 and 0.8. These were analysed by the Budo program using different ϵ_∞ values. The results are summarised in Table (7).

Table (7) Relaxation times and weight factors yielded by the Budo program for a synthetic system with $\tau_1 = 16 \times 10^{-12}$ sec, $\tau_2 = 4 \times 10^{-12}$ sec, the C_1 value indicated, $\epsilon_o = 2.35$ and true $\epsilon_\infty = 2.20$, for different initial estimates of ϵ_∞. Relaxation times are in picoseconds.

Estimated	$C_1 = 0.2$			$C_1 = 0.5$			$C_1 = 0.8$		
ϵ_∞	τ_1	τ_2	C_1	τ_1	τ_2	C_1	τ_1	τ_2	C_1
2.200	16.0	4.0	0.20	16.0	4.0	0.50	16.0	4.0	0.80
2.198	17.2	4.0	0.20	16.4	3.9	0.50	16.3	3.8	0.79
2.194	20.2	3.9	0.20	17.4	3.9	0.50	16.6	3.2	0.79

In Table (7) the following points are notable:

(i) With the correct estimate for ϵ_∞ the program yields the correct answers.

(ii) C_1 is fairly insensitive to ϵ_∞ variation.

(iii) The relaxation time which has the lowest weight factor is more sensitive to ϵ_∞ variation.

(iv) Decrease in the ϵ_∞ value leads to an increase in the longer and a decrease in the shorter relaxation time. Since the Cole-Cole approximation tends to underestimate ϵ_∞ this is relevant to the subsequent discussions. It is clear, however, that methods of analysis using approximations to ϵ_∞ which neglect atomic polarisation are likely to be extremely misleading.

To conclude this section: it seems that determination of ϵ_∞ by the Cole-Cole approximation is valid but tends to yield low ϵ_∞ values when α is finite; that a rough empirical correction can be made in such cases; that estimates of in error by amounts which could be experienced in practice lead to errors in τ_1 and τ_2 by about 20%; and, that the method employed although obviously not ideal, is superior to both arbitrary assignment of ϵ_∞ and methods of assigning ϵ_∞ which neglect all or some atomic polarisation.

Tests on Real Systems.

A rigorous test of the procedure is to choose two solutes, each of which is known to exhibit Debye behaviour in simple binary solutions with non polar solvents, make up ternary mixtures of these with non polar solvents, and analyse the resulting dielectric data. The three parameters τ_1, τ_2, and C_1 are known if the solutes do not interact and can be compared with values emerging from the analysis (17).

Table (8) Relaxation times (in picoseconds) at specified temperatures, dipole moments, mole fractions and weight factors calculated from equation (45) for the individual components of three ternary mixtures with cyclohexane as the inert diluent. The ratio of the relaxation times is also given.

System	Conc$^{\underline{n}}$ (mole f.)	μ(D)	τ_o (sec x 10^{-12})	Temp.	C_1	τ_1/τ_2
a) Chloroform +	0.0458	1.20	4.1*	25°C	0.30	2.8
Bromobenzene	0.0636	1.56	11.5 (20)	20°C	0.70	
b) Chlorobenzene +	0.0522	1.58	7.5 (20)	20°C	0.51	1.5
Bromobenzene	0.0557	1.56	11.5 (20)	20°C	0.49	
c) Thiophen +	0.4290	0.55	3.2*	25°C	0.47	5.5
1-Chloro-naphthalene	0.0506	1.51	17.6*	25°C	0.53	

*Measurements by the author at 5 microwave frequencies.

The solutions were made up in cyclohexane as the inert solvent. Details of expected parameter values appear in Table (8), dipole moment and relaxation times are ~~free~~ from the indicated sources and weight factors are calculated from equation (35) and the relationship:

$$\frac{C_1}{C_2} = \frac{f_1}{f_2} \cdot \frac{\mu_1^2}{\mu_2^2} \qquad \text{............(45)}$$

where f_1 and f_2 are mole fractions and μ_1 and μ_2 are dipole moments. In the final column is the ratio of the two relaxation times.

Results of the analysis are given in Table (9).

Analyses were performed for extreme values of ϵ_∞ yielded by the inequalities (44); the lower value is from the Cole-Cole approximation.

Table (9) Results of Budo analysis of the systems in Table (8). The Cole-Cole α is shown and the analysis performed for estimates of ϵ_∞ given by the Cole-Cole approximation and the maximum value permitted by the inequalities (44).

System	$\frac{\alpha}{\pi/2}$ (radians)	ϵ_∞	τ_1 (sec x 10^{-12})	τ_2 (sec x 10^{-12})	C_1
a)	0.07	2.065	11.8	4.9	0.63
		2.059	13.5	4.9	0.53
b)	0.01	2.066	11.9	7.5	0.50
c)	0.22	2.214	22.4	4.2	0.49
		2.188	12.2	0.3	0.40

(a) Chloroform and Bromobenzene.- The analysis with ϵ_∞ given by the Cole-Cole approximation is in fair agreement with expectation but a considerable improvement results when ϵ_∞ is corrected for the size of α. For this analysis τ_2 is correct to within 20%, C_1 to about 10% and τ_1 is virtually exact. The effect of changing the parameters is indicated in Fig. (4). Whereas the computed parameters give calculated ϵ' and ϵ'' values which are within the experimental errors of the observed values, variation of any of the parameters by ± 20% gives at least one value of ϵ' or ϵ'' outside the error limits.

(b) Chlorobenzene and Bromobenzene.- The α value is small so the Cole-Cole approximation for ϵ_∞ must be used. The parameters yielded by the analysis are in excellent agreement with those expected. This is the more remarkable when it is considered that the ratio of τ_1/τ_2 is only 1.5. C_1 especially is prone to error when τ_1/τ_2 approaches unity. This is made clear by arranging equation (34) to give:

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)\left[C_1 \left\{ \frac{\omega\tau_1}{1+\omega^2\tau_1^2} - \frac{\omega\tau_2}{1+\omega^2\tau_2^2} \right\} + \frac{\omega\tau_2}{1+\omega^2\tau_2^2} \right] \ldots (46)$$

When τ_1 and τ_2 are almost the same, the coefficient of C_1 is small and so careful interpretation of accurate data is required for C_1 to be correctly evaluated. The effect of parameter variation is shown in Fig. (5). Again variation of any of the parameters by ± 20% gives a poorer fit to the data.

(c) Thiophen and 1-Chloronaphthalene.- Both of these compounds do not undergo Debye behaviour in dilute solution. Accurate determination of ϵ' and ϵ'' at a large number of frequencies would, of course, permit analysis by more sophisticated models such as two Cole-Cole absorption regions. This has, in fact, been carried out in the literature (21) with too few data but since two more adjustable parameters are introduced such analyses cannot be justified. However, since it is not certain that the systems subsequently analysed in this work contain two Debye as opposed to other mechanisms, it is interesting to determine the effect on the analysis when this assumption is untrue; whence the analysis of this ternary mixture.

Measurements on a 50% mixture of thiophen with cyclohexane show that α is 0.05 and for a 12% solution of 1-chloronaphthalene in cyclohexane α is 0.06. The distribution coefficient for the mixture is very large (0.22) and the Cole-Cole ϵ_∞ yields a very poor analysis, but use of the upper limit for ϵ_∞ gives quite a creditable analysis. Fig. (6) shows the effect of parameter variation. The calculated dielectric constants and loss are very sensitive to a change of ± 20% in the parameters and some values even appear closer to an adjacent data point than to that for which they were calculated. The assumption of Debye behaviour therefore seems justified in these analyses.

Conclusions.

A detailed appraisal of the accuracy of the apparatus and methods of interpreting the data has been made. It is shown that despite the limitations in the number of frequencies available, the accuracy of the data and the technique of deriving the relaxation parameters, such parameters can be obtained to an accuracy of better than 20%.

In the following chapters this technique is used for the study of systems in many of which two relaxation mechanisms might be expected.

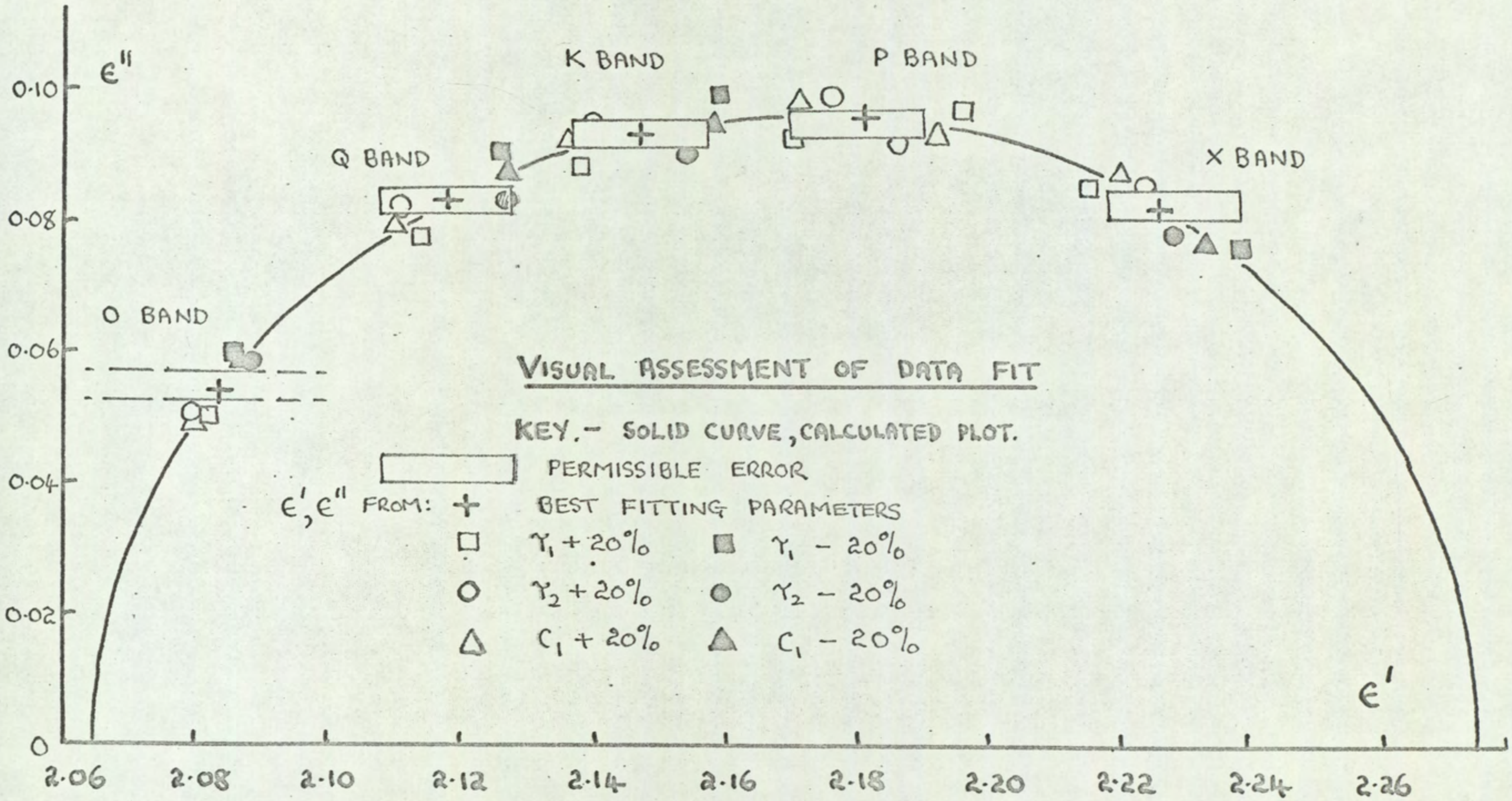


Fig 4. Cole-Cole plot for the system chloroform-bromobenzene-cyclohexane, illustrating the effect on the calculated dielectric constant and loss of variations in the parameters τ_1, τ_2 and C_1.

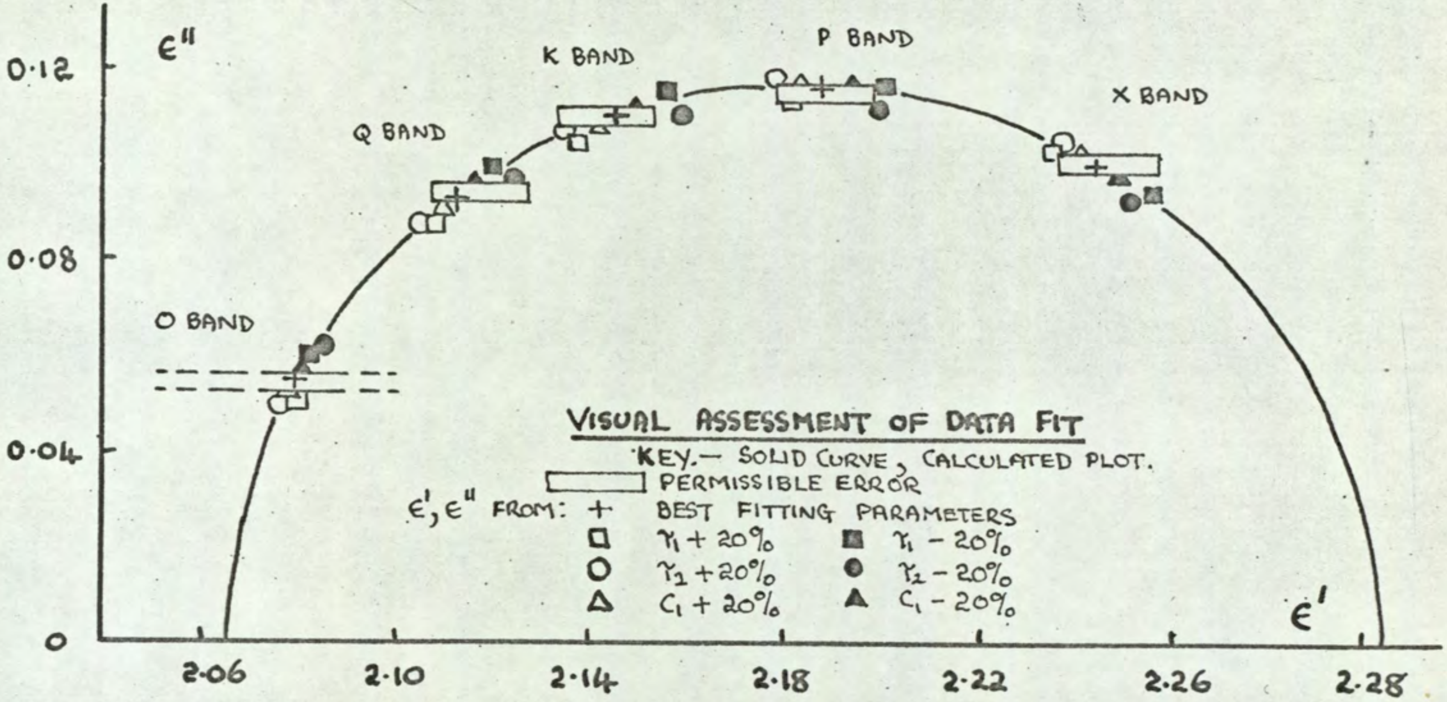


Fig 5. Cole-Cole plot for the system chlorobenzene-bromobenzene-cyclohexane, illustrating the effect on the calculated dielectric constant and loss of variations in the parameters τ_1, τ_2 and C_1 by ±20%.

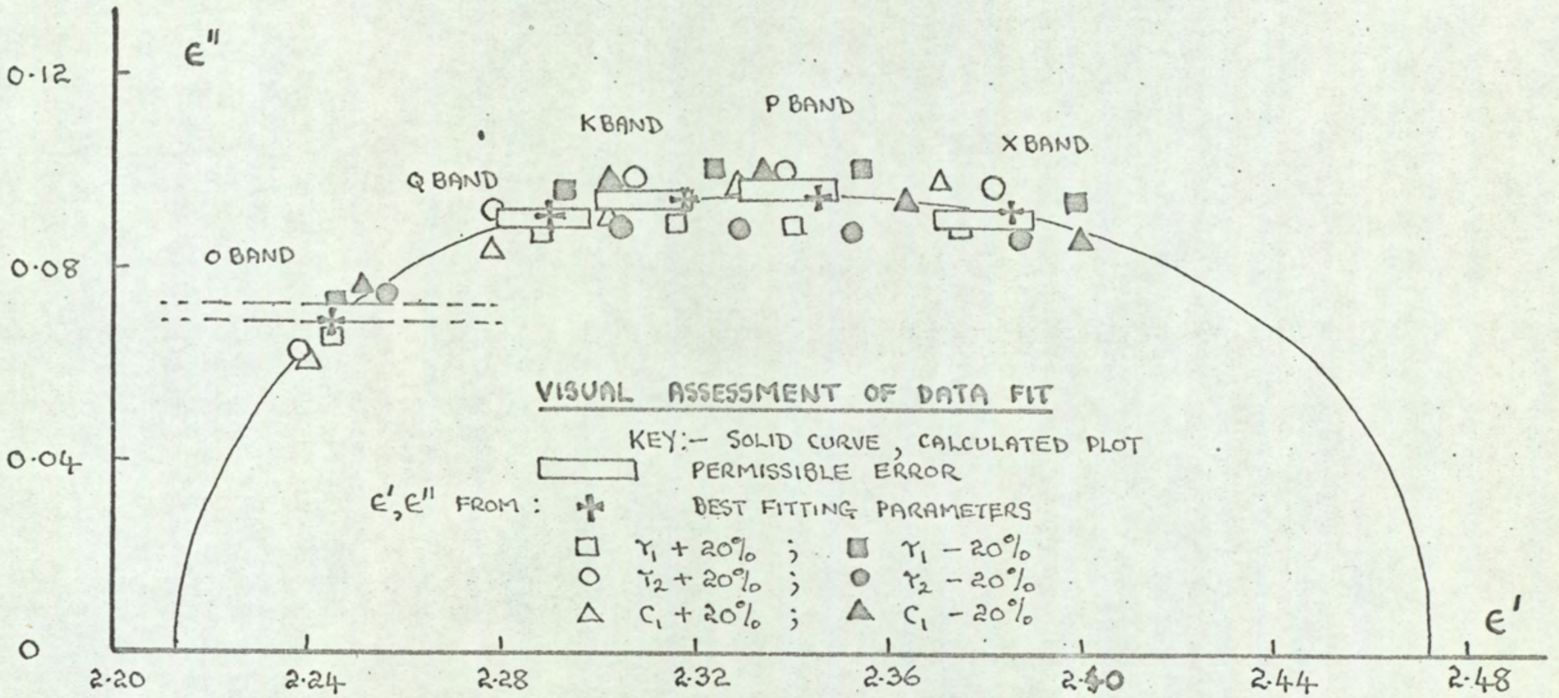


Fig 6. COLE-COLE PLOT FOR THE SYSTEM THIOPHEN - 1-CHLORONAPHTHALENE - CYCLOHEXANE, ILLUSTRATING THE EFFECT ON THE CALCULATED DIELECTRIC CONSTANT AND LOSS OF VARIATIONS IN THE PARAMETERS τ_1, τ_2 AND C_1.

CHAPTER III

INTERPRETATION OF WEIGHT FACTORS.

Introduction.

Interpretation of relaxation times from the analysis is normally fairly straightforward but the significance of weight factors seems often uncertain. In this chapter the meaning of C_1 and C_2 is reviewed to prevent repetition and to facilitate discussion in later chapters. In particular, the effect of solvent electron donor capacity upon the weight factors is investigated.

Budo Theory of C_1 and C_2.

The Debye equation for dilute solutions (equation 42) shows that:

$$\epsilon_0 - \epsilon_\infty = A \, \mathbf{A} f \mu^2 \qquad \text{............}(47)$$

where f is the mole fraction of the polar component of dipole moment μ and A is a constant for a given solvent and temperature:

$$A = \frac{4\pi N}{9kT} \; \frac{(\epsilon_1 + 2)^2 d_1}{M_1} \qquad \text{............}(48)$$

the symbols retaining their previous meaning. In the Debye loss equation (equation 24) the loss is given as:

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)\,\eta'' \qquad \text{............}(49)$$

where η'', a function only of relaxation time and of frequency, is the reduced dielectric loss. It therefore follows for Debye behaviour that:

$$\epsilon'' = A . f \mu^2 . \eta'' \qquad \text{............}(50)$$

For two simultaneous independent Debye mechanisms the loss, according to the Budo theory, is the sum of the individual losses:

$$\epsilon''_{\text{total}} = \epsilon''_1 + \epsilon''_2 \qquad \ldots\ldots\ldots\ldots(51)$$

$$= A.f_1\mu_1^2.\eta''_1 + A.f_2\mu_2^2.\eta''_2 \qquad \ldots\ldots\ldots\ldots(52)$$

subscripts refering to each relaxation mechanism. The dispersion in this case is given by:

$$(\epsilon_o - \epsilon_\infty) = A\ (f_1\mu_1^2 + f_2\mu_2^2) \qquad \ldots\ldots\ldots\ldots(53)$$

From equations (52) and (53) we therefore obtain:

$$\epsilon''_{\text{total}} = (\epsilon_o - \epsilon_\infty)\left[\frac{f_1\mu_1^2}{f_1\mu_1^2 + f_2\mu_2^2}\cdot\eta''_1 + \frac{f_2\mu_2^2}{f_1\mu_1^2 + f_2\mu_2^2}\cdot\eta''_2\right] \ldots(54)$$

Comparing this with equation (34) it is evident that:

$$C_1 = \frac{f_1\mu_1^2}{f_1\mu_1^2 + f_2\mu_2^2} \qquad C_2 = \frac{f_2\mu_2^2}{f_1\mu_1^2 + f_2\mu_2^2} \qquad \ldots\ldots\ldots\ldots(55)$$

$$\frac{C_1}{C_2} = \frac{f_1\mu_1^2}{f_2\mu_2^2} \qquad \ldots\ldots\ldots\ldots(56)$$

thus the Budo theory permits the calculation of C_1 and C_2 from a knowledge of the concentrations and dipole moments of the re-orienting species in a dilute solution.

These equations have already been used in Chapter II when testing the accuracy of the analysis. The good agreement between the analysed and calculated weight factors was produced there as evidence of the validity of the analysis, but conversely it helps to confirm the general truth of the equations, at least in the case of separate dipolar species in solution.

Weight Factors of Nonrigid Molecules.

Most of the compounds studied in this work are phenols and other hydroxylic compounds or related substances, and so the examples given in this section are confined to phenols although most of the principles involved can be extended to other molecules.

(a) Simple Nonrigid Molecules: Phenol.- By simple nonrigid molecules are meant mono-substituted benzene derivatives in which the moment of the substituent (X) does not lie along the Ph-X bond and in which X is free to rotate. Thus the simplest common substituents (X) are -OH, -CHO and $-COCH_3$.

Such molecules are regarded as simple because their dipole moment can be resolved into two components, one of which is perpendicular to the Ph-X bond and is free to rotate intramolecularly while the other is along the Ph-X bond and involves rotation of the whole molecule. Since the components are at right angles the two modes of re-orientation are effectively independent. The rotating species are the group and the molecule so the concentrations of each in equations (55) are equal. Hence:

$$C_1 = \frac{\mu_1^2}{\mu_1^2 + \mu_2^2} \qquad C_2 = \frac{\mu_2^2}{\mu_1^2 + \mu_2^2} \qquad \ldots\ldots\ldots\ldots (57)$$

where μ_1 is the component of the moment along the Ph-X bond and μ_2 is the moment perpendicular to the Ph-X bond.

There are two ways of determining μ_1 and μ_2; from bond moments and bond angles and from group moments and the angle of inclination of the group moment with the Ph-X bond. Use of aliphatic bond moments neglects mesomeric effects while use of group moments introduces an uncertainty with regard to the angle of inclination. When the factors influencing weight factors are well documented, accurate determinations of C_1 and C_2 will doubtless become a useful method for estimating the mesomeric moment and the angle of inclination of the group moment but in the meantime the reverse procedure is to be retained. Group moments seem preferable when calculating C_1 and C_2 since neglect of mesomeric moment is probably serious in aromatic molecules but many workers have favoured the use of bond moments.

The calculation of C_1 and C_2 for phenol is illustrated in Fig. (7). The OH group moment is taken to be 1.54D (22) acting at an angle of 76° (23) from the C-O bond and towards the ring. For bond moment calculations the bond moment values used were 1.5D for OH, 1.0D for C-O and 0.4D for C-H (23) the diagram showing the direction in which they act. The C-O-H angle was assumed to be 115°, the value quoted by Smyth (24), since the value 110° given by Smith (23) seems to give weight factors which differ still more from the group moment calculations. The calculations were repeated with C-H bond moment of zero. It should be noted that neglect of the mesomeric moment when using these bond moments leads to the overall moment being away from the ring whereas the group moment is inclined towards the ring. Evidence that the moment is, in fact towards the ring is supplied by the Hammett σ value, for the OH group, which is negative; groups known to have moments directed away from the ring, such as Cl, have positive σ values (25).

The weight factors, calculated from group moments, of 0.94 for C_2 and 0.06 for C_1 compare with 0.76 for C_2 and 0.24 for C_2 found from bond moments. Agreement is much improved if the C-H bond moment is assumed to be zero but since this is equivalent to admitting a mesomeric moment of 0.4D into the ring, this is not surprising. It is clear, however, that in the absence of extraneous effects such as self association, according to both calculations phenol should undergo relaxation predominantly by group re-orientation.

(b) Substituted Phenols.- The calculation of C_1 and C_2 is facilitated, in most compounds studied, by the substituents (X) having their moment lying along the Ph-X bond because there is then no ambiguity about the relative directions of the group moments.

(i) Para-substituents: p-chlorophenol.- The extra moment introduced by the p-substituent (Cl) lies along the PH-O bond and can be added vectorially to the component of the OH group moment along that bond. C_1 and C_2 follow as in the case of phenol. The calculation is illustrated in Fig. (8). No account is taken of the interaction moment. The bond and group moments used were those listed in (a) above, together with 1.58D as the group moment of C-Cl (23) and 1.5D as the bond moment of C-Cl (23). Group moments give a C_2 of 0.37 while bond moments give 0.59. C-H moments cancel so no ambiguity about their value arises.

(ii) Ortho and meta-substituents: o-chlorophenol.- In o- and m-substituted phenols the molecular component of the moment no longer lies along the axis of group rotation. The contributing moments are now resolved into three components: a molecular moment (μ_1) along the PH-O axis; another rigid moment (μ_3) at right angles to the PH-O axis, the rotating group moment (μ_2) at right angles to the PH-O axis.

The dipole moment corresponding to overall molecular rotation is now the resultant of the two rigid moments which meet at right angles in the benzene ring. C_1 and C_2 are accordingly given by:

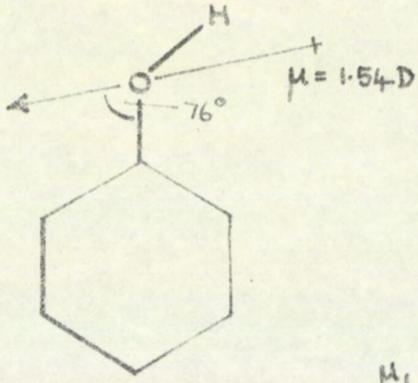
$$C_1 = \frac{\mu_1^2 + \mu_3^2}{\mu_1^2 + \mu_2^2 + \mu_3^2} \qquad C_2 = \frac{\mu_2^2}{\mu_1^2 + \mu_2^2 + \mu_3^2} \quad \ldots\ldots\ldots\ldots(58)$$

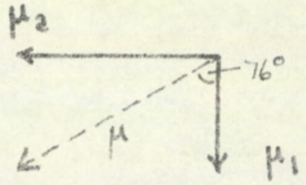
The calculation is illustrated in Fig. (9). No allowance is made for the effect of interaction moments, inductive effects or the presence of some trans form. Hence the denominator in the C_1 and C_2 equations (equations 58) does not generally agree with μ^2obs. The bond and group moments have been given in (a) and (b)(i) above. C_2 from group moments is 0.52 and agrees with the value from bond moments if the C-H moments are neglected but otherwise C_2 is rather different (0.37). Again, neglect of C-H moments is equivalent to assuming a mesomeric moment into the ring, so better agreement with the group moment calculation is expected.

(iii) Polysubstituted phenols.- One of the above procedures can be used depending upon whether the molecular moment lies along the PH-O axis. If so, treatment (i) can be used and if not, treatment (ii).

Effects of Solvent on Weight Factors.

Evidence for a solvent effect on weight factors is primarily based upon values of C_2 found by Fong and Smyth (26, 15) for p-phenylphenol, 1-naphthol and 2-naphthol in benzene solution at 20°C. The expected values should not be greatly different from C_2 calculated for phenol, shown above to be about 0.94, whereas observed values are 0.23, 0.26 and 0.28





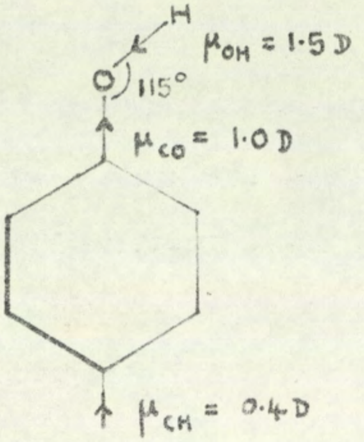
$$\mu_1 = \mu \cos 76$$

$$\mu_2 = \mu \sin 76$$

$$C_1 = \frac{\mu_1^2}{\mu_1^2 + \mu_2^2} = \cos^2 76 = 0{\cdot}06$$

$$C_2 = \frac{\mu_2^2}{\mu_1^2 + \mu_2^2} = \sin^2 76 = 0{\cdot}94$$

Fig 7 (a) CALCULATION OF WEIGHT FACTORS FOR PHENOL FROM GROUP MOMENTS.



$$\uparrow \mu_1 = 1{\cdot}0 + 0{\cdot}4 - 1{\cdot}5 \cos 65$$

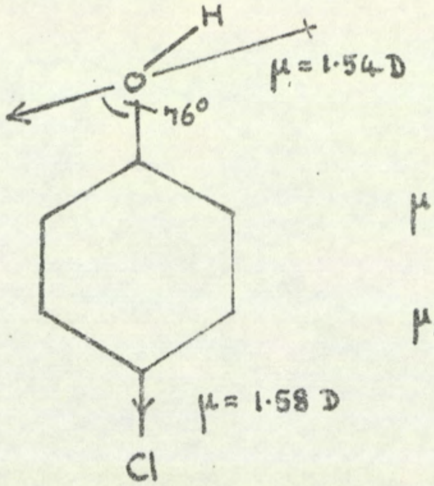
$$= 0{\cdot}76\,D \quad (0{\cdot}36\,D)^*$$

$$\leftarrow \mu_2 = 1{\cdot}5 \sin 65$$

$$= 1{\cdot}36\,D$$

$$C_1 = \frac{\mu_1^2}{\mu_1^2 + \mu_2^2} = \underset{(0{\cdot}05)^*}{0{\cdot}20} \qquad \therefore\ C_2 = \underset{(0{\cdot}95)^*}{0{\cdot}80}$$

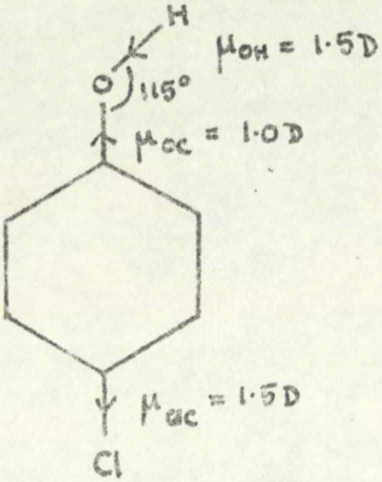
(b) CALCULATION OF WEIGHT FACTORS FOR PHENOL FROM BOND MOMENTS. VALUES DENOTED * ARE CALCULATED NEGLECTING C–H MOMENT.



$$\mu_1 = 1{\cdot}58 + 1{\cdot}54 \cos 76^\circ$$
$$= 1{\cdot}94\ \mathrm{D}$$
$$\mu_2 = 1{\cdot}54 \sin 76$$
$$= 1{\cdot}49\ \mathrm{D}$$

$$C_1 = \frac{\mu_1^2}{\mu_1^2 + \mu_2^2} = 0{\cdot}63 \quad \therefore\ C_2 = 0{\cdot}37$$

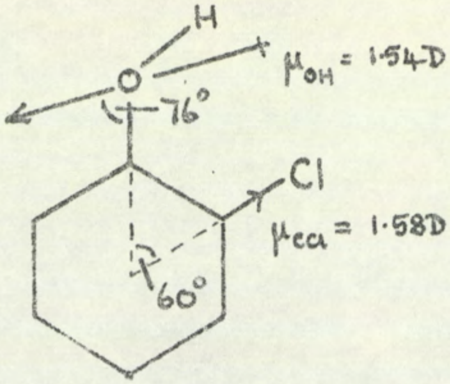
Fig 8 (a) CALCULATION OF WEIGHT FACTORS FOR p-CHLOROPHENOL FROM GROUP MOMENTS



$$\mu_1 = 1{\cdot}5 - 1{\cdot}0 + 1{\cdot}5 \cos 65$$
$$= 1{\cdot}14\ \mathrm{D}$$
$$\mu_2 = 1{\cdot}5 \sin 65$$
$$= 1{\cdot}36\ \mathrm{D}$$

$$C_1 = \frac{\mu_1^2}{\mu_1^2 + \mu_2^2} = 0{\cdot}41 \quad \therefore\ C_2 = 0{\cdot}59$$

(b) CALCULATION OF WEIGHT FACTORS FOR p-CHLOROPHENOL FROM BOND MOMENTS.



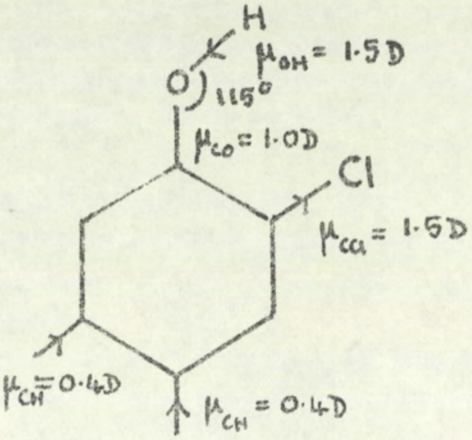
$$\uparrow \mu_1 = 1.58\cos 60 - 1.54\cos 76 = 0.42\,D \quad (\text{FIXED})$$

$$\leftarrow \mu_2 = 1.54\sin 76 = 1.49\,D \quad (\text{MOBILE})$$

$$\rightarrow \mu_3 = 1.58\sin 60^\circ = 1.37\,D \quad (\text{FIXED})$$

$$C_1 = \frac{\mu_1^2 + \mu_3^2}{\mu_1^2 + \mu_2^2 + \mu_3^2} = 0.48 \quad \therefore \quad C_2 = 0.52$$

Fig 9(a) CALCULATION OF WEIGHT FACTORS FOR O-CHLOROPHENOL FROM GROUP MOMENTS.



$$\uparrow \mu_1 = 1.5\cos 60 + 0.4\cos 60 + 0.4 - 1.5\cos 65 = 0.71\,D \quad (0.11\,D)^*$$

$$\leftarrow \mu_2 = 1.5\sin 65 = 1.36\,D \quad (\text{MOBILE})$$

$$\rightarrow \mu_3 = 1.5\sin 60 + 0.4\sin 60 = 1.65\,D \quad (1.30\,D)^*$$

$$C_1 = \frac{\mu_1^2 + \mu_3^2}{\mu_1^2 + \mu_2^2 + \mu_3^2} = 0.63\ (0.48)^* \quad \therefore C_2 = 0.37\ (0.52)^*$$

(b) CALCULATION OF WEIGHT FACTORS FOR O-CHLOROPHENOL FROM BOND MOMENTS. VALUES DENOTED * ARE CALCULATED NEGLECTING THE C-H MOMENTS.

respectively. Such large discrepancies cannot be attributed to experimental error or inaccuracy of the calculated weight factor. The weight factor C_2 for 2,6-dimethylphenol in benzene at 20°C (26), however, is not so seriously in disagreement with the calculated value of 1.0 while 2,4,6-tri-t-butylphenol in decalin at 20°C gives a C_2 value estimated from the relative heights of its two loss maxima of 0.89 (27) in good agreement with the expected value of 0.94. These results are interpreted (26) as showing in the first three molecules mentioned that C_2 is reduced by hydrogen bonding of the -OH to the π electrons of the solvent and that steric protection by the o-groups prevents this in 2,6-dimethylphenol and 2,4,6-tri-t-butylphenol.

The relaxation time of OH in 2,6-dimethylphenol (3.4×10^{-12} sec) is assumed in the subsequent discussion to be the typical value for phenolic OH groups because the observed C_2 value is close to the calculated value, showing perturbing effects to be minimal, and because the methyl groups in the 2 and 6 positions would not be expected to interfere with OH group re-orientation since even the much larger t-butyl group appears not to interfere noticeably in 2,4,6-tri-t-butylphenol.

In order to test the effect of the solvent on the weight factor of phenolic OH the dielectric properties of p-cresol were measured in different solvents at 25°C.

p-Cresol was chosen because the moment of the p-methyl group annuls the component of the OH coment along the Ph-O bond and so $C_1 = 0$ and $C_2 = 1$. The measured mean relaxation time τ_0, in the absence of solvent or other effects, should therefore be close to the typical OH group relaxation time. The observed mean relaxation time for p-cresol in p-xylene solution at 25°C is 16.9×10^{-12} sec which is considerably longer than the typical OH group relaxation time. A large contribution from overall molecular relaxation time is therefore expected. Computer analysis confirms this, $\tau_1 = 32 \times 10^{-12}$sec, $\tau_2 = 8.4 \times 10^{-12}$sec and $C_2 = 0.44$. In p-xylene solutions in which the OH group can interact with the solvent π electrons the C_2 value is apparently decreased and τ_2 is obviously longer than the normal OH relaxation time.

If the increase in C_1 (and τ_2) is due to a hydrogen bonding interaction with the π electrons of the solvent, then the increase would not be expected in carbon-tetrachloride or cyclohexane solutions. The mean relaxation time of p-cresol in carbon tetrachloride at 25°C was 14×10^{-12}sec at a mole fraction of 0.0265. Again this is longer than the anticipated value indicating a contribution from a longer relaxation time. Analysis yields $\tau_1 = 24 \times 10^{-12}$sec, $\tau_2 = 4.2 \times 10^{-12}$sec and $C_2 = 0.34$. τ_2 is close to the normal group relaxation time but C_2 is reduced from the theoretical value more than in p-xylene solution. The solution of p-cresol in cyclohexane was about three times stronger ($f_2 = 0.0638$) than the carbon tetrachloride solution and the mean relaxation time observed was 28×10^{-12} sec, while analysis gave $\tau_1 = 56 \times 10^{-12}$sec, $\tau_2 = 5.7 \times 10^{-12}$sec and $C_2 = 0.31$. C_2 has therefore decreased still further for this solution in the least electron donating solvent. The relaxation times are both longer than expected. The observed solvent effect on C_2 seems to be in opposition to that postulated by Fong and Smyth (26).

Probably the true explanation is given by the relaxation times which indicate self association. This is especially marked in the rather strong cyclohexane solution. Phenols are known from infrared evidence to self associate even in dilute solution and especially in weakly electron donating solvents and Mecke (28) finds that at a mole fraction of about 0.03 in carbon tetrachloride, phenol is about 50% associated. Yet this concentration represents virtually the lower limits of reliable loss measurements for small molecules with a dipole moment of about 1.5D. Furthermore, the relaxation parameters are highly sensitive to association as is illustrated by the mean relaxation time of phenol in p-xylene at 25°C which increases from 11.7×10^{-12}sec at a mole fraction of 0.0221 to 16.7×10^{-12} sec at a mole fraction of 0.0800. Clearly, therefore, the effects of self association cannot be eliminated from the relaxation parameters for phenols.

Naphthols are reported (20) to yield greater association constants than phenols so they are likely to be even more associated in dilute solutions. Fong and Smyth produce infrared evidence for 2-naphthol (15) from which they claim "that the amount of hydrogen bonding between the solute molecules is too small to alter the dielectric results by much more than the probable errors in the measurements." In the light of Mecke's results and the above discussion, however, self association is probably a significant factor.

Having arrived at this conclusion it should be pointed out that because of it the computer analyses given above are not strictly valid since more than two modes of relaxation are likely to be present in self associated systems. Thus although they serve to show association, the parameters obtained are not attributable to any particular species in solution but are probably composite values.

If self association is the cause of the reduction in C_2 then o-substituents would, of course, tend to prevent association because of their steric effect. This would explain the fair agreement between the observed and calculated C_2 values for 2,6-dimethylphenol and 2,4,6-tri-t-butylphenol in benzene and decalin respectively.

The agreement was further substantiated for a solution of 2,6-di-t-butylphenol in p-xylene, a better electron donor than benzene. Taking the moment of m-di-t-butylbenzene to be the same as that of t-butylbenzene (0.5D) (24) and the OH group moment and angle of inclination to the C-O bond to be 1.54D and 76° as before (22,23), the C_2 value of 2,6-di-t-butylphenol is calculated to be 0.74. The microwave measurements gave a mean relaxation time of 8.6×10^{-12} sec, which is very short for a molecule of this size, and a fairly large distribution coefficient of 0.14. This indicates a considerable contribution from a short group relaxation time and is confirmed by computer analysis which gave $\tau_1 = 37 \times 10^{-12}$ sec, $\tau_2 = 6.0 \times 10^{-12}$ sec and $C_2 = 0.69$. The group relaxation time is rather longer than expected but C_2 is in good agreement with the calculated value. These findings therefore confirm Fong and Smyth's conclusion (26) that C_2 is normal for phenols with hydrocarbon substituents in the 2 and 6 positions. Although phenols and naphthols cannot be shown to undergo a solvent effect because of self association it does not follow that the solvent effect is absent.

In a further attempt to detect the solvent effect, cholesterol was chosen for study because: (i) a mesomeric moment is not present to add additional complications in the calculation of C_2, (ii) the large bulk of the molecule seems likely to be sterically unfavourable to self association, (iii) The large bulk of the molecule results in the molecular and group relaxation times being sufficiently separated to enable their absorption peaks to be observed independently and thus enable weight factors to be found with greater accuracy.

The cholesterol was measured at a mole fraction of about 0.03 in solvents of differing electron donor capacity. Two series of solvents were employed.

Series 1. A. Carbon tetrachloride.
B. Cyclohexane + 3.8 mole % 1,4-dioxan.
C. p-Xylene.
D. p-Xylene + 3.6 mole % hexamethylbenzene.
E. Mesitylene.

Series 2. A. p-Xylene.
B. p-Xylene + 8.3 mole % 1,4-dioxan.
C. p-Xylene + 34.6 mole % 1,4-dioxan.
D. p-Xylene + 64.0 mole % 1,4-dioxan.
E. p-Xylene + 83.2 mole % 1,4-dioxan.

In Series 2 the solvent mixture electron donor capacity increases from A to E and this is probably true of Series 1. The solutions containing 1,4-dioxan were corrected for the loss of the dioxan before analysis. The results are summarised in Table (10). For the solvent mixtures dipole moments are approximate since they are calculated by taking the dielectric constant, density and molecular weight of the mixture to be linearly dependent on mole fraction.

Meakins has measured cholestenone in benzene (30) at 20°C obtaining a relaxation time of 233×10^{-12}sec. Cholestenone is virtually the same size and shape as cholesterol, so this value might be expected to be very similar to the overall molecular relaxation time of cholesterol, but the values of τ_1 in Table (10) are, in general, appreciably shorter, approximating to about 100×10^{-12}sec. A straightforward comparison of the relaxation times of cholesterol and cholestenone, however, is not valid since no consideration has been made of the direction of the dipole moment with respect to the main molecular axis. Mr. Cooke in this laboratory has made some measurements on steroids with rigid moments directed at various angles from the main molecular axes. These molecules are considerably prolate in shape and the inclination of the dipole moment from the long axis is critical in determining the overall molecular relaxation time observed. Cooke found that the relaxation time of cholestenone in p-xylene at 20°C was 217×10^{-12}sec and the angle between the dipole and the principal axis was $\sim 10^{\circ}$. For a similar molecule with a dipole angle of $\sim 50^{\circ}$ the relaxation time was only 83×10^{-12} sec while a molecule with a dipole angle of $\sim 70^{0}$ had a relaxation time of 54×10^{-12}sec. The angle of the non-rotating component of the OH dipole in cholesterol from the principal molecular axis is $\sim 50^{\circ}$. Cholesterol should accordingly be compared with Cooke's second compound and should have a relaxation time of the order of 10^{-10}sec just as, in fact is obtained from the analysis (Table (10)).

The group moment of OH attached to aliphatic hydrocarbon groups is about 1.7D and acts at an angle of 62° from the C-O bond (24). The observed moment found in p-xylene is 1.9D so C_2 is given approximately by:

$$C_2 = \frac{(1.7)^2}{(1.9)^2} \cdot \sin^2 62 \qquad \ldots\ldots\ldots\ldots(59)$$

yielding 0.62. Alternatively the aliphatic bond moments of 1.7D for C-O and 1.5D for H-O (23) acting along bonds inclined at 115° (24) may be used to calculate C_2 and also yield 0.62, illustrating the good agreement between the two methods when mesomeric factors are absent.

Table (10) Analysed relaxation parameters, concentrations and approximate dipole moments for cholesterol in different solvent mixtures.

Solvent	f_2 chol.	τ_2 (x 10^{-12}sec)	C_2	τ_1 (x 10^{-12}sec)	μ(D)
I.A	0.0332	3.9	0.24	198	1.7
I.B	0.0238	4.5	0.21	109	1.7
I.C	0.0399	4.8	0.33	93	1.9
I.D	0.0426	4.9	0.24	104	1.8
I.E	0.0547	8.4	0.23	120	1.7
2.A	0.0399	4.8	0.33	93	1.9
2.B	0.0365	5.8	0.26	100	1.9
2.C	0.0382	6.8	0.35	69	1.8
2.D	0.0282	11.5	0.51	98	1.8
2.E	0.0271	16.4	0.63	178	1.8

The analysed C_2 values in Table (10) are generally lower than this estimate, irrespective of the electron donor capacity of the solvent. In series 1, for example, the C_2 value in carbon tetrachloride is practically the same as that in mesitylene, while in series 2, far from decreasing with increasing dioxan concentration, the C_2 value also tends to increase. There must be another explanation of the low C_2 of cholesterol.

According to equation (56) this discrepancy can be due to one of two causes; (i) the effective concentration of rotating groups is lower than the concentration of molecules undergoing overall rotation, which implies self association, or (ii) the rotating component of the dipole moment is smaller than calculated, which requires that either the COH group moment is less than 1.7D (0.9D to 1.25D to account for observed values of C_2) or that the angle of inclination of the group moment from the C–O bond be much less than 62° (27° to 37°), or a combination of these. It seems unlikely that the COH group moment or angle are so much in error: so the possibility of self association must be considered. Infrared spectra were determined for solutions of cholesterol in carbon tetrachloride and p-xylene. At concentrations similar to those necessary for dielectric studies, two OH stretching bands appear for cholesterol solutions in carbon tetrachloride. A sharp band at 3635 cm^{-1} remains even at high dilution but a very broad band centred at about 3340 cm^{-1} disappears at high dilution. The broad band, therefore, seems to be due to a hydrogen bonded OH group and the large bulk of the cholesterol molecule by no means totally inhibits association. In p-xylene a band occurs at 3585 cm^{-1} and a broad band at about 3370 cm^{-1} which seems less intense than the broad band in carbon tetrachloride at similar concentrations. Again the broad band would be attributed to the cholesterol associated by hydrogen bonding. If the extinction coefficient of the hydrogen bonded OH group of cholesterol were substantially the same in the two solvents the apparent reduced intensity in p-xylene would suggest a lower degree of association in that solvent. Thus more free OH would be present in p-xylene and the weight factor C_2 should be higher than in carbon tetrachloride. This is, in fact, found (Table (10)). Self association of the solute therefore interferes with direct interpretation of the results in terms of solvent effects, just as was found for phenols.

Whatever the true cause of the reduction in C_2 it is clear that increasing solvent electron donor capacity is accompanied by a striking increase in the relaxation time τ_2. Such an increase is understandable in terms of hydrogen bonding with the solvent since the rotating group is effectively enlarged. An alternative, and possibly more realistic picture, is that OH group rotation involves breaking of the hydrogen bond followed by rotation as has been proposed by Garg and Smyth (31). The lengthening of the relaxation time is then associated with the increased free energy required to break the hydrogen bond. Comparison can therefore be made with the OH relaxation time of 2,6-dibromophenol (32) which also involves breakage of a hydrogen bond, of 12.7 x 10^{-12}sec at 20°C in benzene. In solution 2.E (17% p-xylene and 83% p-dioxan) at 25°C the OH relaxation time in cholesterol is 16.4 x 10^{-12}sec and in pure dioxan would, of course, be longer.

An apparent reduction in C_2 could easily arise when analyses are being performed manually, e.g. by the Bergmann (14) or double arc method (15). It is necessary to begin with some preconceived idea of the values of τ_1 and τ_2 and the resulting bias may not permit sufficient variation of τ_2 to obtain the best fit, which must then be obtained by changing C_2. This was tested for the cholesterol systems by fixing τ_2 at the p-xylene value of 4.8 x 10^{-12}sec and allowing τ_1, C_1 and ϵ_∞ to change until the best fit was found. For series 1A to E the C_2 values were 0.20, 0.21, 0.33, 0.24 and 0.18 while for series 2A to E they were 0.33, 0.25, 0.30, 0.26 and 0.23. For series 1 most of the values are virtually unchanged because 4.8 x 10^{-12}sec is near to the group relaxation times observed. The mesitylene solution however, has an increased group relaxation time (system 1E Table (10)) and the new C_2 has dropped from 0.23 to 0.18. The change is more marked in series 2. Whereas previously C_2 had tended to increase with greater dioxan concentration, the biased estimate of τ_2 leads to a decrease in C_2.

(d) Conclusions.- Although it has not been possible to show a simple relationship between solvent electron donor capacity and C_2, there does appear to be a correlation with τ_2. A bias towards a fixed τ_2 value in systems in which τ_2 is really varying, can lead to an apparent reduction in C_2 when the analysis is performed manually. Other cases of C_2 lowering might be caused by underestimating the effect of self association.

CHAPTER IV

GROUP ROTATION IN INTRAMOLECULARLY HYDROGEN BONDED PHENOLS AND RELATED COMPOUNDS.

Introduction.

Most physical evidence indicates that the hydroxyl group in intramolecularly hydrogen bonded o-substituted phenols, such as o-nitrophenol and o-hydroxyacetophenone, is in the cis position. Dipole moments (22), infrared (33, 34), N.M.R. (35) and chemical reactivities (36) have not been interpreted as giving evidence for the presence of trans species in those compounds in which the intramolecular hydrogen bond is strong or of medium strength. The dielectric absorption of certain intramolecularly hydrogen bonded phenols in the solid state has been measured at radiofrequencies (37); no relaxation was observed in o-nitrophenol but group rotation occurred in 2,6-disubstituted phenols. Nor is any conclusion drawn from radiofrequency studies regarding the possibility of hydroxyl group re-orientation in xylene solutions of o-nitrophenol (38). Studies on non-intramolecularly hydrogen bonded phenols in solutions at microwave frequencies (26) and at mainly radiofrequencies (27) show that phenolic group rotation leads to dielectric loss in the microwave region. However, little microwave work has been reported on intramolecularly hydrogen bonded phenols in solution.

A useful classification of intramolecularly hydrogen bonded phenols divides them into three categories; strong, medium and weak (39). In this chapter the microwave dielectric loss of some phenols from the different groups is considered with a view to gaining more information on group mobility in intramolecularly hydrogen bonded compounds.

Results.

The results are shown in Table (11). The letters A, B and C denote the group into which the substances have been classified on the strengths of their intramolecular hydrogen bonds. Some investigators have distinguished only two types of intramolecular hydrogen bond, broadly, strong and weak, but Flett (39) preferred a slightly more comprehensive classification into three groups which may be termed strong, medium and weak and correspond with groups A, B and C respectively in Table (11). The differences between these groups are brought out in Fig. (10), adapted from Reeves and Allan (48), where the shift of OH stretching frequency resulting from hydrogen bond formation is plotted against the displacement of the N.M.R. chemical shift caused by the intramolecular hydrogen bond. Separation into three groups is evident.

Assignment of Relaxation times.

Salicylaldehyde.- The observed relaxation time of 11.9 x 10^{-12}sec compares with a value obtained by Fischer (41) from radiofrequency measurements in carbon tetrachloride of 11.6 x 10^{-12}sec at 25°C. Comparison can also be made with quinoline, a rigid molecule of similar size and shape, and

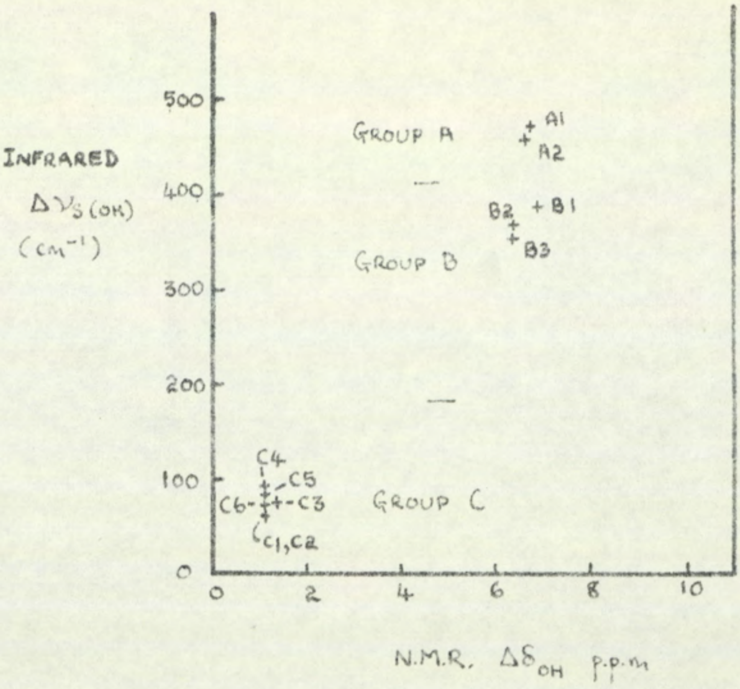


Fig 10. PLOT OF INFRARED OH STRETCHING FREQUENCY SHIFT RELATIVE TO PHENOL AGAINST N.M.R SHIFT OF THE OH CHEMICAL SHIFT ALSO RELATIVE TO PHENOL FOR SEVERAL INTRAMOLECULARLY HYDROGEN BONDED PHENOLS SHOWING THE SEPARATION INTO THREE GROUPS. SOLVENT CCl_4.

KEY TO COMPOUNDS.–

A1. SALICYLALDEHYDE
A2. 5-BROMOSALICYLALDEHYDE

B1. 2,4-DINITROPHENOL
B2. 2-NITROPHENOL
B3. 4-CHLORO-2-NITROPHENOL

C1. 2-CHLOROPHENOL
C2. 2,4-DICHLOROPHENOL
C3. 2,4,6-TRICHLOROPHENOL
C4. 2-BROMOPHENOL
C5. 2,4-DIBROMOPHENOL
C6. 2-METHOXYPHENOL (GUAIACOL)

having a relaxation time of 10.4×10^{-12} sec in p-xylene at 25°C (42). No distribution parameter (α) was obtained for salicylaldehyde, and its dipole moment compares well with the literature value of 2.91D (47); it is concluded that only a single relaxation time occurs - that of overall molecular rotation and the molecule behaves as if rigid. o-Hydroxyacetophenone.- The data is taken from ref (40) in which the authors find the molecule to be rigid. 8-Hydroxyquinoline.- The systems had distribution coefficients and were analysed into two relaxation times. The shorter one in each case is comparable with those obtained (26) for 2,6-dimethylphenol (3.4×10^{-12} sec), and p-phenylphenol (4×10^{-12} sec) and attributed to OH group relaxation. The longer relaxation time (14×10^{-12} sec) in cyclohexane at 25°C compares with the value for o-hydroxyacetophenone in cyclohexane at 20°C of 16.4×10^{-12} sec (40) and that of isoquinoline in cyclohexane at 20°C of 10.5×10^{-12} sec (**25**). Both are molecules of similar size and shape as 8-Hydroxyquinoline. The overall molecular relaxation time in carbon tetrachloride (21×10^{-12} sec) at 25°C is the same as that of isoquinoline in the same solvent at 20°C (44) and a little shorter than the relaxation time of 1-nitronaphthalene (44) in the same solvent and also at 20°C (25×10^{-12} sec). This is in agreement with the relative volumes of the two molecules. The analysed relaxation times of

Table (11) Relaxation time, distribution coefficients, weight factors and dipole moments for some intramolecularly hydrogen bonded phenols in the specified solvents at 25°C. A, B and C denote the hydrogen bond group (see text). cyc = cyclohexane, CTC = carbon tetrachloride, n-hept = n-heptane, benz = benzene and p-xyl = p-xylene. (a) Data of Antony and Smyth (40), (b) Analysed from data of Antony, Fong and Smyth (32), (c) Data of Antony, Fong and Smyth (32). Most values are the average of two or more separate determinations (see full results in the Appendix).

Compound	H-bond group	Solvent	α ($\pi/2$ units)	τ_0	τ_1 (sec x 10^{-12})	τ_2	C_1	μ(D)
Salicylaldehyde	A	p-xyl	0.0	11.9	-	-	-	2.8_8
o-Hydroxyacetophenone (a)	A	cyc	0.0	16.4	-	-	-	2.7_2
8-Hydroxyquinoline	B	cyc	0.04	11.4	14	4	0.81	2.6_1
"	B	CTC	0.05	18.1	21	3.5	0.88	2.6_7
"	B	p-xyl	0.02	14.6	15.3	3.6	0.95	2.5_0
o-Nitrophenol	B	n-hept	0.03	6.6	7.5	2.3	0.78	3.3_8
"	B	cyc	0.03	8.5	9.0	2.7	0.92	3.0_9
"	B	CTC	0.04	14.5	15.7	4.2	0.91	3.1_0
"	B	p-xyl	0.03	13.3	14.9	5.0	0.88	3.0_4
2,4-Dinitrophenol	B	p-xyl	0.12	32	48	15	0.65	2.8_6
2,6-Dinitrophenol	B	p-xyl	0.03	29	41	18	0.62	3.6_6
o-Chlorophenol	C	cyc	0.02	9.1	12	3.6	0.85	1.0_9
"	C	p-xyl	0.08	14.3	18	4.4	0.81	1.2_5
o-Bromophenol	C	p-xyl	0.16	17.6	22	4.8	0.77	1.3_7
2,4-Dichlorophenol	C	p-xyl	0.13	27.6	33	7.2	0.75	1.3_9
2,4-Dibromophenol (b)	C	benz	0.24	23	42	5.4	0.50	1.3_5
2,6-Dibromophenol (c)	C	benz	0.13	23	39	12.7	0.60	1.8_7
2,4,6-Trichlorophenol	C	cyc	0.02	17.2	30	16	0.21	1.0_0
"	C	p-xyl	0.06	22.6	45	15	0.32	1.4_1
2,4,6-Tribromophenol	C	p-xyl	0.13	34	80	15	0.30	1.7_8
Guaiacol	C	p-xyl	0.03	17.4	19	5	0.90	2.3_3
Catechol	C	p-xyl	0.02	15.3	18	6	0.89	-

8-hydroxyquinoline in p-xylene at $25^{\circ}C$ are closely parallelled by those of 1-naphthol in benzene at $20^{\circ}C$ (15×10^{-12} sec and 3.4×10^{-12}sec) (26). 1-Naphthol is very much like 8-hydroxyquinoline except for the intramolecular hydrogen bond in the latter; this seems to be strong evidence for the presence of group relaxation in 8-hydroxyquinoline.

o-Nitrophenol.- All the solutions have small distribution coefficients and analyse into two relaxation times. The shorter relaxation time varies with the solvent but values are close to those quoted (26) for OH relaxation in 2,6-dimethylphenol (3.4×10^{-12}sec), α-naphthol (3.4×10^{-12}sec) and p-phenylphenol (4×10^{-12}sec). The longer relaxation time in n-heptane at $25^{\circ}C$ (7.5×10^{-12}sec) is longer than the relaxation time (6.8×10^{-12}sec) of nitrobenzene (45) in the same solvent at $20^{\circ}C$ as is expected from the volumes of the molecules, and this is true also of the longer relaxation time of o-nitrophenol in cyclohexane at $25^{\circ}C$ (9×10^{-12}sec) since the value for nitrobenzene at $20^{\circ}C$ is 8.8×10^{-12}sec (44) in the same solvent. Whiffen gives 15.2×10^{-12}sec for the relaxation time of nitrobenzene in carbon tetrachloride (45) at $20^{\circ}C$ so that 15.7×10^{-12}sec for o-nitrophenol in that solvent at $25^{\circ}C$ seems reasonable for overall molecular relaxation. In p-xylene at $25^{\circ}C$ the analysed overall relaxation time of o-nitrophenol is 14.9×10^{-12}sec which again is longer than the value for nitrobenzene under the same conditions (13.1 x 10^{-12}sec). The longer relaxation time of o-nitrophenol therefore seems to be due to overall rotation while the shorter is OH group rotation.

2,4-Dinitrophenol.- The relaxation time of 2,4-dinitrophenetole in p-xylene at 25°C was found to be 45 x 10^{-12}sec and since in this molecule Courtaulds models show that the OC_2H_5 group is sterically prevented from rotating it should behave like a rigid molecule. This is confirmed by the absence of a distribution. The longer relaxation time of 2,4-dinitrophenol is expected to be similar to the single relaxation time found for its ether and in fact it was analysed as 48 x 10^{-12}sec in satisfactory agreement although the phenol is a somewhat smaller molecule. The assignment of this relaxation time to overall rotation is borne out by the apparently single relaxation time (32) of 2,6-dichloro-p-nitrophenol, a larger molecule than 2,4-dinitrophenol, of 69 x 10^{-12}sec in benzene at 20°C.

The shorter relaxation time (15 x 10^{-12}sec) of 2,4-dinitrophenol is considerably longer than the normal OH relaxation time but compares with 12.7 x 10^{-12}sec for OH relaxation in 2,6-dibromophenol at 20°C in benzene (32) and an estimate for OH relaxation in 2,4,6-trichlorophenol in xylene mixture at 20°C of 11 x 10^{-12}sec (38).

2,6-Dinitrophenol.- 18 x 10^{-12}sec for the shorter relaxation time in p-xylene at $25^{\circ}C$ is again longer than the normal OH relaxation time (3.4×10^{-12}sec) but compares with the values quoted in the preceding paragraph for OH relaxation in 2,4,6-trichlorophenol and 2,6-dibromophenol. The longer relaxation time of 39×10^{-12}sec is in excellent agreement with the molecular relaxation time of 2,6-dibromophenol (32) which is of closely similar shape.

o-Chlorophenol.- The short relaxation time in both cyclohexane and p-xylene is similar to the normal value (3.4×10^{-12}sec) for OH groups. The longer relaxation time in cyclohexane (12×10^{-12}sec) is rather longer than the relaxation time of o-dichlorophenol (9.5×10^{-12}sec) at $20^{\circ}C$ in cyclohexane (20). A similar effect is observed in p-xylene at $25^{\circ}C$ where the molecular relaxation time (18×10^{-12}sec) is longer than the corresponding value (14.9×10^{-12}sec) for o-nitrophenol, a similar molecule in size and shape, under the same conditions. An attempt to explain these differences is made in the discussion.

o-Bromophenol.- The shorter relaxation time compares with those obtained for o-nitrophenol and o-chlorophenol in p-xylene at $25^{\circ}C$ and attributed to group reorientation. The longer relaxation time is similar to the value for o-chlorophenol under similar conditions and is also rather longer than expected.

2,4-Dichlorophenol.- The smaller volume of the chlorine substituents should result in a shorter overall relaxation time for 2,4-dichlorophenol compared with that of 2,4-dinitrophenol (48 x 10^{-12}sec) and this is found for the overall relaxation time (33 x 10^{-12}sec). The shorter relaxation time (7.2 x 10^{-12}sec) is intermediate between the values for hydroxyl relaxation in 2,6-dimethylphenol (3.4 x 10^{-12}sec) and 2,4-dinitrophenol (15 x 10^{-12}sec), the former molecule in benzene at 20°C (26) and the latter in p-xylene at 25°C.

2,4-Dibromophenol.- Antony, Fong and Smyth (32) did not analyse their data on this compound in benzene but the computer gave satisfactory values. The longer value of 42 x 10^{-12}sec for the overall relaxation time compares with 39 x 10^{-12}sec for that of 2,6-dibromophenol also in benzene at 20°C (32) and 48 x 10^{-12}sec for 2,4-dinitrophenol in p-xylene at 25°C. The shorter value (5.4 x 10^{-12}sec) at 20°C in benzene is similar to that of o-bromophenol (4.8 x 10^{-12} sec) in p-xylene at 25°C.

2,4,6-Trichlorophenol.- The short relaxation times in p-xylene and cyclohexane compare with the value for 2,6-dibromophenol in benzene (32) at 20°C (12.7 x 10^{-12}sec) and other values listed in Table (11) for 2,6-disubstituted phenols. The longer relaxation times in the two solvents seem to be mutually in agreement and the value in p-xylene (45 x 10^{-12}sec) is longer than that of 2,6-dinitrophenol under similar conditions and shorter than the relaxation time of picric acid, which probably acts like a rigid molecule, of 50 x 10^{-12}sec at $18^{\circ}C$ in benzene (46). These data are in agreement with molecular volumes.

2,4,6-Tribromophenol.- The longer relaxation time of 80 x 10^{-12}sec is in reasonable agreement with the relaxation time of 2,6-dichloro-p-nitrophenol, which seems to behave like a rigid molecule, of 69 x 10^{-12}sec in benzene at $20^{\circ}C$ (32). The higher frequency relaxation time agrees with that of 2,4,6-trichlorophenol.

Guaiacol.- The relaxation times of guaiacol (o-methoxyphenol) are similar to those of o-chlorophenol, a molecule which resembles guaiacol, under the same conditions. The origins of the molecular and intramolecular relaxation times are therefore taken to be the same for the two phenols.

Catechol.- The shorter relaxation time is similar to the value obtained for guaiacol and other intramolecularly hydrogen bonded phenols. The longer value agrees with that of similar molecules such as o-chlorophenol and guaiacol and is assumed to be due to overall molecular rotation.

Discussion(43)

Fischer (41) has studied at radiofrequencies both Salicylaldehyde and o-hydroxyacetophenone in carbon tetrachloride at $20^{\circ}C$ finding relaxation times of 11.6 x 10^{-12}sec for salicylaldehyde and 18.7 x 10^{-12}sec for o-hydroxyacetophenone, at infinite dilution. He compares these relaxation times with predicted values from the equation:

$$\tau = 2.89\eta \cdot \frac{V}{kT} \cdot f \qquad \ldots\ldots\ldots\ldots(60)$$

where η is the solvent viscosity, V is the solute molecular volume, k is Boltzmann's constant, T is the absolute temperature and f is a factor expressing the dependence of τ upon the departure of the shape of the molecule from spherical. For salicylaldehyde, for example, equation (60) gives a relaxation time of 13×10^{-12}sec from which Fischer inferred that limited group mobilitywas present since the observed value is lower. The relaxation time which he obtained for o-hydroxyacetophenone, on the other hand, was longer than his expected value so this molecule is rigid. The microwave measurements, however, do not corroborate Fischer's conclusions for salicylaldehyde. No distribution parameter (α) was found in p-xylene and the observed relaxation time seems reasonable compared with similar rigid molecules. Analogous results have been obtained for o-hydroxyacetophenone (40) in cyclohexane and p-dioxan at 20°C, and the dielectric evidence therefore, confirms that molecules in Group A have either rigid structures or that insufficient of the trans rotamer is present to be detected.

Dipole moment work is in support of a strong hydrogen bond in these molecules. A measure of the hydrogen bonding capacity is the difference ($\Delta\mu$) between the dipole moment measured in dioxan and in benzene. $\Delta\mu$ for substances capable of intermolecular hydrogen bonding is distinctive, a mean of sixteen such molecules (47) being as large as 0.52D whereas for fifteen molecules definitely incapable of intermolecular hydrogen bonding $\Delta\mu$ is not greater than 0.12D. The small $\Delta\mu$ obtained for salicylaldehyde (0.11D) and o-hydroxyacetophenone (0.07D) suggest that the intramolecular hydrogen bond in these molecules withstands fission in p-dioxan.

N.M.R. also indicates a very strong hydrogen bond in these molecules. It is found that group A compounds measured at infinite dilution in carbon tetrachloride show a large displacement of the ^{1}H resonance chemical shift ($\Delta\delta$) to low fields relative to the ^{1}H resonance of the OH group in phenöl under the same conditions; the shift is less for weaker intramolecular hydrogen bonds (48). The correlation between $\Delta\delta$ and the shift of the OH stretching frequency ($\Delta\nu_s$) is shown in Fig. (11) but an equally remarkable relationship exists with the shift of the carbonyl group stretching frequency in these compounds (49). In the light of all the evidence it seems indisputable that group A substances are effectively rigid owing to the strength of their intramolecular hydrogen bond.

8-Hydroxyquinoline is classed in group B although the shift of the OH stretching frequency ($\Delta\nu_s$) of 180 cm^{-1} is small compared with most group B compounds such as o-nitrophenol for which $\Delta\nu_s = 368\ cm^{-1}$ (39). Small distribution coefficients for this molecule in the three solvents employed suggest a group relaxation mechanism and the relaxation times (Table (11)) obtained by Budo analysis have been assigned to overall molecular rotation and group rotation. The C_2 value in p-xylene is low but it does seem to be significant because it represents an absorption at 0.86 cm wavelength (Q band) of 0.005 which is about two and a half times the permissible error. C_2 can be calculated as it was for some phenols (Figs. (7) to (9)) by assuming that the angle between the OH group moment and the C-O bond is 76° as in phenol (23) and that the moments of 1-naphthol and quinoline are 1.45D and 2.18D (23) respectively. The resulting value is 0.38 which is clearly appreciably larger than the observed group weight factors for 8-hydroxyquinoline.

o-Nitrophenol has a stronger intramolecular hydrogen bond judged by the OH spectral shift ($\Delta\nu_s = 368\ cm^{-1}$ (39)) but the microwave data still indicate a contribution from group mobility in the solutions listed in Table (11). Radiofrequency work is equivocal on this point. Measurements at infinite dilution in carbon tetrachloride at $25^{o}C$ were taken as showing that, if group mobility occurred, it was slight (41). The relaxation time obtained for o-nitrophenol in a xylene mixture at 20°C however was lower than anticipated, possibly indicating a contribution from a high frequency absorption (38).

Evidence that the short relaxation time obtained by the Budo analysis, is the OH group relaxation time, seems to be given by the agreement between the observed and calculated weight factors. Taking the angle subtended by the OH group moment at the C-O bond to be the customary 76° (23), the OH group moment to be 1.54D (22) as in phenol, the nitro group moment to be 4.01D (23) along the $C-NO_2$ bond and neglecting interaction moments and inductive effects, the weight factor C_1 is calculated to be 0.87 for o-nitrophenol. Agreement is good, the observed value in n-heptane being a little low but the values in other solvent slightly high.

Since OH group mobility implies the presence of some trans species in substances like o-nitrophenol the infrared spectrum of a dried and purified sample in carbontetrachloride was measured. There appeared to be a weak band at 3590 cm^{-1} in dilute solution so the concentration was increased almost to saturation point and the spectrum re-determined. The principle OH stretching frequency observed in this solution was at 3240 cm^{-1} (compare 3243 cm^{-1} in ref. 39), the band being somewhat broadened. The interesting features, however, were the presence of a band at 3513 cm^{-1} and shoulder at 3590 cm^{-1}. The latter could be due to absorption of a proportion of trans OH since the band should be similar to the OH band of p-nitrophenol in carbon tetrachloride ($\nu_s = 3597\ cm^{-1}$ (50)). p-Nitrophenol in benzene however absorbs at 3523 cm^{-1} the shift being attributed to hydrogen bonding association between the OH and the aromatic π-cloud (50). In the strong solution of o-nitrophenol in carbon tetrachloride the band at 3513 cm^{-1} could therefore be due to association between some of the trans hydroxyl groups and the π-cloud of neighbouring solute molecules. If the o-nitrophenol molecules remained strongly intramolecularly hydrogen bonded the origin of both these bands would be difficult to explain.

The dipole moment of o-nitrophenol in the different solvents in Table (11) also suggest the presence of a proportion of trans form. This is because the moment for a rigid cis structure can be calculated (22) from the moment of phenol and its angle of inclination.from the C-O bond (1.54D and $76^{\circ}\phi$) and the moment of nitrobenzene (4.01D). The theoretical value thus obtained is 2.57D and a similar calculation for a rigid trans structure is 5.23D. All of the o-nitrophenol moments in Table (11) are intermediate between the two theoretical values, indicating a contribution from each species. Of course, there is also an interaction moment between the OH and NO_2 groups to be considered but it is expected to be lower in o-nitrophenol than in p-nitrophenol, yet the minimum discrepancy of 0.47D (in p-xylene) between the observed and rigid cis moment is greater than the interaction moment reported for p-nitrophenol (0.46D). That there is no greater shift of charge in o-nitrophenol compared with p-nitrophenol is testified by their similar pKa values, respectively 7.23 and 7.14 (51).

Other workers have studied the variation with temperature of the dipole moment of nitrophenol in toluene solution (52) and this also indicates OH group mobility.

Since an equilibrium exists between the cis and trans species in solution then increasing the temperature should increase the proportion of the higher energy trans form. For p-nitrophenol the observed moment falls by 0.12D when the temperature is increased from 25°C to 75°C whereas the moment of o-nitrophenol increases by 0.10D from 0°C to 75°C. The inference is that the proportion of the higher dipole moment trans species grows with rise in temperature for o-nitrophenol, thus demonstrating the limited mobility of the OH group.

The dipole moments of 8-hydroxyquinoline are of less value in diagnosing the presence of group mobility because the calculated moments for cis and trans species are the same. The infrared spectrum of 8-hydroxyquinoline in carbon tetrachloride, however, showed a weak band at 3585 cm^{-1} besides the main OH band at 3415 cm^{-1} (50). This could be attributed to the presence of a small proportion of trans form.

The trend of the group relaxation time of o-nitrophenol is to increase with increasing proton acceptor ability of the solvent, suggesting that the trans OH is becoming more solvated from n-heptane to p-xylene (compare the behaviour of the alcoholic OH group of cholesterol in Chapter III, Table (10)). With the aid of the graph of relaxation time against free energy barrier in the appendix the difference in free energy between the trans OH of o-nitrophenol in p-xylene and n-heptane can be obtained. This is found to be about 0.5 kcals/mole. Ketelaar (53) obtains 1.4 kcals/mole for the solvation free energy difference of trans o-chlorophenol in the vapour state and in dilute carbon tetrachloride solution. The difference between two solution values is expected to be lower so the estimate from group relaxation times seems reasonable. A similar marked trend of group relaxation time appears not to exist for 8-hydroxyquinoline but may, in fact, be partially masked by the inaccuracy in the determination of the relaxation times. This is especially so of the cyclohexane solution owing to the low solubility of 8-hydroxyquinoline in this solvent.

The group relaxation time of o-nitrophenol seems to be anomalously short when compared with the value for p-nitrophenol (10 x 10^{-12}sec). In p-nitrophenol the double bond character of the C-O bond is enhanced by contributions from quinonoid structures owing to mesomeric interaction between the nitro and OH groups (interaction moment = 0.46D) and the mesomeric interaction in o-nitrophenol should be similar since its pKa value of 7.23 (51) is close to that of p-nitrophenol (7.14). Accordingly the energy barrier opposing OH re-orientation and therefore the group relaxation times of the two molecules should be similar. It seems likely, however, that the trans form of o-nitrophenol is rendered less stable by the strongly dipolar o-substituent which will tend to pull the OH group away from the trans orientation. Thus the energy barrier for a trans→cis re-orientation will be lowered and it is shown later that this will result in a lower group relaxation time. Since the influence of the o-substituent decreases as the square of the moment of the substituent, this is probably only significant for groups, such as nitro, with large dipole moments. Infrared spectral evidence has been presented for the occurrence of related field effects in o-substituted benzene molecules (54).

In 2,4- and 2,6-dinitrophenol the molecular dipole moment lies approximately along the line bisecting the angle between the nitro broups. Molecular models show that the OH group in 2,6-dinitrophenol being between the larger nitro groups, offers little additional resistance to overall rotation than do the nitro groups by themselves. The OH group in 2,4-dinitrophenol, however, adds to the resistance to overall rotation since it is not so well shielded by the nitro groups, so the molecular relaxation time (48 x 10^{-12}sec) might be expected to be longer than that of 2,6-dinitrophenol (41 x 10^{-12}sec).

The group relaxation time of 2,6-dinitrophenol at 25°C in p-xylene (18 x 10^{-12}sec), has been compared with the value for 2,6-dibromophenol of 12.7 x 10^{-12}sec (32). The increases relative to the normal OH relaxation time must be attributed to the intramolecular hydrogen bond which forms when the OH is in both its stable orientations, the hydrogen bond is evidently stronger in 2,6-dinitrophenol in agreement with its infrared classification (group B) relative to the dibromophenol (group C).

The lengthening of the group relaxation time for 2,4-dinitrophenol compared with o-nitrophenol, both in p-xylene at 25°C, is a consequence of the mesomeric contributions due to the p-nitro group. The free energy barrier opposing group re-orientation in 2,4-dinitrophenol and o-nitrophenol can be obtained from the observed relaxation times to be 2.74 and 2.06 kcals/mole, a difference of about 0.7 kcals/mole. Similarly the difference for OH in p-nitrophenol and 'free' OH is about 0.6 kcals/mole. This suggests that the increase in double bond character of the C-O group caused by addition of a p-nitro group to a phenol is constant and corresponds to an increase in free energy barrier of about 0.7 kcals/mole/nitro group. This would explain the apparent rigid behaviour of picric acid (46) because the free energy of activation of OH group rotation in picric acid should be that in 2,6-dinitrophenol (2.8 kcals/mole) plus 0.7 kcals/mole for the additional nitro group, i.e 3.5 kcals/mole. This corresponds to a group relaxation time of more than 50×10^{-12} sec which is close to the relaxation time of overall re-orientation. The constant increment in free energy barrier is also in agreement with the observed constant decrease in pKa of about 2.8 with each addition of a nitro group to phenols (51).

The calculated weight factors C_1 obtained by making the same assumptions as for o-nitrophenol are 0.89 for 2,4-dinitrophenol and 0.86 for 2,6-dinitrophenol. Values in Table (11) are considerably lower. Since the nitrophenols present several unusual features, they were selected for more detailed study by extending the measurements to higher temperatures. The results are shown in Table (12).

Table (12) Relaxation parameters for solutions of o-nitrophenol, 2,4-dinitrophenol and 2,6-dinitrophenol in p-xylene at different temperatures.

Solute	Temp.	τ_o	α	τ_1	τ_2	C_1
	°C.	(sec x 10^{-12})		(sec x 10^{-12})		
o-Nitrophenol	25	13.3	0.03	14.9	5.0	0.88
"	60	9.8	0.07	10.5	1.2	0.86
2,4-Dinitrophenol	25	32	0.12	48	15	0.65
"	37.5	28	0.22	43	8	0.70
"	50	18	0.05	20	6	0.90
"	60	15	0.07	17	2.5	0.87
2,6-Dinitrophenol	25	29	0.03	41	18	0.62
"	37.5	24	0.05	33	15	0.69
"	50	21	0.09	23	7	0.84
"	60	21	0.08	23	6	0.89

In Table (12) the data at the different temperatures seem fairly consistent. The analysed relaxation times diminish with increasing temperature as expected but the weight factors C_1 for the polynitrophenols increase with increasing temperature, whereas constant values are anticipated. At the higher temperatures they approach the calculated values. o-Nitrophenol, on the other hand, has essentially constant weight factors, This seems to suggest the possibility of solute-solvent interaction in the solutions of the dinitrophenols. Polynitro benzene derivatives are known to form molecular complexes with aromatic hydrocarbons (53) and in the case of picric acid, which is closely similar to these phenols, the complexes are often strong. Since the interaction is probably largely of a dipole - induced dipole nature it would be likely to affect the weight factors owing to the charge shifts in the solute attendant upon complex formation. As the temperature is raised, however, thermal agitation would tend to oppose complex formation and the weight factors would approach the calculated values, as is observed. The strength of the interaction depends upon the number of nitro groups in the phenol, decreasing from picric acid to the mononitro phenols, and this probably accounts for the apparent normal behaviour of o-nitrophenol. Evidence for interaction in similar systems has been obtained at radiofrequencies (46).

If interaction between solute and solvent is occurring at room temperature it must be considered whether this and not group rotation is the sole cause of the observed distribution. That this is not the case is shown by; (i) the agreement between observed weight factors and those calculated for group re-orientation at the higher temperatures, (ii) the agreement between calculated and observed values for o-nitrophenol at both temperatures, since a strong interaction is unlikely to be present in this system, and (iii) the second relaxation time being short whereas a longer one would be expected for re-orientation of a complex. The presence of interaction in the dinitrophenol solutions at room temperature means, however, that the analysed overall molecular relaxation time is probably lengthened somewhat, either by an increased microscopic viscosity (η in equation 60) or by a contribution from the relaxation time of the complex.

The remaining molecules in Table (11) belong to Flett's group C of weak intramolecular hydrogen bonded phenols. Physical methods have been used extensively to study solutions of phenols of this type and it seems certain that group mobility occurs in many cases. The results in Table (11) confirm and add to this body of evidence.

o-Chlorophenol solutions have been studied twice by workers in the radiofrequency region. Fischer (41) found that the mean relaxation time of o-chlorophenol in carbon tetrachloride at infinite dilution was 8.5×10^{-12} sec at 25°C. The value predicted by equation (60) is 13×10^{-12} sec and so it was concluded that group relaxation with a short relaxation time must make a significant contribution. The other study (38) also found a shorter mean relaxation time than expected but no conclusions were drawn regarding the possibility of group re-orientation. Infrared evidence (33,53,55) is based upon a splitting of the OH stretching frequency owing to the presence in solution of both the cis species with a hydrogen bonded OH group and the trans species with a free OH group. This splitting is shown by solutions of o-halophenols, catechol and 2,6-dihalophenols in which the halogen substituents in the 2 and 6 positions are different (55). Dipole moment measurements also support group mobility in o-halophenols. Thus the observed moment of o-chlorophenol in cyclohexane found by the Halvenstadt and Kumler procedure, of 1.12D (compare the microwave value in Table (11) of 1.09D) is intermediate in magnitude between the moments calculated for rigid cis (0.44D) and rigid trans (2.89D) showing the presence of both species in solution (56). N.M.R. provides further evidence for the presence of a cis-trans equilibrium in dilute solutions of o-halophenols (48).

The assignment of the relaxation times of o-halophenols in Table (11) has already been discussed and it was mentioned that the overall relaxation times appear longer than those of similar molecules. N.M.R. has shown that o-halophenols self associate in solution (66). Some of those in the trans configuration act as proton donors to the majority in the cis configuration. The longer observed relaxation time can therefore be explained by a contribution from relaxation of a dimer. When the proportion of trans is lower as in o-nitrophenol solutions this effect is not detectable.

2,4-Dibromophenol is a larger molecule than 2,4-dichlorophenol so that the shorter mean relaxation time of the former molecule suggests a greater contribution from group rotation and this is confirmed by computer analysis. The inference is that the intramolecular hydrogen bond in 2,4-dibromophenol is weaker than that in 2,4-dichlorophenol.

Infrared (55), dipole moment (56) and N.M.R. studies show that this is, in fact, the case. The group relaxation times of the 2,4-dihalophenols seem also to reflect the strength of the hydrogen bond since it is longer in 2,4-dichlorophenol. The dipole moments of 2,4-dichlorophenol and 2,4-dibromophenol in Table (11) are between the values calculated for rigid cis (1.17D) and rigid trans 3.08D) again supporting group mobility.

The OH group in 2,6-dibromophenol has been shown, in a microwave study (32), to be mobile. According to atomic volume increments (57) 2,4,6-trichlorophenol is a slightly larger molecule than 2,6-dibromophenol and yet it has slightly the shorter mean relaxation time suggesting that it also has a group relaxation mechanism. Analysis confirms this deduction. Radiofrequency workers (38) have drawn the same conclusion and estimated the group relaxation time to be 11 x 10^{-12}sec in fair agreement with the results of the analysis of the microwave data (Table (11)). The OH relaxation time is therefore longer in 2,6-dihalophenols than the normal OH relaxation time but not so long as the group relaxation time of 2,6-dinitrophenol. Clearly the hydrogen bonds are lengthening the group relaxation time, the biggest increase being for the molecule in group B, 2,6-dinitrophenol (compare p.83.). The weight factor C_2 calculated for 2,6-dibromophenol from group moments is 0.37 and from bond moments is 0.59 while the corresponding values for 2,4,6-trichlorophenol and 2,4,6-tribromophenol are 0.94 and 0.76 respectively. Experimental values in Table (11) are in reasonable agreement with bond moment calculations and are slightly lower than group moment calculations. These results contrast with the weight factors of the unsymmetrically substituted phenols in Table (11) which tend to be significantly lower than values predicted by group and bond moment calculations.

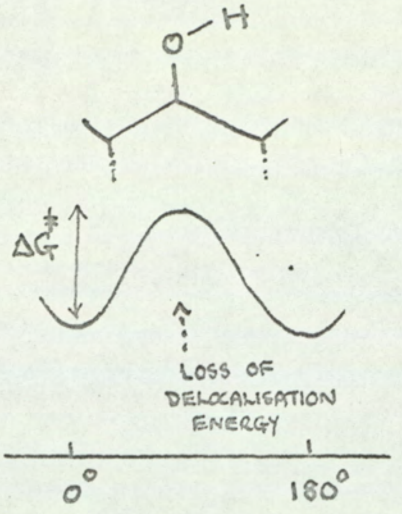
Antony, Fong and Smyth (32) obtained the dielectric constant and loss of solutions of 2,6-dichloro-p-nitrophenol and 2,6-dibromo-p-nitrophenol in benzene but were unable to analyse their data into two relaxation times. Computer analyses were attempted on these data but also failed. Both molecules have an unusually long mean relaxation time in benzene at 20^oC (69×10^{-12}sec and 56×10^{-12}sec respectively) which suggests that group rotation might not be present. It was argued above (p.84) that a p-nitro group adds about 0.7 kcals/mole to the free energy barrier of OH group rotation and that this could account for the apparently rigid behaviour of picric acid shown by radiofrequency measurements (46). The same effect would operate in these molecules. An estimate of the group relaxation time of 2,6-dibromo-p-nitrophenol obtained by adding 0.7 kcals/mole to the group rotational energy barrier of 2,6-dibromophenol is 40 x 10^{-12} sec which is probably too close to the overall relaxation time of the molecule to permit resolution of the two relaxation times with the data available. It is interesting that the mean relaxation time of 2,6-dibromo-p-nitrophenol is longer than that of 2,6-dichloro-p-nitrophenol, despite the smaller volume of the latter. This indicates that group rotation does occur in these molecules and that the group is more mobile in the bromine derivative as expected. The long group relaxation time, however, precludes a really pronounced shortening of the mean relaxation time.

The mobility of the OH group in guaiacol has been a controversial subject for many years. The infrared spectrum of guaiacol in carbon tetrachloride shows a sharp band at 3550 cm^{-1} which may be attributed to hydrogen bonded OH ~~and~~ and the value of $\Delta\nu_s$ of about 60 cm^{-1} indicates that the hydrogen bond is fairly weak (see Fig.(10)). However, there seems to be no band or shoulder near 3600 cm^{-1} attributable to the presence of free OH. The ultraviolet spectrum (58) of guaiacol in p-dioxan shows a marked 'red shift' and erasure of the detailed structure relative to the spectrum in cyclohexane. This can be accounted for by a decrease in the planarity of the molecule in p-dioxan because of the rupture of the hydrogen bond and therefore suggests that the OH group is mobile in p-dioxan. On the other hand the change in dipole moment of guaiacol in p-dioxan relative to benzene (47) is small (0.03D) indicating that the intramolecular hydrogen bond is not ruptured and that the OH group is not mobile. The absence of a significant change may however partly be ascribed to charge rearrangements when the hydrogen bond is broken (58). The observed dipole moment in benzene is 2.37D which is closer to the value calculated for cis (2.45D) than for trans (0.8D) (59). The moment calculated on the basis of free rotation, however, is about 2.5D and so dipole moment evidence is equivocal (58). Radiofrequency measurements seem to indicate mobility of the OH group in eugenol (41,60), a closely related molecule to guaiacol, and possibly also in guaiacol (41).

The microwave data supports mobility of the OH group, but it should be noted that the shorter relaxation time is probably a composite value of the OH relaxation time and the OCH_3 relaxation time. Rotation of the OCH_3 group is not sterically prevented in o-dimethoxy~~phenol~~benzene yet the steric effects are possibly greater than in guaiacol. The most reliable group relaxation time for the OCH_3 group is probably 5.2×10^{-12} sec(61). Since the observed group relaxation time of guaiacol will approximate to the weighted arithmetic mean (see the appendix) and the weight factor of OH relaxation is likely to be greater than that of OCH_3, the OH

Fig 11. GROUP RELAXATION TIME AND FREE ENERGY BARRIER.

(a) SYMMETRICAL

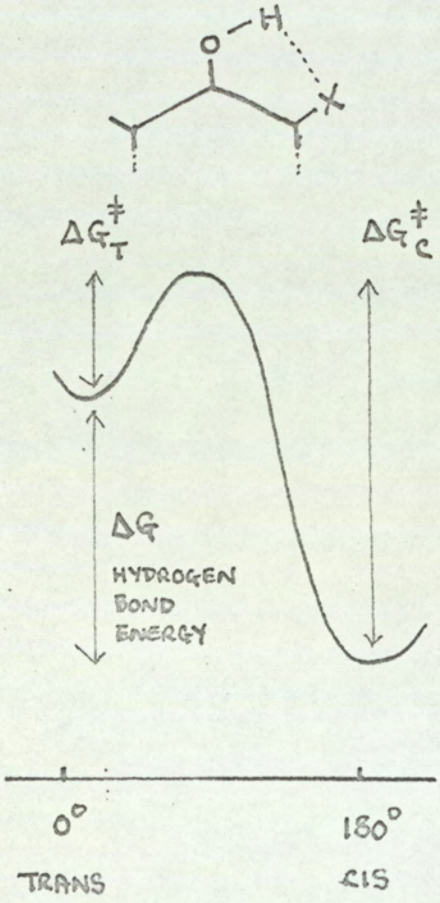


ZERO POINT ENERGY OMITTED FOR CLARITY

$$\tau_2 = \frac{\kappa h}{kT} e^{\Delta G^{\ddagger}/RT}$$

where' κ = transmission coefficient.

(b) ASYMMETRICAL.



$$\tau_2 = \frac{2\tau_T \tau_c}{\tau_T + \tau_c}$$

$$\tau_T = \frac{\kappa h}{kT} e^{\Delta G^{\ddagger}_T/RT}$$

$$\tau_c = \frac{\kappa h}{kT} e^{\Delta G^{\ddagger}_c/RT}$$

$$\frac{\tau_T}{\tau_c} = e^{(\Delta G^{\ddagger}_T - \Delta G^{\ddagger}_c)/RT}$$

$$= e^{-\Delta G/RT}$$

$$= K$$

$$= [\text{TRANS}]/[\text{CIS}]$$

potential energy barrier is symmetrical) then:

$$\tau_2 = \tau_c = \tau_T \qquad \text{.............(62)}$$

and τ_2 is the actual group relaxation time. When the energy curve is extremely asymmetrical then $\tau_c \gg \tau_T$ and

$$\tau_2 = 2\tau_T \qquad \text{.............(63)}$$

so it appears that the group relaxation time does not increase indefinitely as the strength of the o-hydrogen bond increases, as might be expected, but is never longer than twice the relaxation time of a trans → cis re-orientation.

There is a further factor to be considered and that is the change in polarisibility which occurs as the asymmetry of the potential energy barrier increases. The contribution to the group orientational polarisibility (α_{02}) due to the re-orientation of the hydroxyl group is:

$$\alpha_{02} = \cdot \frac{\mu_2^2}{3kT} \cdot \frac{4\tau_T\tau_C}{(\tau_T + \tau_C)^2} \qquad \text{.............(64)}$$

For a symmetrical energy barrier $\tau_T = \tau_C$ and the group orientational polarisibility reduces to $\mu_2^2/3kT$ but when the barrier is very asymmetrical $\tau_c \gg \tau_T$ and equation (64) becomes:

$$\alpha_{02} = \frac{\mu_2^2}{3kT} \cdot \frac{4\tau_T}{\tau_c} \qquad \text{.............(65)}$$

from which it follows that α_{02} approaches zero as τ_c

becomes appreciably longer than τ_T. It is often assumed that the ratio of weight factors C_1/C_2 is proportional to μ_1^2/μ_2^2 where μ_1 and μ_2 are the components of the rotating moments at right angles to their respective axes of rotation. The proportionality, however, is really with the ratio of orientational polarisibilities (65), i.e.

$$\frac{C_1}{C_2} = \frac{\alpha_{01}}{\alpha_{02}} \qquad \text{............(66)}$$

If $\tau_T = \tau_c$ then μ_1^2/μ_2^2 is identical to α_{01}/α_{02} but when $\tau_c > \tau_T$ then α_{02} is reduced according to equation (64) and so C_2 is correspondingly diminished. This simple model seems to account, at least qualitatively, for the following facts:

(i) The apparent absence of a long group relaxation time corresponding to the cis trans re-orientation in o-substituted halophenols. Radiofrequency studies find no evidence for such a relaxation mechanism (38,41) in agreement with equation (61).

(ii) The strong hydrogen bond in o-substituted phenols of group A would undoubtedly severely hinder group rotation but rotation might still be expected to occur at much lower frequencies. No evidence of group rotation is obtained at radiofrequencies (41), however. According to the simple theory group A molecules constitute the special case of $\tau_c \gg \tau_T$ and no intramolecular relaxation process is detectable, C_2 being effectively zero by equations (65) and (66).

(iii) For o-substituted phenols of group C it is probably a reasonable approximation to identify τ_T with the normal OH relaxation time. Equation (61) then predicts that the observed group relaxation time should be longer than the normal value. This is borne out, in general by values in Table (11).

(iv) Molecules with asymmetric energy barriers should have weight factors for group re-orientation lower than the calculated values. This is not so well borne out probably mainly because of the uncertainty in calculated weight factors but large decreases in C_2 were found for o-chloro- and o-bromophenol for which calculated values are near the optimum of 0.5.

(v) For 2,6-disubstituted phenols the symmetry of the OH rotational free energy barrier is restored and the group relaxation time is therefore given by the equations (62). No reduction in C_2 is anticipated by equation (64). This is probably borne out by the data in Table (11), the observed values for 2,4,6-trichlorophenol and 2,4,6-tribromophenol being slightly lower than group moment calculations but in fair agreement with bond moment calculations.

In principle, equations (61) and (64) permit the calculation of τ_T and τ_C from the analysed group relaxation time and weight factor, and the calculated weight factor. In practice, the probable error in analysed parameters and especially the uncertainty in the calculated weight factor vitiates such treatment.

Although relaxation times and weight factors are sensitive to many perturbing influences, some of which have been mentioned in this discussion, the ideas represented by equations (61) to (66) seem to offer a fair basis for the interpretation of the relaxation data for group rotation in o-substituted phenols.

CHAPTER V

INTERACTION OF PHENOLS.

Introduction.

The 'free' Phenolic OH group is well known (29) to form an intermolecular hydrogen bond with suitable bases, as is testified by many physical methods but notably infrared (28), N.M.R. (35) and polarisation measurements (47). The same methods have not been regarded as suggesting that intermolecular association is present when the OH group is bound by an intramolecular hydrogen bond of the strong group A or medium group B categories (39). The study of dielectric behaviour in the microwave region is particularly valuable in the study of association because it yields several parameters each of which might be sensitive to the interactions e.g. relaxation times, weight factors and dipole moments. In this chapter a variety of phenolic systems are considered. Systems known to interact show how the relaxation parameters are affected and hence the behaviour of systems which are less well documented can be interpreted.

Interactions of some Non-Hindered Phenols.

In the discussion of solvent effects on weight factors in Chapter III some measurements were cited on phenols in which the OH group is not sterically hindered. The results are summarised in Table (13).

For p-cresol C_1 should be close to zero so the observed mean relaxation time should be almost that of group relaxation i.e. about 3.4×10^{-12}sec. Observed values are much greater especially for the fairly strong solution in cyclohexane and distribution parameters are pronounced.

Table (13) Relaxation parameters for some phenols in different solvents and at various concentrations at 25°C. cyc = cyclohexane, CTC = carbon tetrachloride, xyl = p-xylene.

Solute	Solvent	Conc$^{\underline{n}}$ (mole fract.)	τ_o (sec x 10^{-12})	α	μ (D)
p-Cresol	cyc	0.0638	28	0.31	1.4_4
"	CTC	0.0265	14	0.16	1.5_0
"	xyl	0.0374	17	0.15	1.6_1
p-Chlorophenol	cyc	0.0211	14	0.16	1.7_7
"	xyl	0.0309	25	0.09	2.2_4

The behaviour of p-cresol seems, in fact, to be very similar to that of p-chlorophenol which it resembles in shape and size but for which a large contribution from overall molecular relaxation is anticipated. Analysis shows that there is apparently a dominant contribution from a long relaxation time for both compounds but parameters are not constant at different concentrations and it was argued in Chapter <u>III</u> that this is best explained by self association. Computer analyses into only two Debye terms are therefore invalid and interpretation must in general be based on mean relaxation times and distribution parameters for strongly interacting systems. However, increases in mean relaxation times and distribution parameters seem sensitive criteria of intermolecular interactions.

Measurements on solutions of p-cresol mixed with acetone in cyclohexane at 25°C substantiate this conclusion. Acetone has a dipole moment about twice that of p-cresol and in order that each molecule might give a reasonable contribution to the relaxation data the mixture was made up with a greater mole fraction of p-cresol than acetone. The results are given in Table (14).

Table (14) Relaxation times and distribution parameters for mixtures of acetone and p-cresol in cyclohexane at different total concentrations and at 25°C. The ratio of acetone to p-cresol was 1 : 1.6 in each case. The average dipole moment should be 2.01D.

Acetone conc$^{\underline{n}}$ (mole fract.)	τ_o (sec x 10^{-12})	α	μ (D)
0.0098	13	0.46	2.1_0
0.0343	35	0.45	2.3_4
0.0515	39	0.43	2.3_6

Acetone has a short relaxation time (see Chapter VI) and consequently the mean relaxation time of the mixture is expected, in the absence of interfering factors, to be shorter than that of p-cresol alone. Furthermore the mean relaxation time should not depend upon the total concentration of the mixture in the cyclohexane but merely upon the proportion of acetone and p-cresol and this is constant, the weight factors corresponding to relaxation of each species, therefore being constant according to equations (55). In fact, the mean relaxation times in Table (14) increase rapidly as the concentration of acetone/p-cresol mixture is increased until it is greater for the mixture than for either component separately. The ratio of the relaxation time of acetone to that of p-cresol is quite large (about five to ten) especially when the concentration of p-cresol is high (Table (13)) and so an appreciable distribution parameter would be expected for mixtures of the two, even in the absence of interactions. An empirical equation (see the Appendix) permits an estimate of the distribution parameter in non interacting systems and it is found that it should not be greater than 0.35 for the strongest solution in Table (14). Yet even the most dilute solution in Table (14) exhibits a distribution parameter greater than this estimate showing that the distribution coefficient is sensitive to interactions. Since a number of relaxation mechanisms are operative in this mixture, computer analysis into two Debye terms is again invalid. In the final column of Table (14) is the mean dipole moment of the mixture. Assuming a value for the dipole moment of p-cresol of 1.44D (Table (13)) and of acetone 2.76D (23) the mean dipole moment should be 2.01D. The larger observed values are also indicative of complex formation.

Association of Phenol.

The results of measurements on phenol at a number of concentrations in p-xylene at 25°C are given in Table (15). The viscosity of the stronger solutions are appreciably greater than the dilute solutions so the reduced relaxation times given by:

$$\tau_{red} = \tau_o \cdot \frac{\eta\ \text{solvent}}{\eta\ \text{solution}} \qquad \ldots\ldots\ldots\ldots(67)$$

are also listed; η represents viscosity. These values are also shown plotted against mole fraction in Fig. (12).

Table (15) Mean relaxation times, viscosities, reduced relaxation times and apparent dipole moment of phenol solutions in p-xylene at 25°C and at the specified mole fraction.

Phenol Conc$^{\underline{n}}$. (mole fract.)	Mean relaxation time (sec x 10^{-12})	Viscosity (c.poise)	Reduced mean relaxation time (sec x 10^{-12})	μ(D)
0.0221	11.7	0.665	10.6	1.51
0.0510	13.8	0.683*	12.1	1.55
0.0800	16.7	0.711	14.1	1.57
0.1674	28.5	0.810	21.1	1.81
0.2751	41	0.928	26.5	1.99

* Interpolated value.

The dependence of the mean relaxation time upon mole fraction of phenol is very nearly linear, deviations being only about 1.5 x 10^{-12} sec at the greatest, but the data of Fischer (67) obtained at lower frequencies confirm that the slight curvature is real. Fischer's measurements were carried out in carbon tetrachloride solution and the curvature he obtained was much more pronounced as might be expected since the phenol would have less tendency to interact with carbon tetrachloride than with p-xylene which has been shown to be a proton acceptor (29). The curvature of the plot of the reduced relaxation is, however, quite definite.

Fig 12. VARIATION OF RELAXATION TIME OF PHENOL WITH CONCENTRATION IN p-XYLENE.

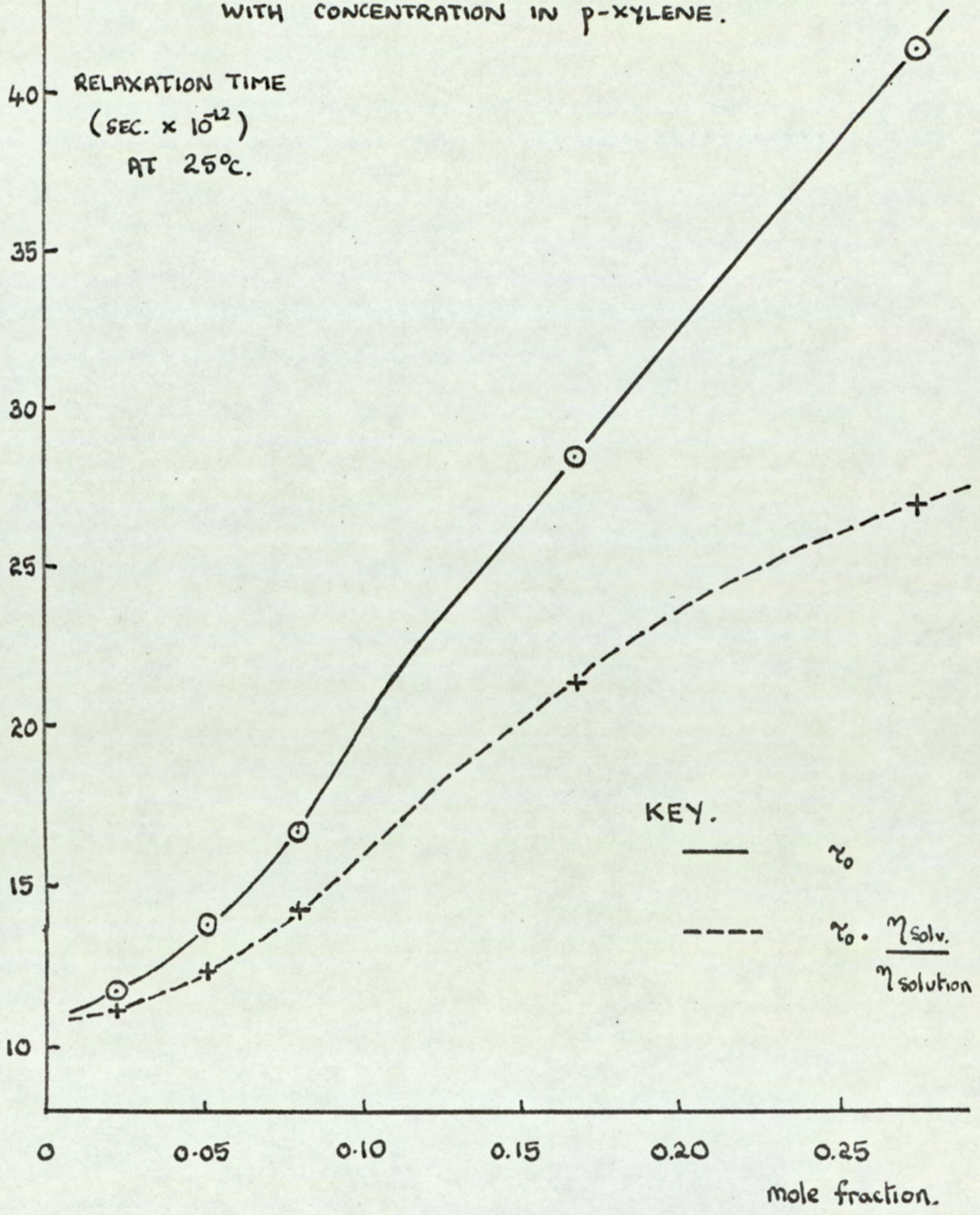
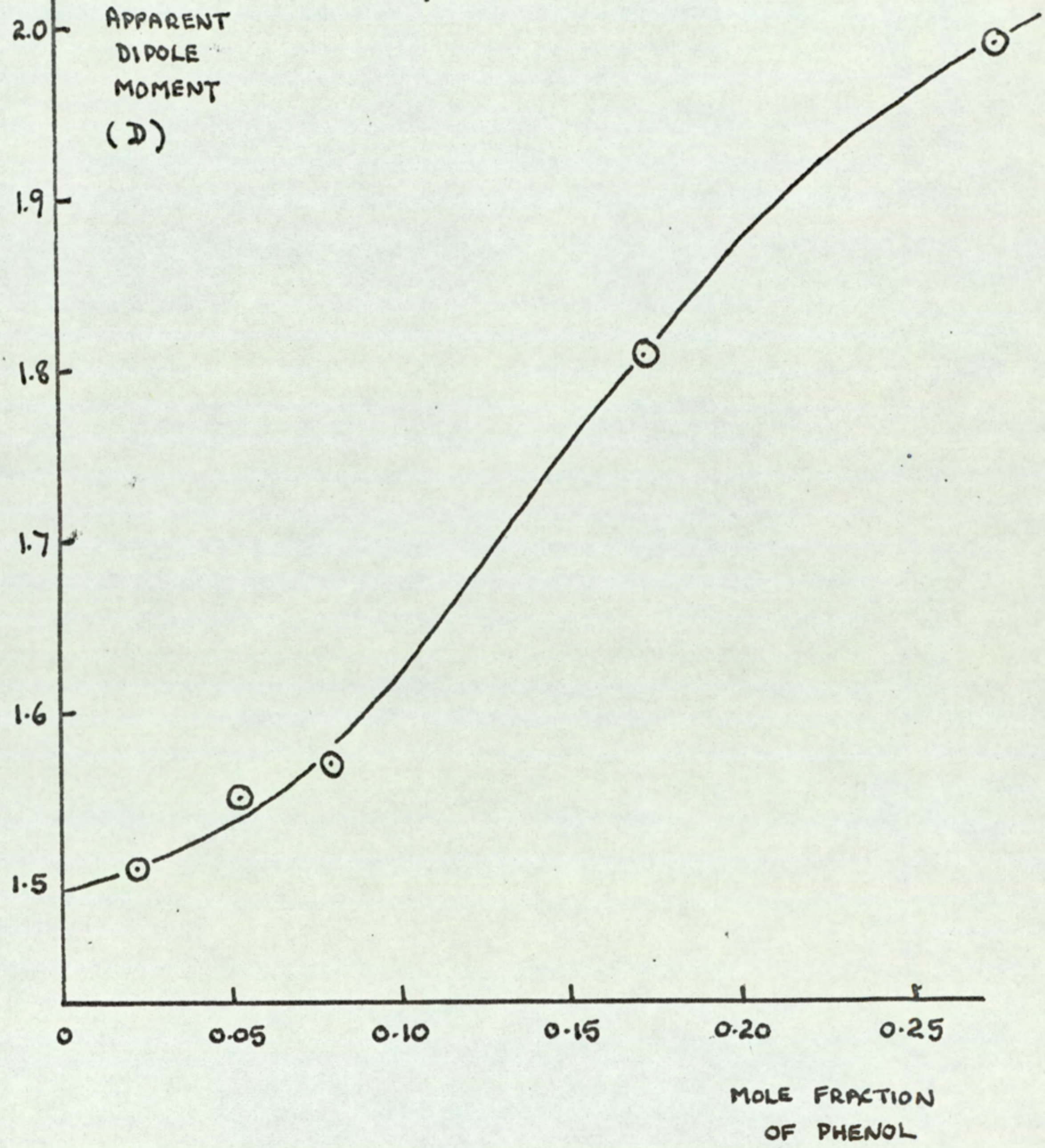


Fig 13. VARIATION OF APPARENT DIPOLE MOMENT OF PHENOL WITH CONCENTRATION IN p-XYLENE.



The limiting value of the relaxation time at infinite dilution seems to be about 11 x 10^{-12}sec. This is similar to the value which would have been expected if phenol were a rigid molecule; compare, for instance, chlorobenzene in cyclohexane at 20°C of 7.5 x 10^{-12}sec (20) and nitrobenzene in p-xylene at 25°C of 13.1 x 10^{-12}sec, both of which are molecules of similar size and shape to phenol. It is shown in Fig. (7) that a contribution of at least 80% from a group relaxation time is anticipated for phenol but self association by intermolecular hydrogen bonding would reduce the apparent group relaxation time contribution (see Chapter III). Mecke (28) finds that the phenol monomer is removed rapidly with increasing concentration even at low concentrations, so that at a concentration of about 0.02 mole fraction in carbon tetrachloride about 40% of the phenol is polymerised thus increasing the observed relaxation time. Another factor is the lengthening of the group relaxation time by interaction with the solvent. Since group relaxation occurs in a variety of other phenols as has been shown in Chapter IV and by Smyth, et al (32), Mansel Davies and Meakins (27) etc., it appears inconceivable that phenol monomer would behave as a rigid molecule and it seems reasonable to conclude that the relaxation time takes a rapid downward turn at concentrations lower than those it has been possible to measure, where association is unimportant.

Evidence for such behaviour comes from radiofrequency studies on eugenol at different concentrations in carbon tetrachloride (41). At concentrations lower than about 1 mole % the relaxation decreases so rapidly that it is not possible to estimate the infinite dilution value with any confidence.

The behaviour of the relaxation time can therefore be described in terms of progressive association with increasing concentration. At very low concentrations the molecules strongly associate probably into principally dimers and cyclic trimers (28,29) the former causing a rapid increase in the mean relaxation time. At slightly higher concentrations, representing the minimum observable by the present dielectric studies, the proportion of cyclic trimers becomes more important. An N.M.R. study finds that the association into cyclic trimers is the most important equilibrium at such concentrations (68). Having a low zero moment the cyclic trimers should not contribute greatly to the mean relaxation time and its value becomes less dependent on concentration. At still higher concentrations linear polymers dominate and the relaxation time increases again with concentration. The reduced relaxation time indicates a levelling out of the relaxation time once again above about 20 mole % concentrations, and Fischer (67) found a slight decrease in reduced relaxation time at the highest concentrations. This is probably due to the growing importance of internal rotational degrees of freedom as the polymer chain lengthens. Workers on the N.M.R. spin-lattice relaxation time have proposed an essentially similar mechanism in terms of molecular 'clusters' (i.e. polymers) which lose their rigidity above about 20 mole % of phenol (69).

Dipole moments.- The apparent dipole moment calculated by equation (42) is plotted against concentration in Fig. (13). The shape of the curve is similar to that obtained from the Onsager equation and refractive indices (67). The apparent moment rises rapidly between 10 mole % and 20 mole % when linear polymers are probably being formed but at low concentrations the increase is slower. This is in agreement with the idea that species of fairly low or zero moment (cyclic trimers) are tending to prevent the orientational polarisation from increasing at concentrations below about 5 mole %.

Solvent effects on Intramolecularly Hydrogen Bonded Phenols.

Results for several intramolecularly hydrogen bonded phenols have already been given in Table (11). The mean relaxation times and dipole moments for these systems are for clarity also given in Table (16) together with results for p-dioxan solutes.

These compounds fall into Flett's group B of moderately

Table (16) Mean relaxation times and dipole moments, determined from ($\epsilon_0 - \epsilon_\infty$), for several intramolecularly hydrogen bonded phenols.

Solute	Solvent	τ_0 (sec x 10^{-12})	μ(D)
o-Nitrophenol	n-heptane	6.6	3.3_8
"	cyclohexane	8.5	3.0_9
"	CTC	14.5	3.1_0
"	p-xylene	13.3	3.0_4
"	p-dioxan	29	2.9_3
8-Hydroxyquinoline	cyclohexane	11.4	2.6_0
"	CTC	18.1	2.6_7
"	p-xylene	14.6	2.5_0
"	p-dioxan	39	2.2_7
2,6-Dinitrophenol	p-xylene	29	3.7_3
"	p-dioxan	47	3.4_1
2,4-Dinitrophenol	p-xylene	32	2.8_6
"	p-dioxan	58	3.3_2

strong intramolecular hydrogen bonds. It has been suggested in Chapter IV that limited OH group mobility nevertheless occurs, and evidence was presented to substantiate this proposal. Hydroxyl group mobility implies the presence of a proportion of trans form in solution, and it was shown that the group relaxation time τ_2 lengthens as the solvating power of the solvent increases, owing to the deepening of the energy trough of the trans OH caused by solvation. Associated with the lowering of the trans energy trough would also be an increase in the proportion of trans form present since ΔG, the free energy difference between the cis and trans orientations, would be reduced. Solvation of the trans OH in p-dioxan occurs by formation of an intermolecular hydrogen bond and should lead to a considerable stabilisation of the trans relative to the cis configuration.

The formation of an appreciable amount of such a complex in solution should cause a disproportionate increase in the measured relaxation time because both the group relaxation time (τ_2) and the overall relaxation time (τ_1) should increase. Direct comparisons between the relaxation times in Table (16) are open to the objection that the relaxation time in p-dioxan is expected to be longer than that in the other solvents because it has the greater viscosity (see equation 60). To allow for this the relaxation times are expressed in Table (17) relative to the value in n-heptane, together with the viscosities of the solvents relative to that of n-heptane and the relaxation times of nitrobenzene relative to the value in n-heptane. Nitrobenzene is a very similar molecule to o-nitrophenol, differing mainly in being slightly smaller and incapable of dielectric relaxation by an intramolecular process in the microwave region. Viscosity effects should be similar for o-nitrophenol and nitrobenzene so that differences in relaxation behaviour are attributable to specific interaction.

From Table (17) it can be seen that the relaxation times of o-nitrophenol have a closely similar dependence on the solvent as those of nitrobenzene for the four relatively inert solvents, n-heptane to p-xylene. For both molecules, their relaxation times in carbon tetrachloride are predicted from the values in n-heptane by equation (60), while in cyclohexane the values are anomalously low. For the two solvents with the greatest ability to interact, however, the relaxation times are high relative to the viscosities, but although in p-xylene the effect on both solutes is the same, in p-dioxan the relaxation time of o-nitrophenol is lengthened more than that of nitrobenzene. It appears that an interaction occurs between o-nitrophenol and dioxan which is smaller or absent between nitrobenzene and p-dioxan.

Table (17) Viscosities of solvents expressed relative to that of n-heptane and relaxation times of o-nitrophenol and nitrobenzene relative to those in n-heptane for solutions in various solvents at 25°C (o-nitrophenol) and 20°C (nitrobenzene). n-hept = n-heptane, cyc = cyclohexane, CTC = carbon tetrachloride, p-xyl = p-xylene, p-diox = p-dioxan.

Solvent	Viscosity relative to n-heptane	o-Nitrophenol relaxation time (τ_o) relative to value in n-heptane	Nitrobenzene relaxation time (τ_o) relative to value in n-heptane (44)
n-hept	1	1	1
cyc	2.3	1.3	1.3
CTC	2.3	2.2	2.3
p-xyl	1.5	2.0	2.1
p-diox	2.8	4.4	3.5

In Table (18) the data for 8-hydroxyquinoline are treated similarly, the relaxation times being expressed relative to carbon tetrachloride as 2.3 so that direct comparison can be made with the previous table.

1-Nitronaphthalene is a rather larger molecule than 8-hydroxyquinoline but of similar shape and, in the absence of unusual interactions, should be more liable to interact by virtue of its large dipole moment. Yet Table (18) indicates a pronounced interaction between 8-hydroxyquinoline and p-dioxan which seems to be absent for 1-nitronaphthalene even though the behaviour of the two solutes is similar in more inert solvents.

Table (18) Viscosities of solvents expressed relative to that of carbon tetrachloride and relaxation times of 8-hydroxyquinoline and 1-nitronaphthalene, relative to their values in carbon tetrachloride, in several solvents at 25°C (8-hydroxyquinoline) and 20°C (1-nitronaphthalene). Values are scaled by a factor of 2.3 to permit comparison with Table (17). cyc = cyclohexane, CTC = carbon tetrachloride, p-xyl = p-xylene, p-diox = p-dioxan.

Solvent	Viscosity relative to CTC	8-Hydroxyquinoline relaxation time (τ_o) relative to value in CTC	1-Nitronaphthalene relaxation time (τ_o) relative to value in CTC (44)
cyc	2.3	1.4	1.5
CTC	2.3	2.3	2.3
p-xyl	1.5	1.9	1.9
p-diox	2.8	5.0	2.1 (2.9)*

* Value corresponding to the relaxation time calculated by the equation of Chau, Le Fevre and Tardif (44).

The dinitrophenols were insufficiently soluble in the inert solvents to permit dielectric measurements of the necessary accuracy so only p-xylene and p-dioxan were used. Their relaxation times in p-dioxan (Table (19)), were almost twice as long as in p-xylene, a ratio which is similar to that of the solvent viscosities. However, the increase in relaxation time is often less than that predicted from solvent viscosities by equation (60) even for rigid molecules. An example is m-dinitrobenzene, a molecule which should offer a good comparison with 2,4- and 2,6-dinitrophenols and which shows an increase in relaxation time from benzene to p-dioxan of 1.5 times, whereas the ratio of viscosities is almost 2 (70). Furthermore 2,4- and 2,6-dinitrophenols seem likely to interact with p-xylene as was pointed out in Chapter IV. The overall relaxation times in p-xylene are therefore longer than expected and any increase in p-dioxan would not appear so pronounced.

Table (19) Mean relaxation times of 2,4-dinitrophenol and 2,6-dinitrophenol in p-xylene and p-dioxan at 25°C. Viscosities of the solvents are given for comparison. DNP = dinitrophenol.

Solute	Solvent	τ_o	Viscosity c.p.
2,4-DNP	p-xylene	34	0.6
"	p-dioxan	64	1.1
2,6-DNP	p-xylene	29	0.6
"	p-dioxan	47	1.1

For 2,6-dinitrophenol there is the further factor of the group relaxation time which should not be directly affected by the solvent in contrast with that of 2,4-dinitrophenol which should be lengthened by solvation of the OH when in the trans configuration. The mean relaxation time of 2,6-dinitrophenol should accordingly be less sensitive to the influence of the solvent as, in fact, is the case in Table (19). Thus, for the dinitrophenols, relaxation data do not unequivocally show interaction with p-dioxan but are probably not incompatible with such an interaction. Low frequency measurements show that picric acid behaves similarly on moving from xylene to p-dioxan (38).

For o-nitrophenol the dipole moment determined by equation (42) and listed in Table (16) tends to decrease as the electron donor capacity of the solvent increases. This is true also of 8-hydroxyquinoline and 2,6-dinitrophenol but not of 2,4-dinitrophenol. These results are in agreement with a previous polarisation study (22). The dipole moments of the molecules can be calculated by assuming values for the moment of phenol and nitrobenzene of 1.54D and 4.01D respectively and taking the angle of the OH moment to be 76° from the C-O bond. Dipole moments obtained in this way and the observed moments are shown in Table (20).

Table (20) Calculated and observed dipole moments and values for four molecules having an intramolecularly hydrogen bonded OH group. The difference in the moment in p-xylene and dioxan is also given.

Compound	Calculated moments		μ(D)	μ(D)	μ(D)
	cis	trans	p-xylene	p-dioxan	
o-Nitrophenol	2.57	5.23	3.0_4	2.9_3	-0.1_1
2,4-Dinitrophenol	3.09	5.51	2.8_6	3.3_2	0.4_6
2,6-Dinitrophenol	3.93		3.7_3	3.4_1	-0.3_2
8-Hydroxyquinoline	2.31	2.31	2.5_0	2.2_7	-0.2_3

To calculate the dipole moment of 8-hydroxyquinoline in Table (20) values of 2.18D and 1.45D (24) were assumed for the dipole moments of quinoline and 1-naphthol respectively and the angle of the OH group moment from the C-O bond was again assumed to be 76^{0} (23).

The $\Delta\mu$ values in Table (20) are larger than those observed for most strongly intramolecular hydrogen bonded phenols such as o-hydroxyacetophenone ($\Delta\mu$ = 0.07D) (47). Fission of the intramolecular hydrogen bond and replacement by an intermolecular hydrogen between o-nitrophenol and p-dioxan would account for the pronounced lengthening of the relaxation time but could not account for the negative $\Delta\mu$ value since any change in the cis-trans equilibrium in p-dioxan in favour of the trans isomer would be accompanied by a substantial increase in the observed dipole moment as shown by the calculated values.

In, 2,6-dinitrophenol the OH group is intramolecularly hydrogen bonded whatever its orientation so the change in moment in p-dioxan cannot be attributed to intermolecular hydrogen bonding as it possibly could for 2,4-dinitrophenol in which $\Delta\mu$ might have been interpreted in terms of a switch from cis to trans. Nor can the change of moment of 8-hydroxyquinoline be attributed to changes in the cis-trans equilibrium since the moment is calculated to be the same in both orientations so the state of the equilibrium would not be expected to effect the observed moment. It appears, therefore, that some type of specific dipole attachment would best account for the relaxation and dipole moment data.

An interaction of this sort was suggested by Bellamy and Hallam (50) to explain their observations of the OH stretching frequency of intramolecularly hydrogen bonded phenols in solvents of differing polarity. Richards and Walker (22) added strongly to this view with extensive polarisation and infrared measurements and were able to calculate the angle made by the additional moment introduced into the nitrophenols as a result of the interaction. The angle was 10° from the C-OH bond in four nitrosubstituted phenols and in view of the increase in OH stretching frequency (suggesting a weaker hydrogen bond as a consequence of the interaction) the most likely site of dipole attachment seems to be approximately along the direction of the N-O bond in the chelated ring with the negative end of the dipole towards the nitrogen atom. The dipole in the p-dioxan molecule which interacts is one of the C-O dipoles of the ether links. Since p-dioxan is predominantly in the chair form it is possible that this interaction is facilitated by the low steric interference from the main body of the p-dioxan which will effectively be bent away from the solute molecule. A similar dipole attachment satisfactorily accounts for much of the data for 8-hydroxyquinoline. Since (i) dipole moments and relaxation times indicate little interaction between nitrobenzene and p-dioxan, (ii) 8-hydroxyquinoline has only a relatively low moment and (iii) the interaction seems to be connected with the chelated ring, it appears that dipole attachment is stabilised in some way by the presence of the chelated ring.

Interactions of Intramolecularly Hydrogen Bonded Phenols with a strong base.

The cis-trans equilibrium of o-nitrosubstituted phenols is apparently not seriously disturbed in p-dioxan but a stronger base might effect the equilibrium significantly. Triethylamine is not suitable because it has a dipole moment of about 0.7D and so would lead to dielectric loss in its own right. 1,4-Diazabicyclo-(2,2,2)-octane (DBO) is a base of comparable strength to triethylamine but with certain improved features. Most important from the dielectric viewpoint is that it is non-polar. Measurements on a solution of DBO ($f_2 = 0.0681$) in p-xylene at Q, K and X bands showed that the loss was greater than that of the pure solvent by only 0.003 at the most. Another feature of DBO compared with triethylamine is the reduced steric hindrance to complex formation owing to the cyclisation of the hydrocarbon chains. The results of observations on a number of compounds are given in Table (21).

DBO has only a low solubility in cyclohexane so only one solution in this solvent was measured. It can be seen from Table (21) that although the total solute concentration was only about 1 mole % the mean relaxation of o-nitrophenol in this mixture has increased substantially. Mean relaxation times can normally be obtained to better than 10% but this difference is more than 20%. The dipole moment has also increased in contrast with the behaviour of o-nitrophenol in p-dioxan.

Table (21) Relaxation times and dipole moments for various phenols and 2,4-dinitrophenetole in three component mixtures with DBO and the specified solvent at 25°C. The results in two component mixtures are also given. * Denotes more than one solution measured. cyc = cyclohexane, xyl = p-xylene, 2,4-DNP = 2,4-dinitrophenetole, 2,6-DTBP = 2,6-di-tert-butylphenol.

Compound	Mole fraction	Solvent	DBO mole fraction	Mean relaxation time (sec x 10^{-12})	μ(D)
o-Nitrophenol	*	cyc	-	8.5	3.0_9
"	0.0054	"	0.0054	10.4	3.1_6
"	*	xyl	-	13.3	3.0_4
"	0.0155	"	0.0155	17	3.3_2
"	0.0232	"	0.0232	17	3.3_1
"	0.0503	"	0.0503	25	3.6_2
2,4-DNP	0.0128	"	-	49	5.4_2
"	0.0123	"	0.0123	47	5.3_6
o-Chlorophenol	*	"	-	14.3	1.2_4
"	0.0729	"	0.0109	30.3	1.7_0
"	0.0655	"	0.0181	40.6	1.9_6
Guaiacol	*	"	-	17.4	2.3_3
"	0.0441	"	0.0441	31	2.2_5
2,6-DTBP	0.0386	"	-	8.6	1.5_6
"	0.0351	"	0.0070	9.2	1.6_2

Higher concentrations can be achieved in p-xylene and a small series of equimolar mixtures of o-nitrophenol and DBO were measured. The mean relaxation time shows a pronounced lengthening in the stronger solutions and the dipole moment increases considerably. When the reacting species are present at a concentration of only 5% the mean relaxation time has almost doubled relative to its value in p-xylene alone, while the dipole moment has increased by 0.6D. The distribution parameter for these systems also increases rapidly and has a value of 0.18 for the strongest solution compared with 0.03 for o-nitrophenol in p-xylene. These values strongly suggest that the OH group of o-nitrophenol is swinging into the high dipole moment trans form (see Table (20)), owing to the stabilisation of the latter by the strong hydrogen bond with the DBO. A qualitative estimate of the proportion of trans form (i.e. complex) present can be obtained by assuming that the observed moment is a weighted average of the moments actually present. To do this one has to know the moments of the cis and trans forms and estimates of these for o-nitrophenol in benzene have been given in Table (20). These may be used in the present calculation except that a small increment of 0.4D is added to the trans moment to allow for the charge shift consequent upon the formation of the hydrogen bond to the strong base. If this is too low then the calculated percentage of trans present will be too high and vice versa but relatively the results have significance. For o-nitrophenol in p-xylene the amount of trans increases from 10% with no DBO added to 18% for the intermediate amounts and 26% for the solution with most DBO added.

The effect of complex formation on the relaxation time is twofold: the intramolecular hydrogen bond lowers the trans energy trough thus increasing τ_2; the volume of the complex is greater than that of the monomer so its relaxation time should be longer by equation (60). In the mixture, of course, some of the free phenol will remain with its two relaxation times and the complex may have internal rotational degrees of freedom so analysis of the dielectric data into two Debye terms would seem invalid. Estimation of the mean relaxation time of the complex is difficult for these reasons and because its shape and dimensions can only be guessed. However, Tucker and Walker (71) found the relaxation times of similar but linear complexes of DBO with pyrrole in cyclohexane and indole in p-xylene to be 42 x 10^{-12}sec and 70 x 10^{-12}sec respectively at 25^{o}C, while the relaxation time of uncomplexed pyrrole in cyclohexane at 25^{o}C is 2.4 x 10^{-12}sec, and that of indole in p-xylene at 25^{o}C is 19 x 10^{-12}sec. Antony and Smyth find a value for the chloroform-DBO complex of about 80 x 10^{-12}sec in chloroform at 20^{o}C (72). Thus long values would be expected for the phenol complexes and the observed sharp increases in mean relaxation time and distribution parameter can be explained by the presence of appreciable amounts of the complex in solution. No changes in relaxation parameters analogous to those of o-Nitrophenol and DBO mixtures should be observed for 2,4-dinitrophenetole and DBO mixtures since 2,4-dinitrophenetole is incapable of proton donation. From Table (21) the equimolar mixture of DBO and 2,4-dinitrophenetole actually showed a slight reduction in relaxation time and dipole moment compared with 2,4-dinitrophenetole in p-xylene, (probably as a result of random error). This is in accordance with expectations and helps confirm the interpretation of the changes for o-nitrophenol.

For o-chlorophenol polarisation data indicate the presence of approximately one molecule of trans to two of cis in p-dioxan solutions (56). A strong base like DBO should therefore readily bring about a switch to the trans configuration. From the series of three mixtures containing o-chlorophenol in Table (21) it is obvious again that a sharp lengthening of the mean relaxation time and increase in dipole moment occurs when DBO is present in the solution. The relaxation time increment is more pronounced than for o-nitrophenol, reflecting the relative strengths of the intramolecular hydrogen bond in the two phenols, for the relaxation times of the complexes are probably of the same magnitude. The moment of trans form of o-chlorophenol can be calculated (56) to be 2.89D by assuming the following values for monosubstituted benzene derivations: 1.54D for the moment of phenol at 76° from the C-O bond; 1.58D for the moment of chlorobenzene. A similar calculation gives

0.44D for the cis form so the proportion of cis is considerably reduced even with addition of 1 mole % of DBO to the solution. The state of the equilibrium can be estimated from the dipole moments, as for o-nitrophenol. The complex moment is again enhanced by 0.4D to make an arbitrary allowance for charge shifts associated with hydrogen bond formation and the proportions of trans (or complex) present is found to be 15% with no DBO, 29% for the intermediate strength solution and 38% for the solution most concentrated in DBO. The relative values may be taken to be significant and illustrate the marked increase in the concentration of trans form. Just as for o-nitrophenol the distribution parameter is also increased by the presence of DBO in the mixture. From a value of 0.08 it rises to 0.24 for the mixture containing 1.09 mole % of DBO, and to 0.26 for the mixture with 1.81 mole % of DBO.

Guaiacol is, like o-chlorophenol, classified in Flett's group C of weak intramolecular hydrogen bonds and, like o-chlorophenol, its mean relaxation time rises sharply when measured in the presence of DBO. An increase in distribution parameter also occurs but not so marked as for o-chlorophenol: in p-xylene it is 0.08 and for the solution containing DBO it is 0.14. The behaviour of the dipole moment, however, is different from o-nitrophenol and o-chlorophenol since it has fallen slightly. Curran (59) quotes the values of the moments of the cis and trans forms of guaiacol to be

2.45D and 0.8D so a disturbance of the equilibrium in favour of the trans form should result, in this case, in a fall in dipole moment as is observed. Rough estimates of the proportions of cis and trans as before yield 12% of trans in the guaiacol solution without DBO and 19% in that with DBO.

The results obtained for 2,6-di-tert-butylphenol confirm the nature of the interaction observed in the phenols discussed. 2,6-Di-tert-butylphenol is found to relax predominantly by an intramolecular mechanism and therefore a hydrogen bonding interaction via the OH group should lead to a marked change in the mean relaxation time. However, it has been noted (Chapter III) that the large contribution from group relaxation in this molecule compared with phenol is due to the suppresion of self association by the steric influence of the bulky ortho substituents; even in the solid state OH group rotation occurs with a short relaxation time (6.1×10^{-12}sec) for 2,4,6-tri-tert-butylphenol at 20°C (73). Infrared spectroscopy also shows that the OH group is sterically protected because the OH stretching frequency is unaltered for such molecules in the crystalline state or in dilute solution in carbon tetrachloride (27). From infrared the equilibrium constants for the reaction of various phenols with the Lewis base diethyl ether have also been determined (74). For phenol the formation constant (K) of the complex is $6.0\,l.mole^{-1}$ but for 2,6-di-tert-butylphenol no complex was formed (K = 0) showing that the OH group is protected from molecules with an electron donor capacity similar to that of diethyl ether. Thus it seems probable that no increase in mean relaxation time should occur for mixtures of 2,6-di-tert-butylphenol and DBO. In fact, a small increase of 0.56×10^{-12} sec is observed but if this is significant it shows interactions to be only slight.

2,4,6-Trihalophenol Interactions.

In 2,4,6-trihalophenol systems, interaction might be expected to be slight since the OH group is intramolecularly hydrogen bonded in both preferred configurations. The relaxation parameters for 2,4,6-trichlorophenol and 2,4,6-tribromophenol in cyclohexane and p-xylene have been given in Table (11). Measurements were also carried out in p-dioxan for these two molecules and in a p-xylene/p-dioxan mixture for 2,4,6-trichlorophenol and the results for these systems are summarised in Table (22).

Table (22) Mean relaxation times, distribution parameters and apparent dipole moments for some systems of 2,4,6-trihalophenols with electron donor molecules at 25°C. TBP = Tribromophenol, TCP = Trichlorophenol.

Solute	Solvent	Solute Conc$^{\underline{n}}$ (mf.)	τ_o (sec x 10^{-12})	α	μ(D)
2,4,6-TBP	Dioxan	0.0209	29	0.29	2.1_5
2,4,6-TCP	1/3 Dioxan + p-xylene	0.0285	39	0.12	1.7_8
"	Dioxan	0.0296	40	0.26	2.0_0

In p-dioxan both molecules show a large increase in the distribution parameter compared with the values in p-xylene and cyclohexane and for 2,4,6-trichlorophenol the relaxation time is also much lengthened, indications of interaction with the solvent. The relaxation time for 2,4,6-tribromophenol is, however, anomalously short and might suggest a considerable contribution from group relaxation. The dipole moments are also increased, in agreement with the work of Goode and Ibbitson (75). Using the Halvenstadt and Kumler approach they found that the moment of 2,4,6-trichlorophenol was greater in p-dioxan than in benzene by 0.45D and the moment of 2,4,6-tribromophenol was greater by 0.43D. Such large values of $\Delta\mu$ are strong evidence of a hydrogen bonding interaction (see p.76).

Since the interaction seemed fairly pronounced in p-dioxan it was decided to use DBO to see whether strong complexes could be formed. A preliminary measurement on a fairly concentrated equi-molar solution of 2,4,6-trichlorophenol and DBO in p-xylene gave an apparent dipole moment for the 2,4,6-trichlorophenol of 3.81D, a mean relaxation time of 176 x 10^{-12}sec and a distribution parameter of 0.40, indicating strong complex formation in the system. Further measurements were carried out in which the 2,4,6-trichlorophenol initial concentration was kept constant while the DBO concentration was varied. The resultant relaxation parameters are summarised in Table (23). It can be seen that the mean relaxation time and distribution coefficient both increase sharply even when very small quantities of DBO are added to the 2,4,6-trichlorophenol. At high concentrations of DBO (greater than that of the 2,4,6-trichlorophenol the relaxation times and distribution parameters are effectively constant. Similar behaviour was observed for all the measured dielectric constants and loss factors.

Table (23) Relaxation times, distribution parameters, viscosities and apparent dipole moments for some systems of 2,4,6-trichlorophenol with DBO in p-xylene solution at 25°C. The 2,4,6-trichlorophenol concentration is 0.3544 moles litre^{-1} in each case. Viscosities are expressed relative to that of the p-xylene solvent.

DBO Conc$^{\underline{n}}$ (moles litre^{-1})	τ_0 (sec x 10^{-12})	α	μ(D)	Viscosity
0.0000	22.6	0.06	1.4_1	1.00
0.0184	38	0.28	1.7_0	1.02
0.0466	86	0.34	2.1_0	1.04
0.0653	91	0.38	2.2_8	1.04
0.0897	141	0.37	2.5_0	1.03
0.3571	152	0.36	3.8_4	1.15
0.7143	146	0.39	4.1_3	1.26

The levelling off at high DBO concentrations is just the sort of behaviour expected if a strong complex were formed since once all the 2,4,6-trichlorophenol were bonded to the DBO, further DBO additions should lead to no more increases in the observed properties. An interesting feature of many of the data is the slightly sigmoid form of the curves, at low DBO concentrations, the rate of increase of the property being lower than at intermediate concentrations. This could be attributed to the formation of a complex of relatively low dipole moment but long relaxation time at low DBO concentrations. DBO has two proton acceptor sites and can in theory bond two 2,4,6-trichlorophenol molecules. Such a complex can adopt either a configuration which might be termed the trans form since the bulk of each 2,4,6-trichlorophenol molecule is on opposite sides of the line through the nitrogen atoms of the DBO, or one which is a cis form since the bulk of the 2,4,6-trichlorophenol molecules are on the same side of the DBO. The trans form of the 2 : 1 complex would have a zero or small dipole moment yet a very long relaxation time and would probably be the sterically preferred form. Thus the predominant formation of this complex when the concentration of 2,4,6-trichlorophenol greatly exceeded that of DBO could explain the form of the data. At intermediate and high DBO concentrations, of course, the 1 : 1 complex would be present in the greater concentration. Assuming that all the 2,4,6-trichlorophenol is complexed when DBO is present in excess, it seems that the moment of the complex is about 4D but if any is left uncomplexed at the highest DBO concentrations, then the true moment of the complex must be greater. The ultraviolet spectrum of the mixture of 2,4,6-trichlorophenol and DBO in cyclohexane, however, did not show any bands which could be attributed to change transfer spectra, although the absorption due to the 2,4,6-trichlorophenol was shifted towards the red.

A number of infrared spectra of mixtures of DBO with trichlorophenol, and DBO with 2,4,6-tribromophenol in various solvents were also recorded. 2,4,6-Trichlorophenol in carbon tetrachloride has a single sharp band due to the OH stretching frequency at 3542 cm^{-1}, while 2,4,6-tribromophenol has the band at 3526 cm^{-1}. Both are, of course, shifted relative to the stretching frequency of uncomplexed phenolic OH at 3611 cm^{-1} (50). In p-xylene both compounds exhibit a doublet in the OH stretching region, bands occurring at 3498 cm^{-1} and 3534 cm^{-1} for 2,4,6-trichlorophenol and at 3498 cm^{-1} and 3514 cm^{-1} for 2,4,6-tribromophenol. This unsuspected doubling of the hydroxyl frequency has been noted for phenols in aromatic solvents by Mecke (28) and attributed to the presence of "association isomerism", i.e. orientation of the solvent with its π-electrons close to the -OH group or with its C-H groups adjacent to the -OH group. Since the solvent has a different polarisibility in the two directions, the interaction energy is different and therefore the frequency shift of the phenolic OH group also is different. This explanation is, perhaps, tantamount to saying that the phenolic OH group is able to form a weak complex with the solvent π-electrons and therefore two bands arise, one due to the 'complex' and one due to unbonded OH. In p-dioxan a much greater change is observed. The 'free' OH peak occurs only as a minor band at 3500 cm^{-1} on the side of a broad band centred at about 3230 cm^{-1} for 2,4,6-trichlorophenol. This compares with the OH stretching frequency of phenol in p-dioxan of 3315 cm^{-1} and of p-nitrophenol in p-dioxan, 3205 cm^{-1} (50). For 2,4,6-tribromophenol the 'free' OH band is at about 3250 cm^{-1} and again is broad. The slightly weaker bond which might be indicated by the lesser shift for 2,4,6-tribromophenol compared with 2,4,6-trichlorophenol is probably attributable to the steric hindrance of the bulky bromine substituents relative to chlorine. The influence of DBO on the infrared spectrum of 2,4,6-trichlorophenol in p-xylene is also striking. To a solution of 2,4,6-trichlorophenol in p-xylene of concentration 0.35 molar was added 0.18 moles per litre of DBO. Thus the molarity of the DBO just exceeded half that of the 2,4,6-trichlorophenol and two OH bands would be expected if a 1:1 complex were formed. In fact, there was only the faintest trace of an uncomplexed band at about 3490 cm^{-1} and a band appeared which was so broad that its maximum was obliterated by the C-H absorption of the solvent. It seems that nearly all the 2,4,6-trichlorophenol was interacting since the normal OH doublet in p-xylene had almost vanished and this can best be explained if much of the 2,4,6-trichlorophenol forms the 2:1 complex with the DBO. Infrared data, therefore, confirm the conclusion made from the relaxation parameters, that a 2:1 complex is present in these mixtures.

It was hoped that a data fitting technique based on the Elliott Applications Program L03 described in Chapter II could be used to fit parameters for the 2,4,6-trichlorophenol/DBO system to the dielectric data and a program was devised to do this but trials showed that the amount of computer time required would be formidable, owing to the large number of unknown parameters. More data would also have been required for accurate results but the trials seemed to indicate that the equilibrium constants for 1:1 and 1:2 complexes were similar in magnitude and the relaxation time of the 1:1 complex was of the order of 100 x 10^{-12}sec.

CHAPTER VI

INTERACTION OF CHLOROFORM WITH ELECTRON DONOR MOLECULES.

Introduction.

It seems fairly well established that the hydrogen atom in chloroform is capable of hydrogen bonding to a suitable electron donor molecule (29). Thus the C-H stretching frequency may be shifted and is considerably intensified in electron donor solvents, these phenomena being characteristic of hydrogen bond formation. Many other physical properties e.g. vapour pressure, N.M.R., dielectric polarisation etc. indicate complex formation in chloroform + base mixtures (29). Dielectric relaxation however has been little used in this field. Acetone-chloroform mixtures have been measured at radiofrequencies (76) and p-dioxan-chloroform mixtures have recently been studied at microwave frequencies (72). No microwave studies have been carried out on ternary mixtures, the third component being inert diluent, nor have attempts been made to estimate equilibrium constants from microwave data. In this work ternary mixtures of chloroform with an electron donor in dilute cyclohexane solution were measured in an attempt to detect complex formation.

Results.

The observed dielectric constants and losses are given in the appendix. The results were analysed in the customary way (see discussion) and the analysed parameters are summarised in Table (24).

Table (24) Relaxation times, distribution functions, weight factors and dipole moments for solutions of bases and chloroform in cyclohexane at the indicated concentration and at 25°C. Concentrations are in mole fractions. TEA = Triethylamine, $CHCl_3$ = Chloroform. Relaxation times are in picoseconds.

Solute 1	Conc$^{\underline{n}}$	Solute 2	Conc$^{\underline{n}}$	τ_o	α	τ_1	τ_2	C_1	μ(D)
Acetone	0.0362	-	-	2.6	0	-	-	-	2.5_6
Ether	0.0966	-	-	2.5	0	-	-	-	1.1_3
TEA	0.234	-	-	8.0	0	-	-	-	0.6_7
$CHCl_3$	0.106	-	-	4.1	0	-	-	-	1.0_9
Acetone	0.0627	$CHCl_3$	0.0627	4.5	0.22	21	3.5	0.29	-
"	0.0355	"	0.0355	3.6	0.20	25	3.5	0.21	-
Ether	0.1114	"	0.1114	7.0	0.08	12.6	4.6	0.43	-
"	0.0637	"	0.0637	5.3	0.11	11.8	3.7	0.36	-
TEA	0.0738	"	0.0532	11.3	0.17	37	6.8	0.39	-
"	0.0510	"	0.0368	8.2	0.19	37	5.9	0.31	-

Discussion.

Chloroform in cyclohexane (f_2 = 0.106) has no distribution of relaxation times since the Cole-Cole semicircle lies on the ϵ' axis. The computer yielded a relaxation time of 4.1×10^{-12} sec at 25°C which is slightly longer than the value of 3.7×10^{-12} sec quoted by Antony and Smyth at 20°C from measurements at only two microwave frequencies (72). The dipole moment obtained from the computed high frequency intercept was 1.09D, in good agreement with values in the literature (23). The acetone results were obtained before P and O bands were operating and the relaxation parameters are therefore based on three frequencies and accordingly may be somewhat less reliable than those of chloroform. The relaxation time was 2.6×10^{-12} sec at 25°C in good agreement with earlier determinations at 20 (3.2×10^{-12} sec)(4).

The dipole moment (2.56D) is low compared with most literature values (2.76D) (23) but compares well with an earlier microwave value of 2.58D also in cyclohexane (4). The value here may be inaccurate owing to the difficulty in fixing ϵ_∞ for molecules with small relaxation times, although the moment of diethylether, a molecule with a similar relaxation time to acetone, also in cyclohexane at 25°C is in agreement with the literature (see below). The computer gave no distribution parameter but a small distribution would be required to give a moment in agreement with the literature. Such a distribution is not impossible since several small and apparently rigid molecules (e.g pyridine and cf. thiophen, Chapter II) yield distributions of doubtful origins in cyclohexane. For the purposes of this discussion however, the zero distribution yielded by the computer will be accepted and the acetone considered to obey Debye's equations.

In contrast, the dielectric data for diethylether seem well represented by Debye's equations with a relaxation time of 2.5×10^{-12} sec and a dipole moment of 1.13D, in good agreement with the literature (23), as observed above. Triethylamine also undergoes Debye behaviour with a relaxation time of 8.0×10^{-12} sec and a dipole moment of 0.67D. The latter agrees with the literature (24) and the former compares with a determination on the same system in this laboratory of 8.5×10^{-12} sec by Miss S.W. Tucker.

From Table (24) it can be seen that the mixtures of chloroform with the electron donor molecules show pronounced distribution coefficients. If no interaction occurred distribution coefficients would be expected since the relaxation times of chloroform and the electron donor are not equal but they should be small. An estimate of the distribution parameter in the absence of interaction can be obtained from an empirical equation given in the Appendix. The ratio of relaxation times (k) is largest for the chloroform-triethylamine system and it is clear that the distribution parameter cannot be greater than about 0.05 whereas the observed values are much greater. Perhaps more significant are the mean relaxation times which can again be estimated empirically for each system. However it is obvious that in the absence of interactions the mean relaxation time should be between the relaxation times of the components, yet in no case in the table is this true; the relaxation time of the mixture is always longer than those of the separate components. This suggests that there is an appreciable contribution from a complex of longer relaxation time in the mixture. An alternative explanation would be that the viscosity of the electron-donor solution had increased considerably on adding the chloroform. Chloroform, however, has a lower viscosity than cyclohexane and would therefore lead to a reduction in viscosity if no interactions occurred. Thus mean relaxation times and distribution coefficients confirm complex formation in these systems.

The joint behaviour of the non-interacting chloroform and electron-donor molecules in the mixture, it has been noted, is quite close to Debye behaviour e.g. for the non-interacting chloroform and acetone α is estimated to be less than 3°, for chloroform and ether - less than 4°, and for chloroform and triethylamine - less than 5°. This seemed justification for an attempt to analyse these sytems into two relaxation times, one characteristic of the complex and the other due to both chloroform and electron-donor, the computer effectively treating these as one species with a mean relaxation time, especially since it was shown in Chapter II that a mixture of two species, each of which had a distribution coefficient could reasonably be analysed into two Debye terms. The results are shown in Table (24). In the table τ_1 is the relaxation time of the complex and τ_2 the composite relaxation time of uncomplexed molecules. It may be seen now that τ_2 lies between the relaxation times of the two reactants as expected, except in the case of the stronger diethyl ether-chloroform solution for which τ_2 is slightly longer than the relaxation time of chloroform, but this is probably merely random error. The longer relaxation time (τ_1) being the relaxation time of the complex offers further justification for the analyses since it is considerably longer than the relaxation times of the parent molecules and under such conditions the analysis is more likely adequately to separate the two distinct absorption regions. Large differences also exist between the relaxation times of the complexes themselves. The diethyl ether-chloroform complex has the shortest relaxation time of about 12×10^{-12} sec, the acetone-chloroform complex is next with about 23×10^{-12} sec, while the triethylamine-chloroform complex has the longest relaxation time with about 37×10^{-12} sec. Estimates of molecular volume from atomic volume increments (57) show that the triethylamine complex is the bulkiest with a volume of $205\ \mathring{A}^3$ and is expected by equation (60) to have the longest relaxation time. Of the 1:1 complexes between chloroform and acetone and ether, however, the latter has the greater volume of $170\ \mathring{A}^3$ compared with $150\ \mathring{A}^3$ for the acetone complex, whereas the acetone complex has a considerably longer relaxation time. Of course, the complexes differ in shape, as well as volume, and this is known to be an important factor determining the magnitude of relaxation times, being represented in equation (60) by the shape factors f. Neglecting possible configurations of the ethyl groups, the diethyl ether and acetone complexes are probably bent but the triethylamine complex is linear. In addition, the hydrogen bond in the acetone complex lies in the plane of the three carbon atoms in acetone but in the ether complex it is inclined at about 50° from the plane of the C-O-C angle. However, these differences seem unlikely to account for the much shorter relaxation time of the diethyl ether complex. The overall maximum length of the complexes can be estimated, from covalent bond distances and van de Waals radii (33), to within about 0.5 Å. These are found to be about 10 Å for all the complexes. In determining the value for triethylamine and diethyl ether it was assumed that the ethyl group was in its extended configuration. It has been suggested, however, by Magat (77) that the ethyl groups of the diethyl ether may partly envelope the chloroform molecule. If this is the case the length of the complex would be only 8.5 Å and would be in better agreement with the observed relaxation time.

Only 1:1 complexes have been considered but much evidence exists demonstrating the presence of complexes of two moleculess of chloroform with one of acetone or diethyl ether. Early vapour pressure determinations on binary mixtures show deviations from ideality which are greater at a mole fraction of chloroform of about 0.6, for both diethyl ether and acetone mixtures (78,91). This could be a result of the presence of a 1:2 complex. Later Wyatt isolated a crystalline compound $(CH_3)_2CO2CHCl_3$ although it has been stated that the freezing point diagram of acetone-chloroform mixtures gives no sign of the 1:2 complex (79,80). The freezing point diagram of diethyl ether-chloroform mixtures does show the 1:2 complex, however (80). More recently infrared studies have confirmed the presence of two complexes (81). The presence of 1:2 complexes in either of the solutions would lengthen the observed relaxation time τ_1, but a possible factor in the longer τ_1 of the acetone-chloroform system compared with the diethyl ether-chloroform system is a greater contribution from 1:2 complexes in the former. It should be remembered that the weight factor is proportional to $\mu^2 f$ and the moment of the 1:2 complex of acetone is about 3.8D but is only about 2.2D for the diethyl ether complex. It is therefore possible that a lower concentration of the acetone complex is present but that owing to its greater moment it nevertheless has a greater effect on τ_1 than the higher concentration of the diethyl ether complex. Fischer and Fessler, working at radiofrequencies, studied the system acetone-chloroform (76) and noted that the mean relaxation time corrected for viscosity variations reached a maximum at about 0.6 mole fraction of chloroform, suggesting that the 1:2 complex has a pronounced influence on the observed relaxation time. Antony and Smyth (72) found the relaxation time of chloroform at infinite dilution in p-dioxan to be 17×10^{-12} sec at 20°C. This is effectively the relaxation time of the p-dioxan-chloroform complex and can be compared with the value for the diethyl ether-chloroform complex of 12×10^{-12} sec. The p-dioxan complex is expected to have the longer relaxation time owing to the greater viscosity of p-dioxan compared with cyclohexane and the slightly lower temperature. The volume of the complex (165

± 5 Å^3) is virtually the same as that of the diethyl ether complex so agreement between the relaxation times is good.

It seems then that the apparent relaxation times of the complexes are compatible with other data on these systems.

Equilibrium Constants.

Measurements in the microwave region yield a number of quantities each of which is a function of the number of polar species in the system under examination. If four microwave frequencies and a low frequency are used, then nine such quantities are obtained. Measurements at different concentration are therefore capable of giving a wealth of information on equilibria in the mixture. Since there are several unknowns the best way of obtaining them would be by fitting the data using a computer. At this stage, however, the experimental accuracy is not generally high enough to justify this (see Chapter $\overline{\underline{\text{II}}}$) unless much time is spent obtaining a large number of data points. The procedure adopted here will therefore be to make a number of simplifying assumptions to obtain the equilibrium constants fairly directly and knowing the inaccuracy thus attempt an assessment of the potential of the exact method.

The equilibrium constants may be evaluated in two ways. The first method utilises the analysed C_1 parameters in Table (24). Equations (55) may be generalised to the form:

$$C_i = \frac{f_i \mu_i^2}{\sum_i f_i \mu_i^2} \qquad \ldots\ldots\ldots\ldots(68)$$

The first assumption is that only a 1:1 complex is formed. There are therefore three species in solution, the two reactants and the complex. Calling the weight factor of the complex C_1, we have:

$$C_1 = \frac{f_1\mu_1^2}{f_1\mu_1^2 + f_2\mu_2^2 + f_3\mu_3^2} \qquad \text{............(69)}$$

where the subscripts 2 and 3 refer to the reactants. If a and b are the amounts of reactants weighed into the solution then $f_2 = (a - f_1)$ and $f_3 = (b - f_1)$.

$$C_1 = \frac{f_1\mu_1^2}{f_1(\mu_1^2 - \mu_2^2 - \mu_3^2) + a\mu_2^2 + b\mu_3^2} \qquad \text{............(70)}$$

Solving for f_1 gives:

$$f_1 = \frac{(a\mu_2^2 + b\mu_3^2)C_1}{\mu_1^2(1 - C_1) + C_1(\mu_2^2 + \mu_3^2)} \qquad \text{............(71)}$$

Making now the usual assumption that each species behaves ideally in solution the equilibrium constant can be evaluated as:

$$K = \frac{f_1}{(a - f_1)(b - f_1)} \qquad \text{............(72)}$$

In equations (71) and (72) a, b, μ_2 and μ_3 are known so only C_1 and μ_1 are required to obtain K. C_1 is put equal to the value obtained from the analysis i.e. the mixture of unreacted molecules is assumed to obey Debye's equations and the complex itself is assumed to undergo Debye

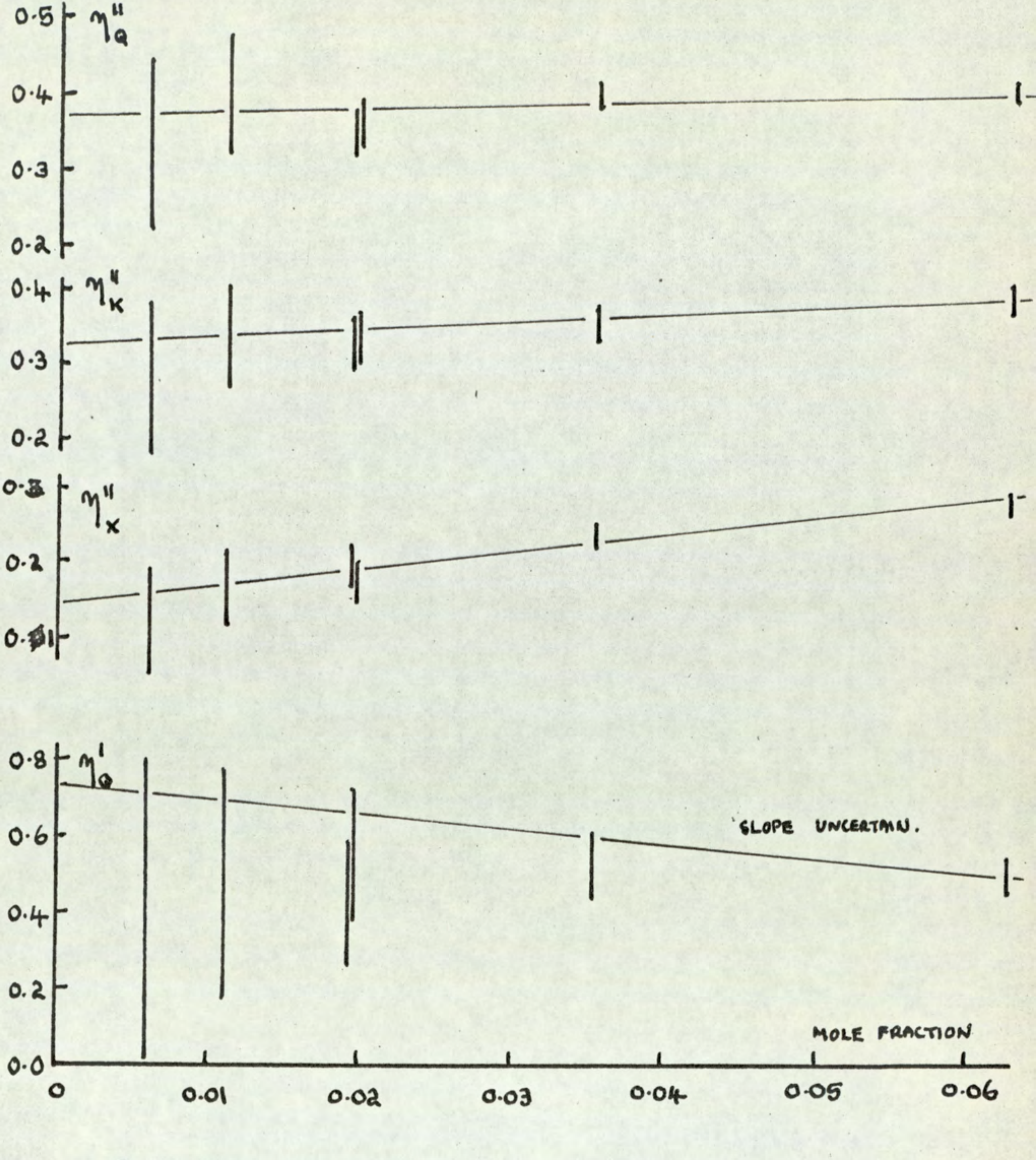


Fig 14. PLOTS OF NORMALISED LOSS FACTORS AT Q, K AND X BANDS AND NORMALISED DIELECTRIC CONSTANT AT Q BAND FOR EQUIMOLAR MIXTURES OF ACETONE AND CHLOROFORM IN CYCLOHEXANE AT 25°C. IF NO INTERACTION OCCURRED PLOTS SHOULD BE HORIZONTAL LINES. DEVIATIONS ARE MORE MARKED FOR η'', AND ESPECIALLY AT X BAND, THAN FOR η' IN WHICH ERRORS ARE PRONOUNCED, THUS MASKING ANY DEVIATIONS.

behaviour. The moment of the complex is estimated to be the vector sum of the moments of the reactant molecules and hence K can be determined. The results by this method are given in Table (25).

Table (25) Equilibrium constants calculated from weight factors.

System	K (mf^{-1})	
Acetone-Chloroform	6.2	7.6
Diethyl ether-chloroform	6.1	7.4
Triethylamine-chloroform	6.5	6.2

The alternative approach is to evaluate K for each experimental point separately beginning with:

$$\eta = c_1\eta_1 + c_2\eta_2 + c_3\eta_3 \qquad \ldots\ldots\ldots\ldots(73)$$

in which represents a normalised dielectric constant or loss. Putting in the expressions for the weight factors:

$$\eta = (\mu_1^2\eta_1 - \mu_2^2\eta_2 - \mu_3^2\eta_3).\frac{f_1}{\sum_i \mu_i^2 f_i} + \frac{a\mu_2^2\eta_2 + b\mu_3^2\eta_3}{\sum_i \mu_i^2 f_i} \quad ..(74)$$

If it is assumed that the increase in $\sum \mu_i^2 f_i$ due to the formation of the complex is small, the second term in equation (74) is the value of η expected if no complex is formed. Hence the first term is the difference between the observed and expected value of η. Denoting the excess (which may be positive or negative) as η_E we obtain:

$$\eta_E = (\mu_1^2\eta_1 - \mu_2^2\eta_2 - \mu_3^2\eta_3).\frac{f_1}{a\mu_2^2 + b\mu_3^2} \qquad \ldots\ldots\ldots(75)$$

Once again each quantity is known or measured except μ_1, f_1

and η_1 but as before μ_1 can be approximated by the vector sum of the component moments. η_1 may be obtained by assuming Debye behaviour for the complex and trying various relaxation times until a value is obtained which gives the most consistent f_1 at different frequencies. Having obtained f_1, K can be obtained from equation (72) or the further approximation can be made that f_1 = Kab and K obtained from the slope of a plot of η_E against $ab/(a\mu_2^2 + b\mu_3^2)$.

The additional assumptions in the second method confine its application to dilute solutions where the experimental accuracy is low. It is also most useful when the reduced dielectric constant or loss of the complex is much different from those of the reactants and when the moment of the complex is large. Measurements on the acetone-chloroform system were extended to lower concentrations to test this method. Since the acetone and chloroform were equi-molar in the mixtures a plot of η against the mole fraction of acetone should approximate to linearity with a slope (m) of:

$$m = \frac{\mu_1^2\eta_1 - \mu_2^2\eta_2 - \mu_3^2\eta_3}{\mu_2^2 + \mu_3^2} \cdot K \quad \ldots\ldots\ldots\ldots(76)$$

Estimates of the error in the η values are included in the graphs which are shown in Fig (14) and it is evident that ϵ' determinations at low concentrations cannot be used to obtain K. In fact only ϵ'' at X band is really of any use for this purpose and from equation (76), assuming a relaxation time for the complex of 23×10^{-12} sec, the equilibrium constant is obtained as 5.0 ± 1 mf^{-1}, the confidence limits being those due to possible variation in placing the slope. The value is compatible with the η slopes for the other bands but of course the inaccuracies in these are higher. Hence, although this method may be potentially useful, improved techniques for low polarity solutions must be awaited and further discussion will be confined to the weight factor method.

The dipole moments used in both methods were those given in Table (24) and in certain cases are somewhat different from accepted values. Since these were obtained from microwave measurements it was thought to be more consistent to employ them in the calculations. In the first method, however, the exact magnitude of the moments is fairly unimportant since errors in the numerator and denominator of equation (71) tend to cancel. The assumption of Debye behaviour for the mixture of unreacted chloroform and base could lead to an inaccurate weight factor (C_1). To test this, the dielectric constant and loss were calculated for a system containing species with moments and relaxation times equal to those presumed present in the systems studied. These data were then analysed by the computer. For example, for the chloroform-triethylamine system data were constructed from parameters $C_1 = 0.39$, $\tau_1 = 37 \times 10^{-12}$ sec, $C_2 = 0.16$, $\tau_2 = 8.0 \times 10^{-12}$ sec, $C_3 = 0.45$, $\tau_3 = 4.1 \times 10^{-12}$ sec.

Analysis into two relaxation times yielded $C_1 = 0.43$, $\tau_1 = 34.5 \times 10^{-12}$sec, $C_2 = 0.57$, $\tau_2 = 4.7 \times 10^{-12}$sec. The value of C_1 yielded by the computer is therefore 0.04 higher than that actually observed; in theother systems agreement was better but C_1 was generally slightly high and consequently so was K. The error in K due to an error in C_1 of 0.04 is about 25%. A selection of literature values of equilibrium constants is given in Table (26) from which it is clear that, infrared determinations apart, values are lower than those in Table (25) and are certainly not within 25% on average.

The remaining factor which can affect K is that the dipole moment (μ_1) of the complex is not the vector sum of the two reactants. In fact, K is found to be very sensitive to deviations of μ_1 from this simple assumption, a difference of 0.4D giving an error in K of about 70%. If μ_1 is greater than the vector sum then the true equilibrium constant is lower than that calculated on the simple assumption. Jumper and Howard (94) have shown that the moment of the complex is greater than the vector sum by amounts up to 0.7D. Thus the high K values in Table (25) possibly substantiate Jumper and Howard's findings. This possibility was examined in more detail by using the equilibrium constants employed by Jumper and Howard (see Table (26), values from ref 82) to calculate the dipole moment of the complex. The results are given in Table (27).

Table (26) Equilibrium constants for chloroform-electron donor systems at 25 ± 5°C determined by various physical methods. In certain cases marked (conv.), the equilibrium constants have been converted from units of 1 mole^{-1} to mf^{-1}. CTC = carbon tetrachloride, cyc = cyclohexane, THF = tetrahydrofuran, TEA = triethylamine. VP = vapour pressure, P = polarisation, IR = infrared, NMR = nuclear magnetic resonance, * indicates $CDCl_3$ used instead of chloroform, MDM indicates a determination by the author.

A. Ternary Mixtures.

Electron Donor	Solvent	Method	K (mf^{-1})	Reference
Acetone	CTC	NMR	2.07	82
"	cyc	IR	11 (conv.)	81
"	cyc	NMR	2.1	MDM
" *	hexane	IR	7 (conv.)	83
Ether	CTC	NMR	1.46	82
"	cyc	"	3.76	82
THF	cyc	"	5.44	84
TEA *	CTC	IR	3.8 (conv.)	85
"	cyc	NMR	4.70	82
"	cyc	"	4.2	86

B. Binary Mixtures.

Electron Donor	Solvent	Method	K (mf^{-1})	Reference
Acetone	-	VP	1.6	87
"	-	"	0.97	88
"	-	NMR	1.8	89
"	-	VP	1.5	90
"	-	P	0.35	79
Ether	-	VP	2.71	91
"	-	P	0.43	79
" *	-	IR	10 (conv.)	92
p-Dioxan	-	VP	1.39 (50°C)	93
TEA	-	NMR	3	89

Fair agreement with Jumper and Howard is obtained except for acetone with chloroform. Unfortunately, however, for acetone the equilibrium constant in cyclohexane solution was not quoted in ref 82 so the value in carbon tetrachloride was used in the calculations. This is probably not justified because the equilibrium constant of the chloroform-diethyl ether complex is 2-3 times greater in cyclohexane than in carbon tetrachloride (see Table (26)), probably because carbon tetrachloride is not really inert and is able to interact with chloroform, thus altering its activity in solution. In fact the equilibrium constant for the chloroform-carbon tetrachloride interaction is found by NMR to be 0.013 mf^{-1} (82). The same interaction may result in a lower equilibrium constant for the acetone complex in carbon tetrachloride solution compared with cyclohexane. The work of Thompson and de Maine (95) confirms the strong solvent dependence of complex equilibrium constants, values commonly being higher in cyclohexane than in carbon tetrachloride.

Table (27) Dipole moment of the chloroform-electron donor complexes calculated from the equilibrium constants of Howard, Jumper and Emerson (82) and by vector addition of the component moments from Table (24) at 25°C in cyclohexane. TEA = Triethylamine, $CHCl_3$ = Chloroform.

Electron Donor	Electron donor Conc$^{\underline{n}}$ (mole fractions)	$CHCl_3$ Conc$^{\underline{n}}$	K (mf^{-1})	μ (compl) (D)	μ Vect. sum (D)	1 Mom Incr (D)	H,J & E Mom Incr (D)
Acetone	0.0627	0.0627	2.07*	5.2	3.2	2	0.4
"	0.0355	0.0355	"	5.2	"	2	"
Ether	0.1114	0.1114	3.76	2.4	2.0	0.4	0.2
"	0.0637	0.0637	"	2.6	"	0.6	"
TEA	0.0738	0.0532	4.70	2.0	1.8	0.2	0.4
"	0.0510	0.0368	"	2.0	"	0.2	"

* Value in carbon tetrachloride.

A determination of the equilibrium constant for the acetone system in cyclohexane was carried out using an approximate NMR technique with a view to showing this increase. The value obtained however was 2.1 mf^{-1} which is very similar to that in carbon tetrachloride.

Since the enhancement of complex moment found for the other two systems are of the same order as those of Jumper and Howard a further test would be to use their moment increment, calculate the equilibrium constant by equation (71) and then compare it with values in Table (26). The resultant values of 4.7 mf^{-1} and 5.1 mf^{-1} for the two solutions are in better agreement with the literature and with Howard, Jumper and Emerson's values for the diethyl ether (3.76 mf^{-1}) and triethylamine (4.70 mf^{-1}) complexes. Remembering that the acetone results still contain an error of 25% due to possible inaccuracy in weight factors and that only a 1:1 complex is considered, the agreement is encouraging.

To summarise, the dielectric constant and loss data do not give good equilibrium constants unless the complex has a moment which is greater than the vector sum of the component moments by about 0.4D. Equilibrium constants are then in reasonable agreement with those found by other physical methods. Thus it would seem worthwhile making extensive microwave measurements on these systems and by a computer data fit, obtain the equilibrium constants and the dipole moments of the complexes independently of other methods.

APPENDIX I

Appendix I

Some relationships useful in the analysis of the data and methods by which they were obtained.

To check the validity of the method of obtaining ϵ_∞ by fitting the Cole-Cole equations to data which really conform to the Budo equations, dielectric constants and losses at the experimental frequencies were calculated using the Budo equations (33) to (35) and inserting selected values of τ_1, τ_2 and C_1. The parameters were chosen to represent the types of system studied practically in this work and the dielectric constant and loss factor for each frequency were rounded off to the number of figures used in real measurements. The results obtained by the Cole-Cole program for the test systems studied are given in Table (28). (i) the inaccuracy of the approximate ϵ_∞ .- Table (28) shows that the approximate ϵ_∞ is consistently low when α is finite. This is shown more clearly in Fig (15) where the depression of ϵ_∞ is plotted against the corresponding distribution coefficient. As the weight factor of the longer relaxation time increases the distribution parameter and depression of ϵ_∞ increase steadily. For weight factors greater than 0.5 however the depression of ϵ_∞ decreases more rapidly than does α . The curves in Fig (15) are therefore loops and the area of each loop becomes greater as the ratio of relaxation times (k) becomes greater. Since each value of α corresponds in general to two values of the approximate ϵ_∞ for a particular value of k it is clear that no definite correction to ϵ_∞ can be made to give a closer estimate of the correct value.

Table (28) Mean relaxation times, distribution parameters and high frequency intercepts (ϵ_∞) obtained by the Cole-Cole program for hypothetical systems with two Debye relaxation regions. The table is in three parts each representing a different ratio of relaxation times (k). The relaxation time τ_2 is put at 4×10^{-12}sec since this is close to the OH relaxation time in many real systems and Cole-Cole parameters are given for various weight factors C_1. ϵ_0 was 2.3500 and ϵ_∞ was 2.200 for all the data. Relaxation times are in picosenconds and distribution parameters in units of $\pi/2$ radians.

(a) $\tau_1 = 8$, $\tau_2 = 4$ i.e. k = 2.

C_1	τ_o	α	ϵ_∞(Cole)
0.00	4.00	0.000	2.200
0.10	4.24	0.017	2.199
0.20	4.52	0.031	2.198
0.30	4.85	0.041	2.197
0.40	5.22	0.045	2.197
0.50	5.63	0.045	2.198
0.60	6.08	0.042	2.198
0.70	6.55	0.035	2.198
0.80	7.03	0.026	2.199
0.90	7.52	0.014	2.200
1.00	8.00	0.000	2.200

(b) $\tau_1 = 16$, $\tau_2 = 4$.

C_1	τ_o	α	ϵ_∞
0.00	4.00	0.000	2.200
0.10	4.29	0.056	2.196
0.20	4.75	0.101	2.194
0.30	5.39	0.140	2.191
0.40	6.35	0.162	2.190
0.50	7.63	0.164	2.192
0.60	9.22	0.152	2.194
0.70	11.03	0.125	2.196
0.80	12.84	0.086	2.198
0.90	14.54	0.043	2.200
1.00	16.00	0.000	2.200

Table (28) Cont'd.

(c) $\tau_1 = 24$, $\tau_2 = 4$.

C_1	τ_o	α	ϵ_∞
0.00	4.00	0.000	2.200
0.10	4.24	0.070	2.196
0.20	4.64	0.142	2.191
0.30	5.38	0.200	2.187
0.40	6.58	0.239	2.186
0.50	8.52	0.255	2.187
0.60	11.30	0.242	2.190
0.70	14.71	0.201	2.195
0.80	18.31	0.140	2.198
0.90	21.48	0.069	2.200
1.00	24.00	0.000	2.200

Of course, k is not known for real systems so no correction could be obtained in any case. Fig (15) does bring out a useful fact, however, and this is that the depression in ϵ_∞ seems not to exceed a particular value for any value of the distribution parameter. This is shown by the straight line in the figure. The depression of ϵ_∞ is also proportional to ($\epsilon_o - \epsilon_\infty$) and so the full empirical expression for the maximum depression obtained from the slope of the line in Fig (15) is:

$$\Delta\epsilon_\infty(\max) = 0.042\,\alpha\,(\epsilon_o - \epsilon_\infty) \qquad \ldots\ldots\ldots\ldots(77)$$

Hence it is possible to quote limits within which ϵ_∞ would be expected to lie and this is a help when carrying out analyses into two relaxation times (see Chapter <u>II</u>).

(ii) The dependence of α on k and C_1.- In Fig (16) the distribution parameters are plotted against corresponding weight factors C_1 for the three different k (τ_1 / τ_2) values.

Fig 15. RELATIONSHIP BETWEEN THE LOWERING OF ϵ_∞ FROM THE COLE-COLE PROGRAM AND THE α VALUE.

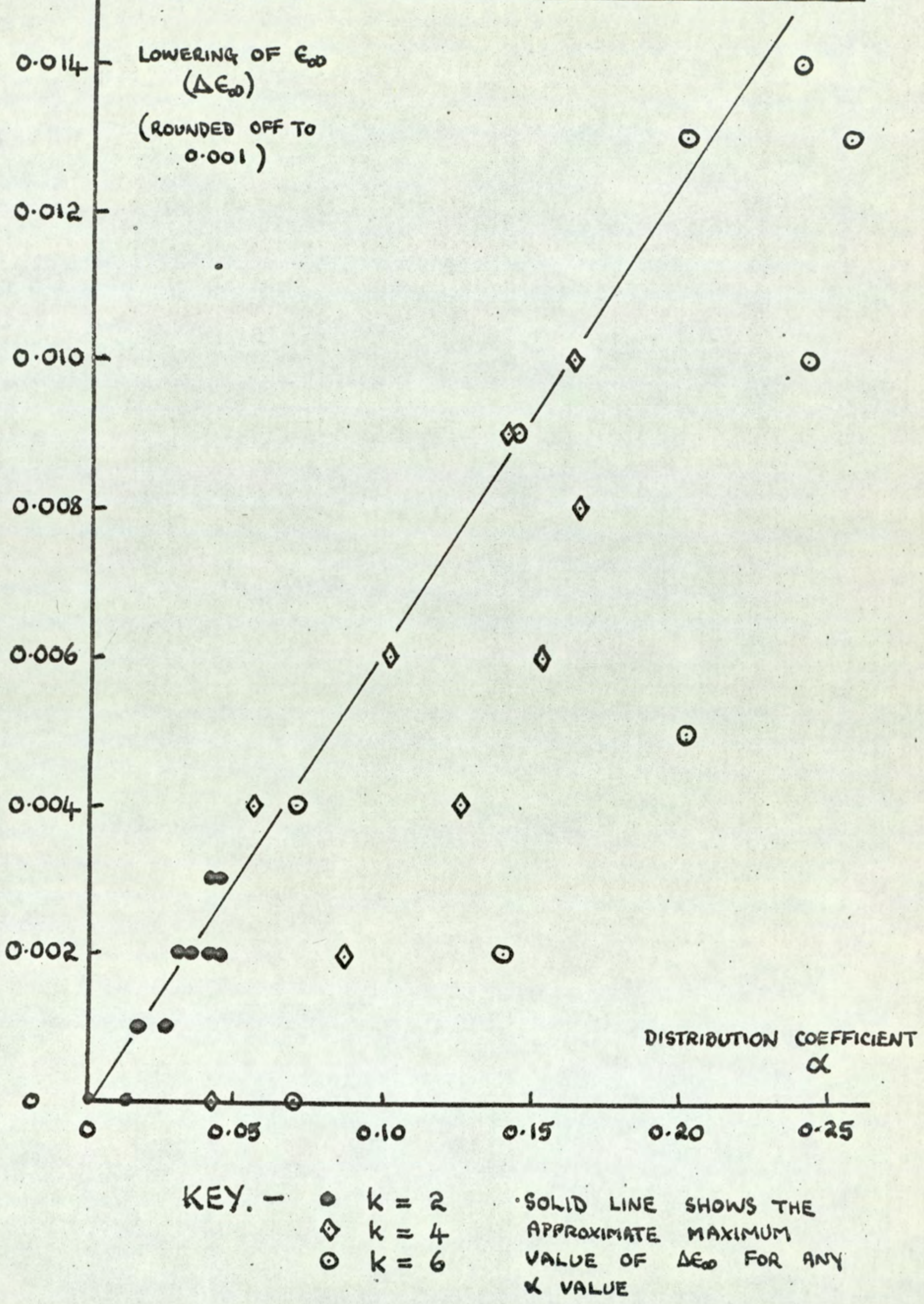
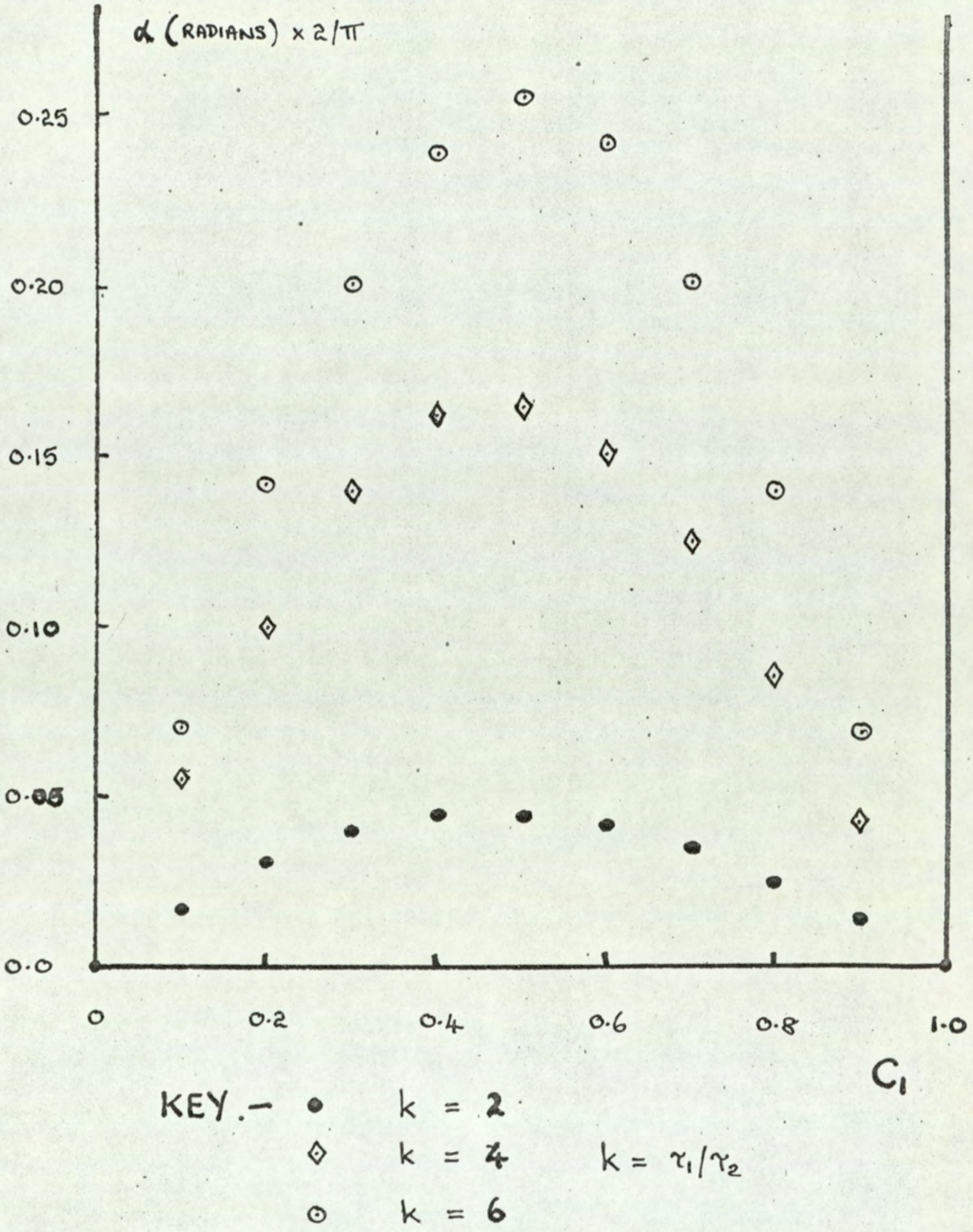


Fig 16. DEPENDENCE OF α UPON C_1 AND k.



GRAPH SHOWING THE VARIATION OF α WITH C_1 FOR THREE SYSTEMS, OF DIFFERING k VALUE. α IS OBTAINED USING THE COLE-COLE PROGRAM.

Each curve is approximately an inverted parabola with its maximum at a weight factor of 0.5 as expected. This suggests a relationship of the sort:

$$\alpha = P\left[1 - (1 - 2C_1)^q\right] \qquad \ldots\ldots\ldots\ldots(78)$$

where P is a function of k and q is close to 2. P is the maximum value of α (when $C_1 = 0.5$) and must be zero when k = 1. When k = 2,4 and 6 the maximum value of α can be obtained from Table (28). By plotting P against k it is found that the relationship between the two is very nearly linear over this range. At high k this relationship will give values of P which are too high since P cannot exceed 1.0, but remembering the range of validity P can be put equal to 0.052 (k - 1). To obtain q equation (78) can be cast in a logarithms form:

$$\log\left(\frac{\alpha}{P} - 1\right) = q \log (2C_1 - 1) \qquad \ldots\ldots\ldots\ldots(79)$$

q can therefore be obtained as the slope of the plot of log $(\frac{\alpha}{P} - 1)$ against log $(2C_1 - 1)$. Good straight lines were obtained and q found to be 1.6. The expression for α is therefore:

$$\alpha = 0.052\,(k - 1)\left[1 - (2C_1 - 1)^{1.6}\right] \qquad \ldots\ldots\ldots\ldots(80)$$

That equation (80) yields distribution parameters easily within the accuracy of their measurement is shown in Table (29) where a selection of the data from Table (28) is compared with the predictions of the equation.

Table (29) Distribution parameters obtained from the Cole-Cole program compared with those calculated by the empirical equation (equation 80).

k	C_1	α(Cole)	α(calc)
2	0.1	0.02	0.02
2	0.7	0.04	0.04
4	0.2	0.10	0.09
4	0.6	0.15	0.14
6	0.4	0.24	0.25
6	0.9	0.07	0.08

No general validity is claimed for equation (80) since it has been obtained for a particular set of conditions. Distribution parameters obtained for real systems are sensitive to random error in the data but the equation is useful for comparing expected distributions with those observed for mixtures of molecules. Observed values considerably in excess of those predicted by equation (80) probably indicate interactions (see Chapter V).

(iii) Dependence of τ_0 on τ_1, τ_2 and C_1.- For a Cole-Cole distribution of relaxation times τ_0 has a theoretical meaning as the mode of the distribution of relaxation times as well as a practical meaning as the reciprocal of the angular frequency at which the loss is a maximum ($1/\omega$ max). Consequently τ_0 has been called the most probable relaxation time irrespective of the true behaviour of the system (32). For the Budo theory applied to two concurrent Debye relaxation processes the most probable relaxation time is that with the greatest weight factor. In this work τ_0 is commonly termed the mean relaxation time and is obtained by fitting the data to the Cole-Cole equations. It is therefore relevant to ask how this compares with the value of $1/\omega$ max and whether any explicit relationships between τ_o and τ_1, τ_2 and C_1 exist.

The exact relationship between τ max (defined as $1/\omega$ max) and τ_1, τ_2 and C_1 can be obtained by differentiating the Budo loss equation (34) with respect to angular frequency (ω) and setting the result equal to zero since the loss is a maximum. The equation which emerges is cubic in x where x is the relationship between τmax and τ_2.

$$x = \left(\frac{\tau_2}{\tau_{max}}\right)^2 \qquad \text{............(81)}$$

The cubic is:

$$Px^3 + Qx^2 + Rx + S = 0 \qquad \text{............(82)}$$

and the coefficients are:

$$P = k^3 (k - 1) C_1 - k^4 \qquad \text{...........(82a)}$$

$$Q = (1 - k)(1 + 3k + k^2) kC_1 + (k^2 - 2)k^2 \qquad \text{...........(82b)}$$

$$R = (1 - k)(1 + 3k + k^2) C_1 + (2k^2 - 1) \qquad \text{...........(82c)}$$

$$S = (k - 1) C_1 + 1 \qquad \text{...........(82d)}$$

and k is of course the ratio of relaxation times τ_1/τ_2. Equation (82) has one real and two complex roots when k is not too large. The system has therefore only one loss maximum. For large k there are three real roots representing two loss maxima and a loss minimum i.e. the two relaxation regions are sufficiently far apart for them to be separately detectable and the loss curve is bimodal.

A simpler but more approximate expression can be obtained if it is assumed that the reduced dielectric constant is always a half at the frequency $1/\tau_o$. This is true of Debye and Cole-Cole behaviour but in general is not true of Budo behaviour although the approximation is probably not great in most cases. From equation (33):

$$\frac{C_1}{1 + (\tau_1/\tau_o)^2} + \frac{(1 - C_1)}{1 + (\tau_2/\tau_o)^2} = \frac{1}{2} \qquad \ldots\ldots\ldots\ldots(83)$$

Substituting $k = \tau_1/\tau_2$, $x = (\tau_2/\tau_o)^2$ and rearranging yields a quadratic in x from which τ_o may be estimated:

$$k^2x^2 + (k - 1)(1 - 2C_1)\, x - 1 = 0 \qquad \ldots\ldots\ldots\ldots(84)$$

The mean relaxation time obtained from this expression is expected to be similar to that obtained from the Cole-Cole program. The values are not exactly the same since the ϵ_∞ used in the Cole-Cole program is that which enables the data to be fitted best and is not necessarily correct whereas the derivation of equation (84) assumes that ϵ_∞ is the correct value. A still simpler relationship is the logarithmic equation (85) which is obtained intuitively from a comparison of the phenomena of dielectric relaxation and viscosity (the latter sometimes being logarithmically additive) and the symmetrical dependence of dielectric constant and loss on log (frequency):

$$\log \tau_o = C_1 \log \tau_1 + C_2 \log \tau_2 \qquad \text{............(85)}$$

or in terms of k:

$$\frac{\tau_o}{\tau_2} = k^{C_1} \qquad \text{............(86)}$$

Finally there is the simple linear relationship between τ_1, τ_2, C_1 and τ_o:

$$\tau_o = C_1\tau_1 + C_2\tau_2 \qquad \text{............(87)}$$

$$\text{or } \frac{\tau_o}{\tau_2} = C_1(k - 1) + 1 \qquad \text{............(88)}$$

These equations are obtained by considering that the mean relaxation time obtained from low frequency measurements by assuming Debye behaviour is the same as the microwave mean relaxation time. From the Budo loss equation (34) applied to low frequencies the loss is obtained as:

$$\epsilon'' = (\epsilon_o - \epsilon_\infty)\left[C_1 \tau_1 + C_2 \tau_2\right] \qquad \text{............(89)}$$

because $\omega^2\tau^2 \ll 1$. Comparing equation (89) with the Debye loss equation at similar frequencies:

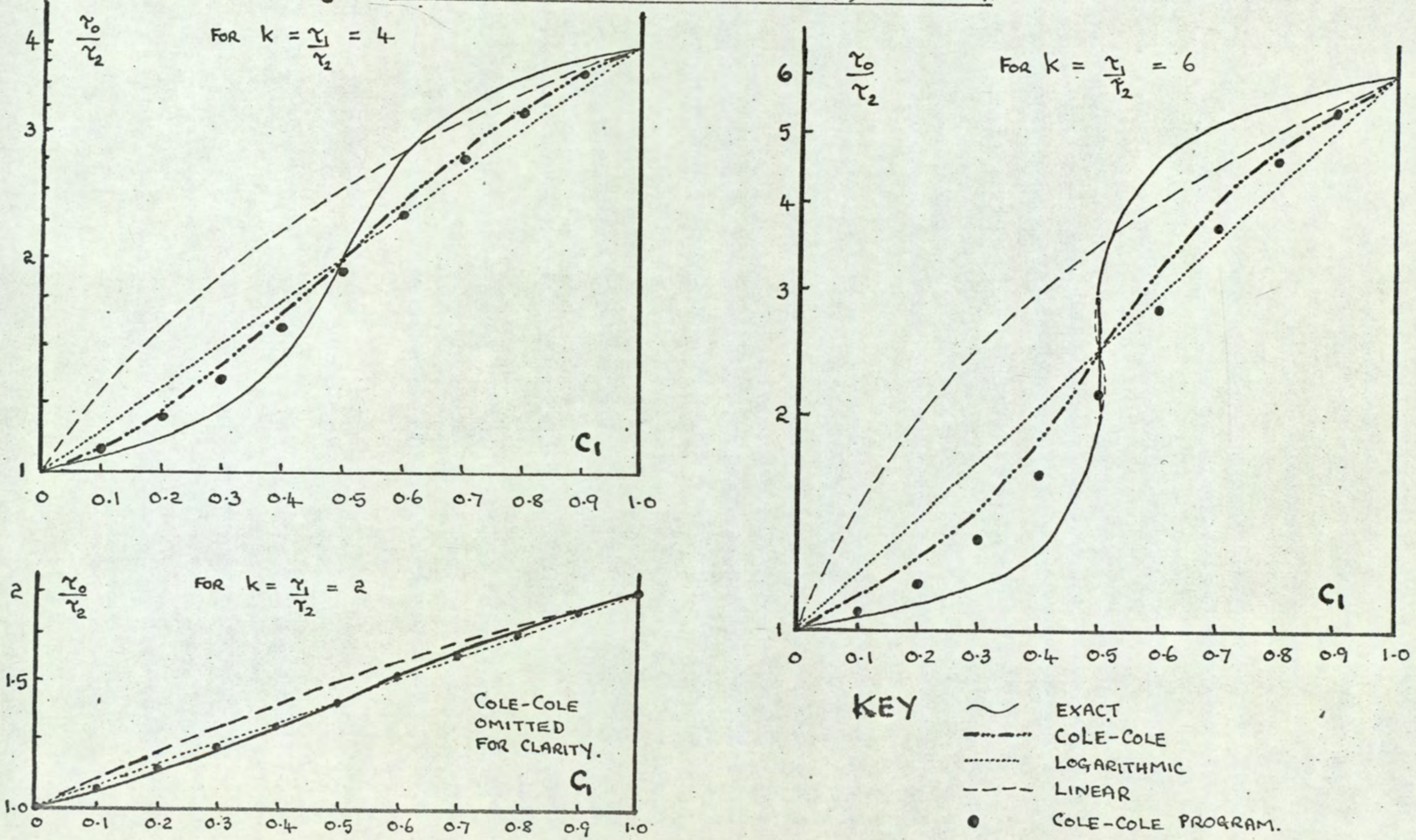
$$\epsilon'' = (\epsilon_o - \epsilon_\infty)\,\omega\tau_o \qquad \text{............(90)}$$

it is evident that the measured relaxation time is a mean value given by equation (87).

We have therefore four expressions for mean relaxation times (τ_o) one of which is an exact expression for τ max, the quantity which one presumes τ_o is approximating. The values of τ_0 given by each expression and those obtained from the Cole-Cole program are illustrated in Fig (17) for the systems in Table (28). The dependence upon C_1 of the relaxation time obtained from the exact equation (82) is sigmoid in shape and increasingly so as k increases. For k = 6 and $C_1 = 0.5$ there are already three real roots of equation (82), showing that the loss curve is bimodal. Further increases in k would exaggerate the bowing of the curve so that three roots would be present over a greater range of weight factors until the curve becomes a square S (S) and the loss curve would be bimodal whatever the weights of each relaxation region. Under these conditions τ_1 and τ_2 are so different that the absorption regions are totally separated. Fig (17) shows that non of the approximate expressions are very good unless k is quite small and that the closeness of the approximation falls as the degree of refinement of the expression decreases. As expected the values yielded by the Cole-Cole program and equation (84) are similar. This may therefore be useful for checking analyses or even writing into a Budo program as a condition which must be fulfilled by the parameters τ_1, τ_2 and C_1. The logarithmic relationship (85) may also be useful as a rapid check on a Budo analysis if k is fairly small since it then gives values fairly close to those of the Cole-Cole program. The linear relationship is generally the poorest approximation if C_1 is large it accidentally becomes the best approximation to τ max. In this work a large C_1 is the most frequently occurring case and equation (87) is often applicable but for systems with a weight factor C_1 of about 0.3, attempts to estimate τ_o by this relationship can be misleading. When interpreting dielectric data without a computer the first impression of the behaviour of the system is obtained from the mean relaxation time given by one of equations (36) to (39). It is natural, at this stage, to compare the experimental value with values expected of possible relaxation mechanisms and if two relaxation mechanisms are anticipated, the mean relaxation time is usually compared with the predictions of equation (87). Fig (17) shows that for systems with weight factors C_1 of 0 to 0.5 the estimated and observed mean relaxation time can be greatly at variance. Suppose, for example that the system under investigation relaxes by two mechanisms with relaxation times of 4×10^{-12} sec and 24×10^{-12} sec (i.e. $k = 6$) and C_1 is 0.3. Suspecting this the estimate of the mean relaxation time based on equation (87) would be about 10×10^{-12} sec (see Fig 17) but a value of about 5.5×10^{-12} sec would be obtained experimentally. The difference between this and the lower relaxation time could easily be neglected in view of random errors and environment effects and the true mechanism might be rejected, despite the 30% contribution from the longer relaxation time.

To summarise, it seems that Cole-Cole approximations to data which really conform to Budo behaviour may not achieve their presumed object of estimating τ max except when the ratio of Budo relaxation times is approaching unity. It may eventually be better, with more accurate Budo analyses to obtain τ max from equation (82) but equation (82) should in any case be useful, owing to the sparse frequency coverage, for deciding from the analysis whether the loss is bimodal. For example, it seems from equation (82) and the analysed parameters that the loss curve of 2,6-di-tert-butylphenol is likely to be bimodal. Equation (85) seems useful as a rapid check that the Budo relaxation times are consistent with the Cole-Cole mean relaxation time while equation (84) may be similarly useful as a more accurate check and might be included in a program as a restraint on the analysed parameters.

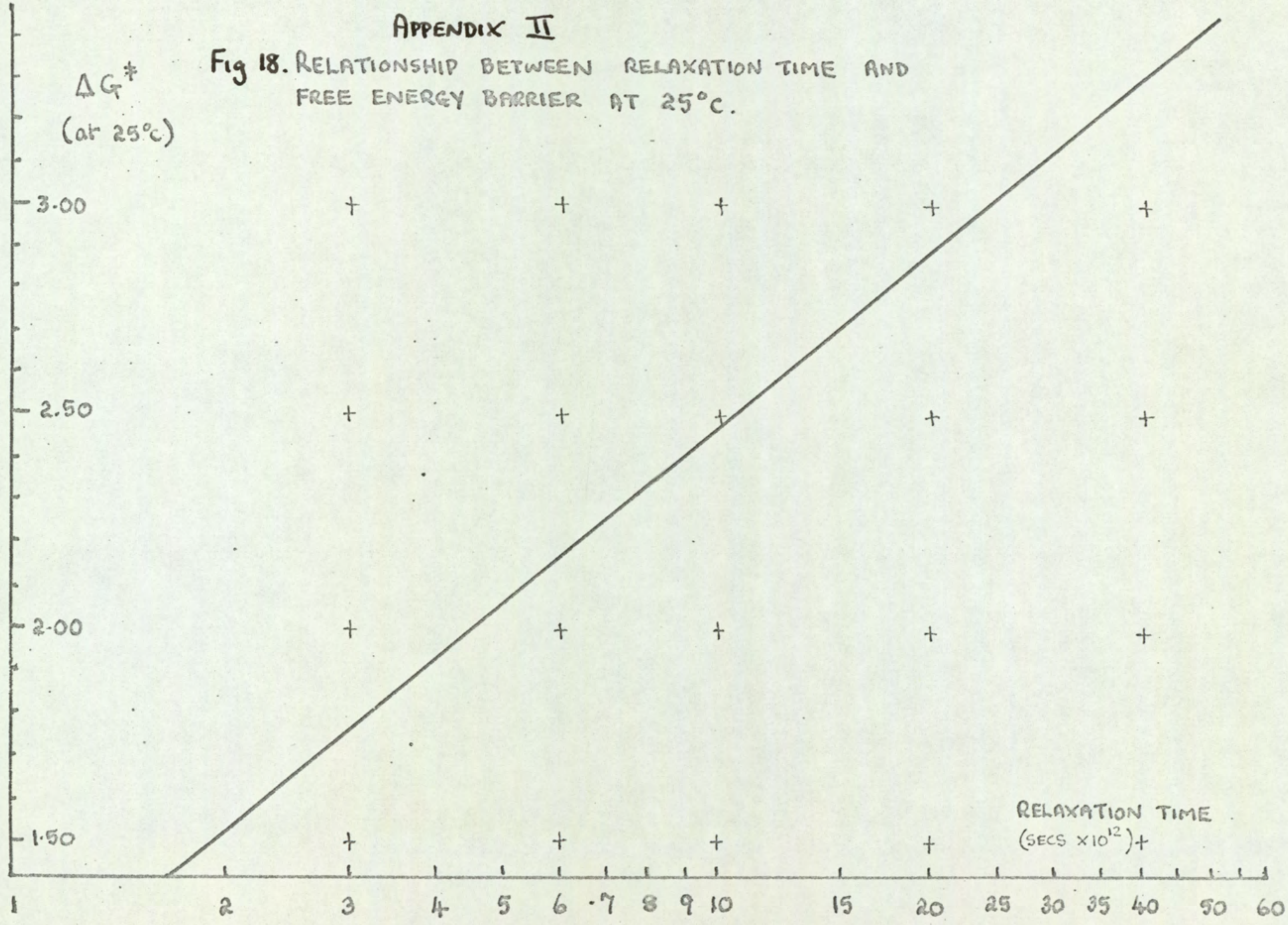
Fig 17. RELATIONSHIPS BETWEEN τ_0 AND τ_1, τ_2 AND C_1.



APPENDIX II

APPENDIX II

Fig 18. RELATIONSHIP BETWEEN RELAXATION TIME AND FREE ENERGY BARRIER AT 25°C.



APPENDIX III

RESULTS

Unless otherwise stated the temperature is 25°C.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ(D)
1. Chloroform (f_2 = 0.1070) in cyclohexane.											
4.07	-	-	-	O	2.0_9	2.08_1	0.054_7	0.054_5	2.178_6	2.05_1	1.0_9
				Q	2.12_6	2.12_2	0.063_2	0.063_6			
(Debye)				K	2.14_3	2.14_4	0.057_6	0.057_1			
(behaviour)				P	2.16_0	2.16_0	0.046_7	0.045_2			
				X	2.17_1	2.17_2	0.028_3	0.028_8			
2. Thiophen (f_2 = 0.4952) in cyclohexane.											
3.15	-	-	-	O	2.0_9	2.23_2	0.058_0	0.058_0	2.315_7	2.18_4	0.5_1
				Q	2.25_9	2.27_1	0.058_8	0.057_3			
(Cole-Cole)				K	2.28_0	2.28_7	0.047_7	0.048_9			
(behaviour)				P	2.28_7	2.30_0	0.036_6	0.038_1			
(α = 0.053)				X	2.29_6	2.30_9	0.022_1	0.024_6			
3. 1-Chloronaphthalene (f_2 = 0.1173) in cyclohexane.											
17.6	-	-	-	O	2.0_7	2.11_1	0.040_9	0.040_9	2.397_1	2.10_1	1.5_8
				Q	2.13_7	2.12_8	0.070_9	0.073_3			
(Cole-Cole)				K	2.15_6	2.14_8	0.096_1	0.095_7			
(behaviour)				P	2.18_7	2.18_0	0.119_0	0.118_7			
(α = 0.057)				X	2.25_3	2.24_6	0.133_2	0.135_4			
4. Chloroform (f_2 = 0.0458) + bromobenzene (f_2 = 0.0636) in cyclohexane.											
8.57	11.8	4.93	0.63	O	2.08_0	2.08_3	0.054_6	0.054_3	2.274_9	2.06_5	-
				Q	2.11_8	2.11_8	0.083_2	0.083_3			
				K	2.14_7	2.14_7	0.094_3	0.093_7			
				P	2.18_0	2.18_1	0.095_1	0.096_0			
				X	2.22_8	2.22_6	0.082_9	0.082_3			

5. Chlorobenzene (f_2 = 0.0522) + bromobenzene (f_2 = 0.0557) in cyclohexane.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
9.41	11.9	7.46	0.50	O	1.9_6	2.08_0	0.053_4	0.055_1	2.303_9	2.06_6	–
				Q	2.11_8	2.11_4	0.094_1	0.092_7			
				K	2.14_4	2.14_7	0.110_0	0.109_6			
				P	2.18_9	2.19_0	0.114_6	0.115_7			
				X	2.24_7	2.24_6	0.099_9	0.099_4			

6. Thiophen (f_2 = 0.4290) + 1-chloronaphthalene (f_2 = 0.0506) in cyclohexane.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
8.01	22.4	4.19	0.49	O	2.1_5	2.24_5	0.070_5	0.068_3	2.473_3	2.21_4	–
				Q	2.28_9	2.29_1	0.089_9	0.090_8			
				K	2.31_0	2.31_9	0.094_5	0.094_3			
				P	2.34_0	2.34_7	0.096_4	0.094_4			
				X	2.38_0	2.38_6	0.090_0	0.091_7			

7. Cholesterol (f_2 = 0.0322) in carbon tetrachloride.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
–	198	3.94	0.76	Q	2.27_4	2.27_5	0.015_5	0.015_1	2.371_6	2.26_0	1.6_5
				K	2.27_5	2.28_0	0.013_5	0.014_5			
				P	2.28_8	2.28_3	0.013_8	0.013_4			
				X	2.28_7	2.28_6	0.013_1	0.013_1			

8. Cholesterol (f_2 = 0.0238) + 1,4-dioxan (f_2 = 0.0380) in cyclohexane.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
–	109	4.54	0.79	Q	2.05_4	2.06_4	0.008_8	0.008_3	2.118_3	2.05_8	1.7
				K	2.06_5	2.06_7	0.007_9	0.008_7			
				P	2.07_4	2.06_9	0.008_3	0.009_0			
				X	2.07_8	2.07_1	0.010_9	0.010_4			

τ_0	τ_1	τ_2	c_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ(D)
9. Cholesterol (f_2 = 0.0399) in p-xylene.											
-	93	4.82	0.67	O	2.2_1	2.29_8	0.019_4	0.019_0	2.422_4	2.29_0	1.8_2
				Q	2.31_0	2.31_1	0.025_1	0.026_1			
				K	2.31_9	2.31_9	0.028_1	0.027_0			
				P	2.32_8	2.32_6	0.026_3	0.026_5			
				X	2.33_0	2.33_3	0.027_1	0.027_1			
10. Cholesterol (f_2 = 0.0426) + hexamethylbenzene (f_2 = 0.0355) in p-xylene.											
-	104	4.94	0.76	O	2.2_2	2.29_5	0.012_9	0.013_0	2.410_5	2.29_0	1.8
				Q	2.29_8	2.30_4	0.018_6	0.018_4			
				K	2.30_9	2.30_9	0.019_1	0.019_7			
				P	2.31_6	2.31_4	0.019_4	0.020_2			
				X	2.32_8	2.31_9	0.022_9	0.022_4			
11. Cholesterol (f_2 = 0.0547) in mesitylene.											
-	120	8.43	0.77	Q	2.30_1	2.30_7	0.018_7	0.017_7	2.439_2	2.29_9	1.7
				K	2.30_7	2.31_2	0.020_0	0.021_7			
				P	2.32_6	2.31_8	0.024_8	0.024_8			
				X	2.33_1	2.32_7	0.028_2	0.027_9			
12. Cholesterol (f_2 = 0.0365) + 1,4-dioxan (f_2 = 0.0831) in p-xylene.											
-	100	5.77	0.74	Q	2.28_9	2.29_3	0.021_2	0.019_6	2.401_3	2.30_0	1.9
				K	2.29_5	2.29_9	0.022_0	0.021_7			
				P	2.30_8	2.30_5	0.020_3	0.022_6			
				X	2.32_0	2.31_2	0.027_5	0.024_5			

τ_o	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_o	ϵ_∞	μ
13. Cholesterol (f_2 = 0.0382) + 1,4-dioxan (f_2 = 0.3456) in p-xylene.											
-	69	6.82	0.65	Q	2.29_2	2.28_7	0.024_6	0.025_0	2.395_9	2.27_3	1.8
				K	2.29_5	2.29_4	0.026_8	0.028_9			
				P	2.30_5	2.30_3	0.032_7	0.031_2			
				X	2.32_1	2.31_4	0.033_3	0.033_5			
14. Cholesterol (f_2 = 0.0282) + 1,4-dioxan (f_2 = 0.6404) in p-xylene.											
-	98	11.5	0.49	Q	2.28_0	2.27_2	0.019_1	0.019_0	2.360_8	2.26_5	1.8
				K	2.28_1	2.27_8	0.022_2	0.024_4			
				P	2.29_1	2.28_6	0.032_5	0.028_8			
				X	2.28_5	2.30_0	0.029_5	0.030_6			
15. Cholesterol (f_2 = 0.0271) + 1,4-dioxan (f_2 = 0.8320) in p-xylene.											
-	178	16.4	0.37	Q	2.26_3	2.26_2	0.017_8	0.018_6	2.366_0	2.25_7	1.8
				K	2.26_8	2.26_7	0.025_7	0.025_4			
				P	2.28_1	2.27_6	0.033_5	0.032_5			
				X	2.29_0	2.29_4	0.031_9	0.038_9			
16. Salicylaldehyde (f_2 = 0.0277) in p-xylene.											
11.9	-	-	-	Q	2.32_7	2.32_1	0.076_9	0.077_3	2.521_2	2.29_1	2.8_8
				K	2.34_7	2.34_6	0.097_9	0.098_1			
	(Debye)			P	2.39_0	2.38_5	0.113_4	0.113_2			
	(behaviour)			X	2.45_1	2.44_6	0.109_6	0.107_9			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
17. 8-Hydroxyquinoline (f_2 = 0.0033) in cyclohexane.											
14	14	4	0.81	Q	2.02_1	2.02_4	0.007_2	0.008_1	2.042_6	2.02_0	2.6_0
				K	2.02_3	2.02_7	0.008_8	0.009_6			
				X	2.03_0	2.03_6	0.009_2	0.010_7			
18. 8-Hydroxyquinoline (f_2 = 0.0049) in cyclohexane.											
11.4	14	4	0.81	Q	2.02_6	2.02_4	0.011_1	0.011_4	2.051_9	2.01_8	2.6_1
				K	2.02_7	2.02_8	0.013_1	0.013_6			
				P	2.03_8	2.03_2	0.016_9	0.015_3			
				X	2.04_1	2.04_0	0.014_9	0.015_1			
19. 8-Hydroxyquinoline (f_2 = 0.0111) in carbon tetrachloride.											
17.5	21	3.5	0.89	Q	2.23_5	2.24_4	0.023_2	0.023_4	2.330_8	2.23_3	2.6_9
				K	2.24_3	2.25_0	0.031_5	0.029_5			
				P	2.26_5	2.25_9	0.044_7	0.044_6			
				X	2.28_7	2.27_8	0.039_2	0.036_8			
20. 8-Hydroxyquinoline (f_2 = 0.0216) in carbon tetrachloride.											
18.6	21	3.5	0.87	Q	2.25_2	2.26_0	0.044_7	0.044_7	2.423_2	2.23_8	2.6_5
				K	2.26_3	2.27_1	0.055_4	0.055_9			
				P	2.29_0	2.28_7	0.068_9	0.069_3			
				X	2.33_6	2.32_4	0.083_4	0.083_8			

τ_o	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_o	ϵ_∞	μ
21. 8-Hydroxyquinoline ($f_2 = 0.0118$) in p-xylene.											
14.5	15.3	3.6	0.95	Q	2.27_9	2.27_9	0.021_8	0.021_5	2.346_1	2.27_1	2.5_2
				K	2.27_7	2.28_5	0.027_4	0.027_8			
				X	2.32_0	2.31_4	0.036_0	0.036_4			
22. 8-Hydroxyquinoline ($f_2 = 0.0180$) in p-xylene.											
14.7	15.3	3.6	0.95	Q	2.28_4	2.29_1	0.033_6	0.031_6	2.390_3	2.27_9	2.4_8
				K	2.29_3	2.30_0	0.037_6	0.040_9			
				P	2.32_8	2.31_5	0.050_5	0.049_9			
				X	2.34_5	2.34_3	0.054_6	0.053_8			
23. o-Nitrophenol ($f_2 = 0.0066$) in n-heptane.											
6.4	7.4	2.4	0.75	Q	1.93_1	1.93_0	0.022_4	0.022_5	1.960_6	1.90_9	3.4_0
				K	1.93_7	1.93_8	0.023_2	0.023_2			
				P	1.94_3	1.94_6	0.021_9	0.021_5			
				X	1.96_1	1.95_4	0.015_5	0.015_8			
24. o-Nitrophenol ($f_2 = 0.0119$) in n-heptane.											
6.8	7.6	2.2	0.81	Q	1.94_5	1.94_6	0.039_4	0.039_3	2.003_4	1.91_2	3.3_6
				K	1.95_3	1.96_0	0.041_8	0.041_7			
				P	1.98_0	1.97_5	0.038_5	0.039_4			
				X	1.99_7	1.99_1	0.030_2	0.029_6			

25. o-Nitrophenol (f_2 = 0.0051) in cyclohexane.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
8.4	8.8	3.1	0.94	O	1.9_9	2.02_5	0.013_0	0.012_7	2.070_4	2.02_1	3.1_0
				Q	2.03_5	2.03_3	0.021_5	0.020_4			
				K	2.03_5	2.04_0	0.021_8	0.023_5			
				P	2.05_3	2.05_0	0.025_5	0.023_9			
				X	2.06_1	2.06_1	0.019_6	0.019_4			

26. o-Nitrophenol (f_2 = 0.0071) in cyclohexane.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
8.6	9.2	2.7	0.92	O	1.9_8	2.02_8	2.018_7	0.017_6	2.091_2	2.02_2	3.1_0
				Q	2.03_7	2.03_9	2.028_1	0.027_8			
				K	2.04_4	2.04_9	2.030_7	0.032_1			
				P	2.06_4	2.06_1	2.034_6	0.033_1			
				X	2.08_0	2.07_7	2.027_5	0.027_3			

27. o-Nitrophenol (f_2 = 0.0079) in cyclohexane.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
8.4	8.9	2.2	0.92	O	2.0_1	2.03_1	0.020_0	0.019_8	2.100_0	2.02_4	3.0_8
				Q	2.04_0	2.04_3	0.031_6	0.030_7			
				K	2.05_1	2.05_4	0.034_7	0.035_3			
				P	2.06_5	2.06_8	0.036_7	0.036_1			
				X	2.08_3	2.08_5	0.029_1	0.029_5			

28. o-Nitrophenol (f_2 = 0.0202) in carbon tetrachloride.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
14.4	16.4	4.3	0.86	Q	2.27_2	2.27_2	0.073_9	0.070_5	2.480_0	2.23_9	3.1_2
				K	2.28_2	2.29_2	0.084_8	0.087_5			
				P	2.31_9	2.32_2	0.103_3	0.103_8			
				X	2.38_8	2.37_9	0.112_6	0.111_4			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
29. o-Nitrophenol ($f_2 = 0.0250$) in carbon tetrachloride.											
14.5	15.0	4.1	0.96	Q	2.27_9	2.28_0	0.086_3	0.083_7	2.539_2	2.24_9	3.0_8
				K	2.29_7	2.30_4	0.105_4	0.108_4			
				P	2.34_4	2.34_3	0.132_8	0.131_8			
				X	2.42_1	2.41_8	0.140_6	0.140_4			
30. o-Nitrophenol ($f_2 = 0.0069$) in p-xylene.											
12.9	14.5	4.9	0.88	Q	2.27_3	2.27_5	0.019_5	0.019_6	2.329_8	2.26_7	3.0_4
				K	2.28_1	2.28_1	0.024_2	0.024_5			
				P	2.29_5	2.29_0	0.028_9	0.028_7			
				X	2.31_1	2.30_6	0.029_8	0.029_3			
31. o-Nitrophenol ($f_2 = 0.0099$) in p-xylene.											
13.1	14.5	5.0	0.90	Q	2.28_2	2.28_0	0.027_5	0.027_9	2.359_0	2.26_8	3.0_3
				K	2.28_9	2.28_8	0.034_7	0.035_3			
				P	2.30_5	2.30_1	0.043_2	0.041_7			
				X	2.32_7	2.32_4	0.043_1	0.042_9			
32. o-Nitrophenol ($f_2 = 0.0146$) in p-xylene.											
13.1	14.6	4.7	0.88	Q	2.29_5	2.29_3	0.042_1	0.041_9	2.408_5	2.27_4	3.0_4
				K	2.30_1	2.30_5	0.052_4	0.052_2			
				P	2.32_5	2.32_4	0.060_4	0.061_0			
				X	2.36_0	2.35_8	0.063_0	0.062_5			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
33. o-Nitrophenol (f_2 = 0.0206) in p-xylene											
13.8	15.9	5.5	0.84	Q	2.30_6	2.30_5	0.058_1	0.058_0	2.471_9	2.28_0	3.0_5
				K	2.32_0	2.32_2	0.074_0	0.072_4			
				P	2.34_4	2.34_8	0.082_8	0.085_2			
				X	2.40_3	2.39_5	0.090_8	0.089_3			
34. p-Nitrophenol (f_2 = 0.0065) in p-xylene.											
41	46	10	0.94	Q	2.26_6	2.26_8	0.018_0	0.018_4	2.427_2	2.26_5	4.9_4
				K	2.27_5	2.27_0	0.024_0	0.025_7			
				X	2.29_7	2.29_0	0.056_6	0.054_0			
35. 2,4-Dinitrophenol (f_2 = 0.0132) in p-xylene.											
30	40	16	0.67	O	2.2_2	2.27_3	0.011_4	0.008_9	2.379_2	2.27_2	2.8_5
				Q	2.26_4	2.27_6	0.017_8	0.017_3			
				K	2.27_4	2.27_9	0.023_0	0.024_0			
				P	2.29_5	2.28_6	0.030_5	0.032_3			
				X	2.30_7	2.30_2	0.044_3	0.032_3			
36. 2,4-Dinitrophenol (f_2 = 0.0278) in p-xylene.											
34	55	14	0.63	Q	2.29_1	2.30_3	0.037_7	0.036_3	2.520_4	2.29_4	2.8_6
				K	2.30_5	2.31_2	0.049_4	0.049_1			
				P	2.32_4	2.32_6	0.062_9	0.063_5			
				X	2.35_6	2.35_6	0.080_6	0.080_7			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
37. 2,4-Dinitrophenetole (f_2 = 0.0128) in p-xylene.											
49	-	-	-	Q	2.29_3	2.29_8	0.038_9	0.035_2	2.671_6	2.29_5	5.4_2
				K	2.31_1	2.30_2	0.060_7	0.050_6			
	(Debye)			P	2.29_7	2.31_0	0.060_3	0.073_4			
	(behaviour)			X	2.34_5	2.33_6	0.120_8	0.118_2			
38. 2,6-Dinitrophenol (f_2 = 0.0077) in p-xylene.											
29	41	20	0.63	Q	2.26_4	2.26_6	0.016_3	0.016_4	2.371_6	2.26_3	3.7_5
				K	2.27_0	2.26_9	0.020_0	0.022_9			
				P	2.28_2	2.27_5	0.032_3	0.031_6			
				X	2.30_2	2.29_0	0.044_6	0.044_3			
39. 2,6-Dinitrophenol (f_2 = 0.0101) in p-xylene.											
29	41	18	0.62	Q	2.26_3	2.27_1	0.022_0	0.021_7	2.306_1	2.26_7	3.7_0
				K	2.28_0	2.27_5	0.028_7	0.030_3			
				P	2.29_4	2.28_3	0.039_7	0.041_3			
				X	2.31_7	2.30_4	0.057_7	0.056_8			
40. o-Chlorophenol (f_2 = 0.0332) in cyclohexane.											
9.1	12	3.6	0.85	Q	2.03_6	2.04_0	0.013_2	0.012_9	2.069_4	2.03_3	1.0_9
				K	2.04_1	2.04_4	0.014_6	0.015_3			
				P	2.05_5	2.05_1	0.017_2	0.016_9			
				X	2.05_7	2.06_2	0.011_1	0.015_6			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ

41. o-Chlorophenol (f_2 = 0.0594) in p-xylene.

14.3	18	4.4	0.79	Q	2.28_1	2.29_4	0.026_0	0.026_7	2.370_0	2.27_9	1.2_4
				K	2.29_0	2.30_1	0.031_9	0.032_1			
				P	2.31_2	2.31_2	0.038_6	0.037_3			
				X	2.34_2	2.33_1	0.037_7	0.040_4			

42. o-Chlorophenol (f_2 = 0.0791) in p-xylene.

14.3	18	4.4	0.83	O	2.32_9	2.30_0	0.023_6	0.021_4	2.417_4	2.29_4	1.2_5
				Q	2.30_1	2.31_1	0.033_9	0.035_0			
				K	2.31_9	2.32_1	0.042_9	0.043_0			
				P	2.32_6	2.33_5	0.052_9	0.051_0			
				X	2.36_6	2.36_2	0.056_2	0.056_2			

43. o-Bromophenol (f_2 = 0.0277) in p-xylene.

16.4	22	4.8	0.75	O	2.28_0	2.28_2	0.008_7	0.009_0	2.331_6	2.27_9	1.3_8
				Q	2.28_6	2.28_7	0.013_8	0.014_3			
				K	2.28_4	2.29_1	0.016_6	0.017_0			
				P	2.29_5	2.29_6	0.022_2	0.019_7			
				X	2.30_6	2.30_6	0.019_6	0.022_4			

44. o-Bromophenol (f_2 = 0.0359) in p-xylene.

18.7	22	4.8	0.79	O	2.28_5	2.28_8	0.010_5	0.010_9	2.351_7	2.28_5	1.3_6
				Q	2.28_0	2.29_3	0.017_3	0.017_6			
				K	2.28_8	2.29_8	0.021_7	0.021_3			
				P	2.30_4	2.30_5	0.026_0	0.025_3			
				X	2.31_9	2.31_8	0.025_7	0.029_4			

45. 2,4-Dichlorophenol (f_2 = 0.0230) in p-xylene.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
28.7	33	7.2	0.75	O	2.24_0	2.27_4	0.003_6	0.005_2	2.315_7	2.27_3	1.3_6
				Q	2.26_1	2.27_7	0.008_1	0.009_2			
				K	2.27_2	2.27_9	0.012_2	0.011_5			
				P	2.28_0	2.28_2	0.014_5	0.013_8			
				X	2.28_8	2.28_9	0.016_8	0.016_9			

46. 2,4-Dichlorophenol (f_2 = 0.0283) in p-xylene.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
26.4	33	7.2	0.75	Q	2.25_4	2.27_8	0.012_4	0.012_1	2.329_6	2.27_3	1.4_1
				K	2.26_7	2.28_1	0.014_6	0.015_2			
				P	2.28_3	2.28_6	0.021_8	0.018_3			
				X	2.29_8	2.29_4	0.022_9	0.022_4			

47. 2,4-Dibromophenol in benzene at 20°C. 'a' values.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
23	42	5.4	0.50	3.22*	1.8	2.0	0.72	0.72	3.1	0.85	1.3_5
				10*	2.5	2.7	0.63	0.66			
				25*	3.05	3.00	0.35	0.37			
				50*	3.05	3.07	0.20	0.20			

*Wavelength in cm. See ref (32).

48. 2,4,6-Trichlorophenol (f_2 = 0.0414) in cyclohexane.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
17.2	30	16	0.21	Q	2.04_5	2.04_2	0.009_4	0.010_2	2.080_5	2.03_9	1.0_0
				K	2.04_6	2.04_4	0.012_2	0.013_7			
				P	2.05_1	2.04_9	0.020_2	0.017_5			
				X	2.06_1	2.05_9	0.021_4	0.020_3			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
49. 2,4,6-Trichlorophenol ($f_2 = 0.0364$) in p-xylene.											
22.6	45	15	0.32	Q	2.28_7	2.29_0	0.015_0	0.017_2	2.362_8	2.28_5	1.4_6
				K	2.28_0	2.29_4	0.021_8	0.023_2			
				P	2.30_2	2.30_2	0.027_4	0.029_5			
				X	2.32_3	2.31_8	0.033_1	0.034_6			
50. 2,4,6-Trichlorophenol ($f_2 = 0.0439$) in p-xylene.											
22.6	46	15	0.32	Q	2.29_9	2.30_7	0.020_7	0.020_5	2.393_6	2.30_1	1.4_5
				K	2.32_3	2.31_2	0.023_6	0.027_6			
				P	2.31_0	2.32_2	0.032_2	0.035_1			
				X	2.33_8	2.34_1	0.042_2	0.041_2			
51. 2,4,6-Tribromophenol ($f_2 = 0.0074$) in p-xylene.											
34	80	15	0.30	Q	2.26_4	2.27_1	0.003_6	0.005_0	2.292_4	2.26_9	1.7_8
				K	2.26_9	2.27_2	0.004_9	0.006_7			
				P	2.27_0	2.27_5	0.008_5	0.008_4			
				X	2.27_8	2.28_1	0.007_4	0.009_5			
52. Guaiacol ($f_2 = 0.0606$) in p-xylene.											
16	19	5	0.90	Q	2.31_6	2.32_8	0.079_9	0.083_6	2.624_6	2.29_6	2.3_3
				K	2.34_4	2.34_9	0.105_4	0.108_0			
				P	2.38_1	2.38_2	0.122_4	0.134_0			
				X	2.47_6	2.45_9	0.158_3	0.156_1			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
53. Guaiacol ($f_2 = 0.0615$) in p-xylene.											
18.7	19	5	0.90	O	2.28_5	2.31_0	0.049_8	0.047_9	2.633_2	2.30_0	2.3_3
				Q	2.32_3	2.33_2	0.083_4	0.084_7			
				K	2.34_5	2.35_4	0.107_2	0.109_2			
				P	2.40_5	2.38_7	0.135_0	0.135_8			
				X	2.46_8	2.46_5	0.160_7	0.158_2			
54. Catechol (solution saturated at 20°C) in p-xylene.											
15.3	18	5	0.91	Q	2.26_5	2.27_0	0.011_7	0.012_9	2.314_3	2.26_5	-
				K	2.27_5	2.27_3	0.015_5	0.016_6			
				P	2.28_6	2.27_9	0.024_1	0.020_6			
				X	2.29_4	2.29_0	0.022_4	0.023_5			
55. Nitrobenzene ($f_2 = 0.0129$) in p-xylene.											
13.2	-	-	-	Q	2.29_2	2.29_0	0.058_7	0.058_7	2.460_0	2.27_0	3.8_4
				K	2.30_5	2.30_8	0.076_8	0.076_2			
	(Debye)			P	2.33_2	2.33_8	0.091_0	0.091_0			
	(behaviour)			X	2.39_8	2.38_9	0.090_0	0.091_9			
56. o-Nitrophenol ($f_2 = 0.0162$) in p-xylene at 60°C.											
9.8	10.5	1.2	0.86	Q	2.23_8	2.24_6	0.049_3	0.049_2	2.349_6	2.20_8	3.1_0
				K	2.25_6	2.26_2	0.059_0	0.058_5			
				P	2.28_8	2.28_4	0.061_7	0.063_2			
				X	2.31_5	2.31_6	0.055_5	0.055_8			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
57. 2,6-Dinitrophenol ($f_2 = 0.00961$) in p-xylene at 37.5°C.											
24	33	15	0.59	Q	2.25_8	2.26_4	0.022_8	0.023_0	2.378_0	2.25_8	3.6_0
				K	2.26_5	2.26_9	0.031_2	0.031_6			
				P	2.28_0	2.27_9	0.041_8	0.041_7			
				X	2.30_7	2.30_1	0.052_9	0.053_2			
58. 2,6-Dinitrophenol ($f_2 = 0.00914$) in p-xylene at 50°C.											
21	23	7	0.84	Q	2.22_8	2.23_8	0.029_7	0.028_0	2.348_7	2.22_8	3.7_6
				K	2.24_2	2.24_5	0.036_1	0.036_4			
				P	2.25_5	2.25_6	0.044_5	0.045_5			
				X	2.28_2	2.28_0	0.055_6	0.055_1			
59. 2,6-Dinitrophenol ($f_2 = 0.00961$) in p-xylene at 60°C.											
21	23	6	0.89	Q	2.20_0	2.21_0	0.027_0	0.027_0	2.322_0	2.20_1	3.6_6
				K	2.21_0	2.21_7	0.036_1	0.035_3			
				P	2.22_0	2.22_7	0.043_5	0.044_8			
				X	2.26_2	2.25_1	0.054_2	0.055_6			
60. 2,4-Dinitrophenol ($f_2 = 0.0179$) in p-xylene at 37.5°C.											
28	43	8	0.70	Q	2.27_9	2.27_7	0.027_0	0.028_5	2.406_4	2.26_5	2.8_4
				K	2.28_3	2.28_5	0.031_7	0.035_7			
				P	2.30_3	2.29_6	0.039_2	0.042_0			
				X	2.32_0	2.31_3	0.047_6	0.050_2			

τ_o	τ_1	τ_2	C_1		ϵ'obs	ϵ'calc	ϵ''obs	ϵ''calc	ϵ_o	ϵ_∞	μ
61. 2,4-Dinitrophenol (f_2 = 0.0123) in p-xylene at 50°C.											
18	20	6.	0.90	Q	2.23_2	2.23_5	0.021_6	0.023_2	2.320_9	2.22_7	2.8_4
				K	2.23_7	2.24_1	0.031_8	0.030_3			
				P	2.24_9	2.25_1	0.038_7	0.038_0			
				X	2.27_1	2.27_2	0.043_2	0.044_9			
62. 2,4-Dinitrophenol (f_2 = 0.0179) in p-xylene at 60°C.											
15	17	2.5	0.87	Q	2.23_0	2.23_7	0.028_3	0.027_9	2.323_5	2.22_1	2.4_7
				K	2.24_1	2.24_5	0.033_4	0.034_6			
				P	2.26_1	2.25_6	0.042_6	0.041_8			
				X	2.28_0	2.27_9	0.045_5	0.046_8			
63. p-Cresol (f_2 = 0.0638) in cyclohexane.											
28	-	-	-	Q	2.08_1	2.07_6	0.026_4	0.025_8	2.192_0	2.05_4	1.4_4
	(Cole-Cole)			K	2.07_2	2.08_3	0.029_5	0.030_4			
	(behaviour)			P	2.09_9	2.09_2	0.035_5	0.034_9			
	(α = 0.31)			X	2.10_6	2.10_8	0.039_2	0.039_8			
64. p-Cresol (f_2 = 0.0265) in carbon tetrachloride.											
14	-	-	-	Q	2.25_1	2.25_4	0.021_9	0.020_7	2.314_3	2.24_1	1.5_0
	(Cole-Cole)			K	2.25_3	2.26_1	0.023_5	0.024_5			
	(behaviour)			P	2.28_0	2.26_9	0.026_0	0.027_5			
	(α = 0.16)			X	2.28_4	2.28_2	0.029_1	0.028_2			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
65. p-Cresol (f_2 = 0.0209) in p-xylene.											
16.3	-	-	-	Q	2.26_9	2.27_6	0.015_6	0.015_1	2.326_0	2.26_8	1.6_7
	(Cole-Cole)			K	2.27_3	2.28_0	0.017_3	0.018_7			
	(behaviour)			P	2.29_3	2.28_7	0.023_5	0.022_0			
	(α = 0.12)			X	2.30_2	2.29_8	0.021_9	0.023_9			
66. p-Cresol (f_2 = 0.0374) in p-xylene.											
17	-	-	-	Q	2.28_7	2.29_1	0.024_5	0.024_5	2.372_9	2.27_6	1.6_1
	(Cole-Cole)			K	2.28_9	2.29_8	0.030_5	0.030_0			
	(behaviour)			P	2.31_5	2.30_8	0.033_8	0.035_0			
	(α = 0.15)			X	2.33_0	2.32_5	0.038_0	0.038_0			
67. p-Chlorophenol (f_2 = 0.0211) in cyclohexane.											
14	-	-	-	Q	2.07_6	2.07_1	0.033_2	0.033_5	2.16_0	2.04_8	1.7_7
	(Cole-Cole)			K	2.07_7	2.08_1	0.039_7	0.039_7			
	(behaviour)			P	2.09_4	2.09_4	0.045_8	0.044_4			
	(α = 0.16)			X	2.10_9	2.11_6	0.044_2	0.045_4			
68. p-Chlorophenol (f_2 = 0.0309) in p-xylene.											
25	-	-	-	Q	2.28_6	2.28_3	0.030_3	0.032_1	2.437_6	2.27_2	2.2_4
	(Cole-Cole)			K	2.29_2	2.29_1	0.043_7	0.042_4			
	(behaviour)			P	2.31_7	2.30_3	0.057_1	0.054_6			
	(α = 0.09)			X	2.30_9	2.33_1	0.067_3	0.068_9			

τ_o	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_o	ϵ_∞	μ
69. p-Cresol (f_2 = 0.0163) + acetone (f_3 = 0.0098) in cyclohexane.											
13	-	-	-	O	2.0_9	2.05_5	0.025_6	0.024_7	2.159_4	2.02_1	(2.1_0)
				Q	2.07_6	2.06_8	0.027_8	0.028_8			
	(Cole-Cole)			K	2.08_5	2.07_6	0.028_9	0.030_4			
	(behaviour)			P	2.09_2	2.08_5	0.029_6	0.031_4			
	(α = 0.46)			X	2.09_7	2.09_7	0.023_5	0.031_3			
70. p-Cresol (f_2 = 0.0566) + acetone (f_3 = 0.0343) in cyclohexane.											
35	-	-	-	O	2.0_6	2.15_3	0.068_8	0.068_5	2.615_1	2.07_4	(2.3_4)
				Q	2.18_7	2.18_8	0.090_9	0.087_7			
	(Cole-Cole)			K	2.20_4	2.21_1	0.096_0	0.098_0			
	(behaviour)			P	2.23_7	2.23_8	0.105_1	0.107_9			
	(α = 0.45)			X	2.26_8	2.28_2	0.120_5	0.118_7			
71. p-Cresol (f_2 = 0.0835) + acetone (f_3 = 0515) in cyclohexane.											
39	-	-	-	O	2.1_2	2.20_0	0.098_1	0.097_9	2.909_8	2.09_5	(2.3_6)
				Q	2.24_3	2.24_8	0.129_3	0.128_5			
	(Cole-Cole)			K	2.28_9	2.28_1	0.144_7	0.145_4			
	(behaviour)			P	2.32_6	2.32_2	0.159_4	0.162_4			
	(α= 0.43)			X	2.38_3	2.38_9	0.185_1	0.181_9			
72. Phenol (f_2 = 0.0221) in p-xylene.											
11.7	-	-	-	Q	2.26_7	2.27_6	0.015_1	0.016_9	2.319_3	2.26_9	1.5_1
				K	2.27_1	2.28_2	0.020_2	0.021_4			
	(Debye)			P	2.30_1	2.29_0	0.028_2	0.024_6			
	(behaviour)			X	2.30_3	2.30_3	0.020_5	0.023_2			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
73. Phenol (f_2 = 0.0510) in p-xylene.											
13.8	-	-	-	Q	2.30_2	2.30_2	0.037_2	0.036_8	2.408_4	2.28_1	1.5_5
	(Cole-Cole)			K	2.30_7	2.31_3	0.043_4	0.044_8			
	(behaviour)			P	2.33_5	2.32_9	0.053_2	0.051_2			
	(α= 0.11)			X	2.35_1	2.35_5	0.051_0	0.052_4			
74. Phenol (f_2 = 0.0800) in p-xylene.											
16.7	-	-	-	Q	2.30_2	2.32_1	0.049_7	0.050_0	2.501_1	2.30_5	1.5_7
	(Cole-Cole)			K	2.32_2	2.33_4	0.065_0	0.066_5			
	(behaviour)			P	2.37_5	2.35_8	0.085_0	0.083_6			
	(α= 0.02)			X	2.40_8	2.40_5	0.092_9	0.094_8			
75. Phenol (f_2 = 0.1674) in p-xylene.											
28.5	-	-	-	Q	2.35_8	2.37_6	0.094_5	0.095_7	2.866_9	2.33_2	1.8_1
	(Cole-Cole)			K	2.38_8	2.39_9	0.122_9	0.123_3			
	(behaviour)			P	2.46_3	2.43_4	0.156_8	0.155_3			
	(α= 0.15)			X	2.51_3	2.50_9	0.194_0	0.195_5			
76. Phenol (f_2 = 0.2751) in p-xylene.											
41.4	-	-	-	Q	2.42_5	2.44_4	0.143_4	0.151_0	3.468_6	2.37_9	1.9_9
	(Cole-Cole)			K	2.47_2	2.47_6	0.199_5	0.197_0			
	(behaviour)			P	2.55_4	2.52_6	0.264_5	0.254_4			
	(α= 0.17)			X	2.63_4	2.63_9	0.334_3	0.341_3			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
77. o-Nitrophenol (f_2 = 0.0063) in 1,4-dioxan.											
30	–	–	–	Q	2.23_6	2.24_5	0.010_8	0.011_6	2.317_5	2.24_3	2.9_6
	(Cole-Cole)			K	2.25_0	2.24_7	0.015_8	0.016_2			
	(behaviour)			P	2.25_5	2.25_1	0.024_0	0.022_4			
	(α = 0.02)			X	2.26_2	2.26_2	0.030_6	0.031_6			
78. o-Nitrophenol (f_2 = 0.0072) in 1,4 dioxan.											
28	–	–	–	Q	2.25_4	2.25_3	0.012_4	0.013_0	2.331_6	2.23_5	2.8_8
	(Debye)			K	2.25_3	2.25_5	0.015_4	0.018_3			
	(behaviour)			P	2.26_6	2.26_0	0.027_5	0.025_4			
				X	2.27_1	2.27_3	0.036_8	0.036_1			
79. o-Nitrophenol (f_2 = 0.0120) in 1,4-dioxan.											
30	–	–	–	Q	2.26_0	2.26_0	0.022_4	0.022_2	2.396_1	2.25_5	2.9_5
	(Cole-Cole)			K	2.26_6	2.26_4	0.031_3	0.030_7			
	(behaviour)			P	2.27_5	2.27_2	0.041_4	0.042_0			
	(α = 0.04)			X	2.28_7	2.29_3	0.059_1	0.058_8			
80. 2,6-Dinitrophenol (f_2 = 0.0058) in 1,4-dioxan.											
47	–	–	–	Q	2.23_1	2.24_3	0.010_4	0.010_9	2.337_4	2.24_0	3.5_2
	(Cole-Cole)			K	2.26_0	2.24_4	0.014_1	0.014_9			
	(behaviour)			P	2.25_2	2.24_8	0.021_4	0.020_6			
	(α = 0.08)			X	2.26_4	2.25_6	0.029_7	0.030_4			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
81. 2,4-Dinitrophenol (f_2 = 0.0099) in 1,4-dioxan.											
53	-	-	-	Q	2.25_3	2.25_6	0.010_7	0.012_4	2.398_6	2.25_5	3.2_8
				K	2.25_7	2.25_7	0.018_1	0.017_8			
		(Debye)		P	2.26_2	2.26_0	0.026_5	0.025_9			
		(behaviour)		X	2.27_0	2.26_9	0.042_1	0.042_2			
82. 2,4-Dinitrophenol (f_2 = 0.0158) in 1,4-dioxan.											
64	-	-	-	Q	2.26_6	2.27_0	0.018_1	0.017_0	2.509_0	2.26_8	3.3_6
				K	2.26_8	2.27_1	0.019_6	0.024_5			
		(Debye)		P	2.27_4	2.27_4	0.037_6	0.035_9			
		(behaviour)		X	2.29_1	2.28_4	0.060_3	0.059_7			
83. 8-Hydroxyquinoline (f_2 = 0.0078) in 1,4-dioxan.											
38	-	-	-	Q	2.22_1	2.23_6	0.002_7	0.006_2	2.286_6	2.23_5	2.2_2
		(Debye)		K	2.24_0	2.23_7	0.005_6	0.008_8			
		(behaviour)		X	2.24_1	2.24_4	0.023_5	0.019_5			
84. 8-Hydroxyquinoline (f_2 = 0.0113) in 1,4-dioxan.											
39	-	-	-	Q	2.23_6	2.23_9	0.003_3	0.009_2	2.318_2	2.23_7	2.3_1
				K	2.24_7	2.24_0	0.010_1	0.013_2			
				P	2.24_6	2.24_2	0.017_7	0.018_9			
				X	2.25_0	2.25_0	0.034_9	0.029_5			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
85. o-Nitrophenol (f_2 = 0.0054) + DBO (f_3 = 0.0054) in cyclohexane.											
10.4	-	-	-	Q	2.02_4	2.03_0	0.019_6	0.019_4	2.073_7	2.01_9	3.1_6
	(Cole-Cole)			K	2.03_5	2.03_6	0.022_8	0.023_3			
	(behaviour)			P	2.04_1	2.04_5	0.025_4	0.025_2			
	(α = 0.05)			X	2.05_9	2.05_8	0.022_3	0.022_8			
86. o-Nitrophenol (f_2 = 0.0155) + DBO (f_3 = 0.0155) in p-xylene.											
17	-	-	-	Q	2.29_2	2.30_3	0.043_4	0.043_3	2.454_0	2.28_3	3.3_2
	(Cole-Cole)			K	2.31_3	2.31_5	0.054_1	0.054_6			
	(behaviour)			P	2.33_9	2.33_3	0.065_1	0.065_5			
	(α = 0.10)			X	2.37_6	2.36_8	0.072_3	0.072_7			
87. o-Nitrophenol (f_2 = 0.0232) + DBO (f_3 = 0.232) in p-xylene.											
17	-	-	-	Q	2.33_3	2.35_5	0.062_8	0.064_4	2.558_3	2.30_4	3.3_1
	(Cole-Cole)			K	2.34_9	2.35_3	0.082_9	0.081_4			
	(behaviour)			P	2.38_2	2.38_0	0.098_1	0.097_7			
	(α = 0.10)			X	2.43_0	2.43_1	0.107_2	0.108_4			
88. o-Nitrophenol (f_2 = 0.0503) + DBO (f_3 = 0.0503) in p-xylene.											
25	-	-	-	Q	2.43_1	2.43_6	0.131_2	0.130_7	3.021_7	2.36_4	3.6_2
	(Cole-Cole)			K	2.46_8	2.46_9	0.163_7	0.163_6			
	(behaviour)			P	2.51_8	2.51_8	0.197_0	0.199_0			
	(α = 0.18)			X	2.62_3	2.61_4	0.238_8	0.237_8			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
89. 2,4-Dinitrophenetole ($f_2 = 0.0123$) + DBO ($f_3 = 0.0123$) in p-xylene.											
47	-	-	-	Q	2.28_9	2.29_7	0.039_6	0.037_1	2.655_8	2.29_1	5.3_6
	(Cole-Cole)			K	2.31_9	2.30_2	0.054_9	0.052_5			
	(behaviour)			P	2.30_1	2.31_1	0.069_9	0.074_5			
	($\alpha = 0.03$)			X	2.34_2	2.34_1	0.116_9	0.115_8			
90. o-Chlorophenol ($f_2 = 0.0729$) + DBO ($f_3 = 0.0109$) in p-xylene.											
30	-	-	-	Q	2.33_5	2.33_9	0.039_1	0.039_8	2.534_6	2.31_3	1.7_0
	(Cole-Cole)			K	2.34_8	2.34_9	0.049_5	0.048_8			
	(behaviour)			P	2.36_7	2.36_3	0.058_8	0.058_6			
	($\alpha = 0.24$)			X	2.39_3	2.39_0	0.069_5	0.070_1			
91. o-Chlorophenol ($f_2 = 0.0655$) + DBO ($f_3 = 0.0181$) in p-xylene.											
41	-	-	-	Q	2.33_3	2.34_1	0.041_3	0.041_1	2.585_6	2.31_5	1.9_6
	(Cole-Cole)			K	2.34_3	2.35_1	0.050_2	0.050_9			
	(behaviour)			P	2.37_9	2.36_5	0.061_9	0.062_2			
	($\alpha = 0.26$)			X	2.40_2	2.39_2	0.077_4	0.077_6			
92. Guaiacol ($f_2 = 0.0441$) + DBO ($f_3 = 0.0441$) in p-xylene.											
31	-	-	-	Q	2.29_4	2.31_4	0.038_8	0.038_6	2.527_6	2.29_8	2.2_5
	(Cole-Cole)			K	2.32_7	2.32_3	0.052_9	0.050_1			
	(behaviour)			P	2.33_5	2.33_7	0.058_6	0.063_9			
	($\alpha = 0.14$)			X	2.39_1	2.36_7	0.083_2	0.082_4			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
93. 2,6-Di-tert-butylphenol (f_2 = 0.0386) in p-xylene.											
8.63	37	6.0	0.31	O	2.2_4	2.27_8	0.023_7	0.023_3	2.364_2	2.27_0	1.5_6
				Q	2.29_4	2.29_4	0.032_7	0.034_8			
				K	2.30_3	2.30_7	0.037_1	0.037_4			
				P	2.32_9	2.31_9	0.036_1	0.036_1			
				X	2.34_5	2.33_3	0.031_5	0.031_5			
94. 2,6-Di-tert-butylphenol (f_2 = 0.0351) + DBO (f_2 = 0.0070) in p-xylene.											
9.19	35	4.85	0.43	O	2.2_1	2.28_0	0.021_6	0.022_8	2.362_2	2.27_0	1.6_2
				Q	2.29_5	2.29_5	0.030_1	0.031_3			
				K	2.30_6	2.30_6	0.031_3	0.032_3			
				P	2.32_6	2.31_5	0.030_9	0.031_1			
				X	2.34_3	2.32_6	0.029_4	0.029_3			
95. 2,4,6-Tribromophenol (f_2 = 0.0209) in 1,4-dioxan.											
29	-	-	-	Q	2.29_6	2.29_7	0.026_6	0.027_8	2.427_2	2.27_6	2.1_5
	(Cole-Cole)			K	2.30_5	2.30_5	0.036_5	0.033_2			
	(behaviour)			P	2.31_3	2.31_4	0.036_3	0.038_8			
	(α = 0.29)			X	2.33_3	2.33_2	0.044_9	0.045_1			
96. 2,4,6-Trichlorophenol (f_2 = 0.0285) + 1,4-dioxan (f_3 = 0.2778) in p-xylene.											
39	-	-	-	Q	2.28_2	2.28_8	0.013_2	0.013_5	2.382_6	2.28_3	1.7_8
	(Cole-Cole)			K	2.28_8	2.29_0	0.017_9	0.018_1			
	(behaviour)			P	2.29_9	2.29_5	0.024_4	0.024_0			
	(α= 0.12)			X	2.31_0	2.30_5	0.033_0	0.033_3			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
97. 2,4,6-Trichlorophenol ($f_2 = 0.0296$) in 1,4-dioxan.											
40	-	-	-	Q	2.29_5	2.29_4	0.027_4	0.027_5	2.456_0	2.27_6	2.0_0
	(Cole-Cole)			K	2.30_5	2.30_0	0.035_6	0.034_1			
	(behaviour)			P	2.30_6	2.31_0	0.039_8	0.041_5			
	($\alpha = 0.26$)			X	2.32_3	2.32_8	0.052_1	0.051_6			
98. 2,4,6-Trichlorophenol (0.3544 molar) + DBO (0.0184 molar) in p-xylene.											
38	-	-	-	Q	2.30_2	2.30_5	0.022_0	0.022_6	2.430_2	2.28_9	1.7_0
	(Cole-Cole)			K	2.30_6	2.31_1	0.028_6	0.027_5			
	(behaviour)			P	2.32_3	2.31_8	0.032_2	0.032_9			
	($\alpha = 0.28$)			X	2.33_9	2.33_3	0.039_6	0.039_9			
99. 2,4,6-Trichlorophenol (0.3544 molar) + DBO (0.466 molar) in p-xylene.											
86	-	-	-	Q	2.31_6	2.32_1	0.022_5	0.022_1	2.512_8	2.30_4	2.1_0
	(Cole-Cole)			K	2.32_3	2.32_6	0.025_6	0.027_1			
	(behaviour)			P	2.33_6	2.33_3	0.034_1	0.033_0			
	($\alpha = 0.34$)			X	2.35_7	2.34_6	0.041_5	0.042_1			
100. 2,4,6-Trichlorophenol (0.3544 molar) + DBO (0.0653 molar) in p-xylene.											
91	-	-	-	Q	2.33_5	2.33_8	0.026_6	0.026_9	2.563_6	2.31_4	2.2_8
	(Cole-Cole)			K	2.34_2	2.34_4	0.032_8	0.032_3			
	(behaviour)			P	2.35_4	2.35_2	0.038_3	0.038_6			
	($\alpha = 0.38$)			X	2.37_5	2.36_8	0.048_0	0.048_1			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
101. 2,4,6-Trichlorophenol (0.3544 molar) + DBO (0.0897 molar) in p-xylene.											
141	-	-	-	Q	2.33_4	2.33_8	0.024_7	0.024_2	2.607_7	2.31_9	2.5_0
	(Cole-Cole)			K	2.34_2	2.34_3	0.028_2	0.029_6			
	(behaviour)			P	2.35_5	2.35_1	0.037_1	0.036_2			
	($\alpha = 0.37$)			X	2.37_1	2.36_4	0.046_6	0.046_9			
102. 2,4,6-Trichlorophenol (0.3544 molar) + DBO (0.3571 molar) in p-xylene.											
152	-	-	-	Q	2.42_2	2.43_0	0.055_6	0.054_6	3.070_6	2.38_8	3.8_4
	(Cole-Cole)			K	2.44_5	2.44_1	0.067_3	0.067_0			
	(behaviour)			P	2.46_1	2.45_7	0.079_5	0.082_3			
	($\alpha = 0.36$)			X	2.49_2	2.48_8	0.107_0	0.107_5			
103. 2,4,6-Trichlorophenol (0.3544 molar) + DBO (0.7143 molar) in p-xylene.											
146	-	-	-	Q	2.45_9	2.46_2	0.067_2	0.067_7	3.199_5	2.40_5	4.1_3
	(Cole-Cole)			K	2.48_1	2.47_7	0.082_9	0.082_1			
	(behaviour)			P	2.50_1	2.49_7	0.099_5	0.099_4			
	($\alpha = 0.39$)			X	2.52_7	2.53_4	0.126_7	0.127_0			
104. 2,4,6-Trichlorophenol ($f_2 = 0.0876$) + DBO ($f_2 = 0.0886$) in p-xylene.											
176	-	-	-	Q	2.60_1	2.59_8	0.108_3	0.106_9	3.848_7	2.50_5	3.8_1
	(Cole-Cole)			K	2.61_3	2.62_2	0.126_3	0.129_0			
	(behaviour)			P	2.66_1	2.65_4	0.156_7	0.155_8			
	($\alpha = 0.40$)			X	2.71_2	2.71_2	0.199_1	0.199_8			

105. Diethyl ether (f_2 = 0.0966) in cyclohexane.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
2.46	-	-	-	Q	2.13_9	2.13_8	0.050_0	0.051_0	2.165_4	2.04_3	1.1_3
				K	2.15_7	2.15_1	0.041_6	0.039_8			
	(Debye) (behaviour)			P	2.16_1	2.15_8	0.028_9	0.028_7			
				X	2.16_8	2.16_3	0.016_4	0.017_2			
				P							

106. Triethylamine (f_2 = 0.234) in cyclohexane.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
8.00	-	-	-	O	1.9_2	2.02_3	0.028_9	0.027_4	2.119_3	2.01_5	0.6_7
				Q	2.02_7	2.04_1	0.047_0	0.044_9			
	(Debye) (behaviour)			K	2.05_0	2.05_8	0.053_4	0.051_2			
				P	2.08_8	2.07_8	0.055_8	0.051_1			
				X	2.09_5	2.10_1	0.040_7	0.040_0			

107. Acetone (f_2 = 0.0362) in cyclohexane.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
2.58	-	-	-	Q	2.3_5	2.24_1	0.083_6	0.083_6	2.288_0	2.05_1	2.5_6
				K	2.26_5	2.26_2	0.066_6	0.065_9			
				X	2.27_3	2.28_4	0.026_6	0.028_8			

108. Chloroform (f_2 = 0.0627) + acetone (f_2 = 0.0627) in cyclohexane.

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
4.5	21	3.5	0.29	Q	2.42_2	2.40_3	0.223_3	0.226_5	2.70_9	2.14_6	-
				K	2.46_1	2.47_2	0.215_8	0.211_8			
				X	2.58_7	2.59_3	0.157_7	0.159_0			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
109. Chloroform (f_2 = 0.0355) + acetone (f_2 = 0.0355) in cyclohexane.											
3.6	25	3.5	0.21	Q	2.24_1	2.24_5	0.113_3	0.114_8	2.38_1	2.10_6	–
				K	2.29_2	2.28_0	0.105_0	0.103_6			
				X	2.32_9	2.33_3	0.069_3	0.069_4			
110. Chloroform (f_2 = 0.1114) + diethyl ether (f_2 = 0.1114) in cyclohexane.											
7.0	12.6	4.6	0.43	Q	2.24_8	2.24_8	0.159_6	0.160_8	2.496_7	2.11_6	–
				K	2.29_5	2.29_7	0.169_8	0.169_3			
				P	2.35_8	2.35_5	0.164_6	0.163_1			
				X	2.41_2	2.42_4	0.131_5	0.133_1			
111. Chloroform (f_2 = 0.0637) + diethyl ether (f_2 = 0.0637) in cyclohexane.											
5.3	11.8	3.7	0.36	Q	2.15_3	2.14_8	0.083_0	0.082_6	2.254_8	2.06_5	–
				K	2.17_2	2.17_4	0.080_4	0.080_9			
				P	2.20_5	2.20_0	0.074_3	0.073_6			
				X	2.22_0	2.22_8	0.057_0	0.056_8			
112. Chloroform (f_2 = 0.0532) + triethylamine (f_2 = 0.0738) in cyclohexane.											
11.3	37	6.8	0.39	O	1.8_4	2.04_8	0.030_0	0.029_0	2.179_9	2.04_0	–
				Q	2.05_9	2.06_7	0.050_6	0.047_1			
				K	2.06_5	2.08_3	0.051_6	0.054_0			
				P	2.10_9	2.10_2	0.056_8	0.056_1			
				X	2.11_8	2.12_6	0.052_5	0.052_7			

τ_0	τ_1	τ_2	C_1		ϵ'_{obs}	ϵ'_{calc}	ϵ''_{obs}	ϵ''_{calc}	ϵ_0	ϵ_∞	μ
113. Chloroform (f_2 = 0.0368) + triethylamine (f_2 = 0.0510) in cyclohexane.											
8.2	37	5.9	0.31	O	1.9_9	2.03_3	0.025_9	0.023_5	2.119_0	2.02_5	-
				Q	2.04_7	2.05_0	0.033_8	0.034_9			
				K	2.05_7	2.06_2	0.034_5	0.037_2			
				P	2.08_6	2.07_5	0.038_5	0.035_8			
				X	2.08_5	2.08_8	0.031_8	0.031_1			
114. Chloroform (f_2 = 0.0197) + acetone (f_2 = 0.0197) in cyclohexane.											
4.8	-	-	-	Q	2.13_8	2.15_7	0.057_4	0.056_5	2.217	2.10_4	-
	(Debye)			K	2.18_0	2.17_7	0.052_6	0.054_0			
	(behaviour)			X	2.21_0	2.20_9	0.028_6	0.029_8			
115. Chloroform (f_2 = 0.0195) + acetone (f_2 = 0.0195) in cyclohexane.											
3.2	-	-	-	Q	2.11_9	2.14_7	0.054_4	0.053_9	2.211	2.05_1	-
	(Cole-Cole)			K	2.16_2	2.16_2	0.049_6	0.049_6			
	(behaviour)			X	2.19_1	2.18_9	0.029_9	0.032_6			
	(α = 0.23)										
116. Chloroform (f_2 = 0.0112) + acetone (f_2 = 0.0112) in cyclohexane.											
4.2	-	-	-	Q	2.07_7	2.09_2	0.032_7	0.031_8	2.121	2.05_7	-
	(Debye)			K	2.10_6	2.10_3	0.027_5	0.028_8			
	(behaviour)			X	2.10_9	2.11_7	0.013_5	0.014_7			
117. Chloroform (f_2 = 0.0061) + acetone (f_2 = 0.0061) in cyclohexane.											
4.8	-	-	-	Q	2.04_5	2.06_2	0.017_3	0.016_3	2.079	2.046	-
	(Debye)			K	2.06_7	2.06_8	0.014_2	0.015_5			
	(behaviour)			X	2.06_1	2.07_7	0.006_4	0.008_5			

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