The influence of the chemical nature of dispersed phase on stability in oil-in-water emulsions

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SUMMARY

Some of the problems arising from the inherent instability of emulsions are discussed. Aspects of emulsion stability are described and particular attention is given to the influence of the chemical nature of the dispersed phase on adsorbed film structure and stability.

Emulsion stability has been measured by a photomicrographic technique. Electrophoresis, interfacial tension and droplet-rest-time data were also obtained. Emulsions were prepared using a range of oils, including aliphatic and aromatic hydrocarbons, dispersed in a solution of sodium dodecyl sulphate. In some cases a small amount of alkane or alkanol was incorporated into the oil phase.

In general the findings agree with the classical view that the stability of oil-in-water emulsions is favoured by a closely packed interfacial film and appreciable electric charge on the droplets. The inclusion of non-ionic alcohol leads to enhanced stability, presumably owing to the formation of a "mixed" interfacial film which is more closely packed and probably more coherent than that of the anionic surfactant alone.

In some instances differences in stability cannot be accounted for simply by differences in interfacial adsorption or droplet charge. Alternative explanations are discussed and it is postulated that the coarsening of emulsions may occur not only by coalescence but also through the migration of oil from small droplets to larger ones by molecular diffusion.

The viability of using the coalescence rates of droplets at a plane interface as a guide to emulsion stability has been researched. The construction of a suitable apparatus and the development of a standard testing procedure are described. Coalescence-time distributions may be correlated by equations similar to those presented by other workers, or by an analysis based upon the log-normal function. Stability parameters for a range of oils are discussed in terms of differences in film drainage and the nature of the interfacial film. Despite some broad correlations there is generally poor agreement between droplet and emulsion stabilities. It is concluded that hydrodynamic factors largely determine droplet stability in the systems studied. Consequently droplet rest-time measurements do not provide a sensible indication of emulsion stability.

MEMORANDUM

This dissertation, which is being submitted for the degree of Doctor of Philosophy in the University of Aston in Birmingham, is an account of work done under the supervision of Dr. S.S. Davis in the Department of Pharmacy of the University of Aston in Birmingham from October 1970 to July 1974. Except where acknowledged by references in the text, the work described herein is claimed to be original and has not been submitted for any other award.

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INTRODUCTION

1.1 EMULSIONS IN PHARMACY

The most concise and most frequently cited definition of the emulsion system is that of Becher (1a):

> "An emulsion is a heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets whose diameters, in general, exceed 0.1μm. Such systems possess minimal stability, which may be accentuated by such additives as surface active agents, finely divided solids etc."

1.1.1 Emulsions as drug delivery systems

Emulsions have been in use as pharmaceutical and cosmetic preparations and vehicles for a considerable period of time. In fact their history has been traced back at least as far as the second century, to the Greek physician Galen whose records contain statements on the emulsifying power of beeswax and the formulation of the first topical cold cream (1b,2,3). However, the title of "emulsion" (or rather "emulction") was not ascribed to liquid-liquid dispersions until the early seventeenth century (4).

The emulsion is undoubtedly one of our most versatile formulation techniques. In addition, as a drug delivery system, emulsions possess a number of potential advantages over other formulations. These have led to a resurgence of interest in emulsions which has resulted in a number of important developments in recent years.

For many years water-insoluble liquids have been rendered more palatable for oral administration by emulsification within an aqueous medium. Studies on the effect of oral dosage forms on the bioavailability of an oil soluble drug (indoxole) in man has shown that higher blood levels can be obtained from an oil-in-water (o/w) emulsion formulation than from an aqueous suspension or a capsule (5,6). A comparable effect was observed many years ago for orally administered sulphonamides (7). Higher and more sustained blood levels, and consequently an enhanced therapeutic effect, was observed when these drugs were formulated into an o/w emulsion rather than an aqueous suspension. Observations have been recorded recently for the absorption of the sparingly soluble drug griseofulvin (8). The very slow dissolution rate of this drug gives rise to erratic and incomplete absorption. When administered to rats the plasma concentrations increased in the order aqueous suspension < oil suspension < o/w emulsion containing the suspended drug. The mechanism by which absorption of such an essentially oil-insoluble drug is enhanced remains in some doubt. Even more remarkable is the intestinal absorption of heparin (in rats) from the aqueous phase of an emulsion of a digestible oil in water , since this acidic macromolecular substance is not absorbed from aqueous solution (9,10). Absorption was believed to depend upon some unknown association with the oil.

A multiple emulsion is one in which a primary water phase is dispersed in oil and then the resulting water-in-oil (w/o) emulsion is itself dispersed in an aqueous medium to produce a w/o/w multiple emulsion (1c). Engel _et al_ (11) have reported that such a system, with the drug dissolved in the internal aqueous phase, will facilitate the gastro-intestinal absorption of insulin, another water soluble substance which is not normally absorbed.

The use of o/w emulsions for intravenous nutrition is now common practice (12). Jeppsson and others (13,14) have shown how such an emulsion may be used to deliver lipid soluble drugs (eg. barbituric acids) directly into the blood. The principal advantage of this preparation was reported to be the more effective penetration of cell membranes by such drugs rather than the more conventional water soluble salts. It was also suggested that oil droplets might serve as a mobile depot, possibly acting as a bridge for the uncharged drug between the circulatory system and the blood brain barrier. One important possibility is that drugs may be protected from hydrolytic degradation or protein binding (14). These workers have extended the technique of delivering oil soluble drugs to other sites (eg. intramuscularly and subcutaneously) (15) and to the new possibility of intravascular administration of lipophilic vasoactive drugs (16).

By dispersing a drug in the aqueous phase of an oil continuous (w/o) emulsion, the formulator can achieve a gradual release of drug over a prolonged period (sustained release). The oil medium retards the diffusion of the aqueous phase from the site of action to the surrounding fluids. Vaccines, in particular, have been administered in this form (17,18,19a). A less viscous, and therefore more easily injected, sustained release preparation has been obtained by incorporation of the antigen into the primary aqueous phase of a multiple w/o/w emulsion (20). In this form toxic reactions are fewer because less oil is injected. The use of a number of drugs in the form of a multiple emulsion has been developed. Cancer chemotherapeutic agents (methotrexate sodium, cytosine arabinosate, vinblastine) in this formulation were found to be more effective and less toxic than up to five daily injections of aqueous solution at the same dose level (21, 22).

The majority of emulsion formulations in use are dermatological and cosmetic lotions and creams. The possibility of using such preparations as vehicles for the administration of drugs through the skin (percutaneous absorption) is of increasing interest. According to Beckett et al (23) this route will become increasingly important in drug therapy, particularly when the release characteristics of the drug are understood. Significant absorption of a number of ephedrine compounds was achieved simply by applying the drug (as the free base) beneath an occlusive patch.

1.1.2 Other uses of emulsions

Emulsions are receiving an increasing degree of attention because of their potential use as model systems for research, and as analogues for the biological cell or membrane.

For example, Stossel et al (24) have shown how an emulsion of liquid paraffin, stabilized with bovine serum albumin, can be used as a substrate to measure the rate of phagocytosis by leucocytes. The rate was shown to depend upon the nature of the droplet surface or its electric charge. Furthermore, it was suggested that improvements in the technique would provide additional information on the mechanism of phagocytosis.

It seems likely that further refinements in the study of diffusion from emulsion droplets will provide invaluable information regarding the transport of drugs through membranes (25,26) and the rate of release of drugs from emulsions (27).

Of increasing interest is the emulsification of fluorocarbon oils into which oxygen is highly soluble (28), for use as a blood substitute. This possibility has been enhanced by the discovery of certain fluorocarbons which are eliminated gradually from the body rather than being deposited in body tissues. Indeed, transfused blood substitutes of this type have been used to sustain mice for several days. The substitute was gradually replaced by regenerated erythrocytes and the animals then survived to normal healthy lives (29,30). One advantage of such a formulation for humans is that accident victims could be treated until their blood grouping was ascertained. Even more significant is the potential saving of real blood during lengthy operations such as open heart surgery (30,31).

1.1.3 The problem of stability

Despite the advantages and versatility of the emulsion, and a long history of use as a vehicle for the incorporation of drugs, the formulation has never been a pharmaceutical favourite. Furthermore, something of a decline in the importance of emulsions as a drug dosage form has been evident in recent years. This trend has been caused largely by the restrictions imposed by stability problems. These assume considerable importance since emulsions are, by definition, inherently unstable.

Emulsions manifest instability in a number of ways, therefore the term "emulsion stability" is somewhat ambiguous (Section 1.2.1.) and problems arise in deciding an appropriate index of stability (Section 1.2.2.). Sherman (32,33) has pointed out that instability may exert a profound effect on the consistency and performance of emulsions long before visible changes occur. A number of properties may be chosen as a measure of stability and not all of these will change at the same rate. Perhaps this partly accounts for the fact that emulsion theory is insufficiently advanced to enable the a priori prediction of stability (1d). Consequently the approach to emulsion formation is, of necessity, largely empirical.

The principal problem to the formulator is one of maintaining stability, which requires that the appearance of the product is retained as far as is possible, but more importantly, that the characteristics of the emulsion in use should be unchanging during storage. Changes in the particle size and total surface area of dispersed droplets are a particular cause of changes in emulsion properties. For example, droplet size increases have been shown to alter the intestinal adsorption rate of heparin (10) or cause rapid release of antigen from influenza vaccine (18). Bollinger (34ab) investigated the factors affecting removal of vaccines from the site of injection. He showed not only that instability may increase toxic effects (34a) but that the emulsion stabilizer might diffuse from tissues more rapidly than the dispersed phase, thus decreasing stability (34b). Droplet size is of considerable importance in emulsions for intravenous use because of the risk of obstructing the blood vessels. Emulsion droplets which are any larger than erythrocytes ($\simeq 10\mu m$) will not pass through the capillaries, and thus increase the risk of embolism (31). A direct relationship has been reported between the toxic effects caused by intravenous fluorocarbon emulsion and droplet size (35). Similarly, emulsions employed for intravenous feeding require refrigerated storage conditions whilst the addition of any supplements (eg. antibiotics, vitamins, drugs) involves the grave risk of instability (14,36,37a).

The formulation of multiple emulsions has been largely an empirical exercise. The sustained release of drugs has been achieved (21,22) but the mechanism of drug release is by no means certain and there remains the possibility that release is due to instability of the formulation rather than transport through the different phases.

Changes in the size of dispersed droplets can also cause changes in the rheological properties of emulsions (38-40) which is particularly important in lotions and creams whose performance and acceptability are determined by such properties (32,33).

Any alteration in the appearance of a product is of somewhat less fundamental importance than the change of emulsion properties in use, though both must be considered from the aspect of general acceptability of the product. Instability can affect the appearance of an emulsion through any of the mechanisms considered below (Section 1.2.1).

1.2 EMULSION STABILITY

1.2.1 Definition

The clasical definition of a stable emulsion is that there should be "no observable change with time" (41,42). Within this description an emulsion may manifest "change" through a number of processes, each proceeding independently by different mechanisms, but any of which may be inter-related. The most recent reviews of emulsion stability have been compiled by Becher (1bc), Florence & Rogers (37ab), Garrett (41), Vold & Groot (43), Lange (44), and Kitchener & Mussellwhite (45).

Instability processes fall into two categories, those resulting in reversible changes in the emulsion and those which give rise to irreversible changes.

Creaming (or sedimentation) of dispersed droplets will occur under gravitational forces in any fluid system in which the dispersed and continuous phases are of differing densities. The factors which affect creaming are summarized in the equation derived by Stokes (46) for the sedimentation of a single rigid sphere, moving under gravity in an infinite liquid medium, viz:

$$v = 2gr^2 (p_1 - p_2)/9\eta_2, \qquad 1.1$$

where v is the sedimentation velocity, g is the acceleration due to gravity, r is the particle radius, p_1 and p_2 are the densities of the sphere and liquid respectively and η_2 is the viscosity of the liquid. Creaming will occur when $p_1 < p_2$. The applicability of Equation 1.1 to the droplets in a liquid-liquid dispersion has been discussed by Becher (1c). Garrett (47) found that the creaming rate followed the Stokes relation provided the emulsion was dilute. The form of the equation is changed in the case of concentrated emulsions though the qualitative dependance of creaming rate on the variables should be maintained (48). Thus, it can be concluded that stability with respect to creaming is favoured by small droplet size, small density difference (Δp) between the phases and by high viscosity of the continuous medium. In fluid pharmaceutical emulsions the first of these factors is of most advantage to the formulator, though creaming should be readily reversible with moderate shaking.

The term aggregation is a general one which describes the sticking together of droplets into three dimensional clusters within the bulk emulsion.The ease with which aggregation can be reversed depends upon the type and strength of interaction between the droplets. "Flocculation" describes the same process, this term often being used to describe association within the secondary minimum of the interaction energy curve (Section 1.2.3.2).

Coalescence is the name given to the process of spontaneous and irreversible joining of droplets, leading to a decrease in the number of dispersed droplets and, ultimately,to separation of the dispersed material. The dispersion of one liquid as droplets within another results in a greater interfacial area between the phases and a correspondingly greater interfacial free energy (Section 1.2.3.2). Coalescence leads to a reduction in interfacial free area until there is complete separation of the two phases. This is the condition of minimum interfacial free area and free energy.

An irreversible change in droplet size can also result from a process known as molecular diffusion (49). Small droplets in an emulsion possess a higher vapour pressure than large droplets and as a result small droplets are thermodynamically unstable and tend to "distill" into the larger ones. Higuchi & Misra (49) have claimed that this mechanism of droplet growth may be significant even at fairly low solubilities of the dispersed material.

It should be noted that coalescence, leading to an irreversible increase in particle diameter represents the fundamental and ultimate instability process, and as such the phenomenon has received considerable attention. Irreversible changes within the emulsion are also more significant with respect to the usefulness of an emulsion for drug delivery (Section 1.1.3). Indeed, Tingstad,(50) defines a stable pharmaceutical emulsion for oral use as "one that can be homogeneously redispersed to its original state with moderate shaking and can be easily poured at any time during its shelf life". However, all aspects of stability should be considered in any evaluation of emulsions, since aggregation and creaming may affect the rate at which irreversible changes occur (41).

1.2.2 Measurement of stability

From the previous section it will be obvious that no single parameter will express the relative stabilities of a range of emulsions. A number of properties may be chosen that can be measured as a function of time, and not all of these will change at the same rate (41). The problem of choosing a suitable parameter for the comparison of dissimilar systems has been discussed by a number of authors (43,50-52). King (53) decided that there was "no single property of an emulsion other than the rate of coalescence or separation of internal phase that can be considered to constitute stability". More recently Lachman (54) has stated that the degree of stability may be measured by the "variation of the distribution of sizes of the dispersed droplets with time".

The irreversible changes in droplet sizes can be measured or deduced in a number of ways.

1.2.2.1 Phase separation

The extent of separation of the dispersed phase can be used as a useful measure of stability provided that the ejection of oil is relatively fast and well defined (53,55,56). Zografi (57) has pointed out that this technique may only be useful in detecting very unstable systems during formulation. The results of Rowe (58) for mineral oil emulsions stabilized by various concentrations of sodium dodecyl sulphate (SDDS) or polysorbate 80 were used to illustrate this point. Groves (42) has conceded that the technique, although requiring no specialized equipment, is of limited usefulness in ranking the relative stabilities of any series of emulsions. One disadvantage of applying phase separation as a measure of stability is that free oil is difficult to detect initially, or accurately enough to follow the kinetics of coalescence (42). Menczel et al (59) included an oil soluble dye into the dispersed phase and followed changes in optical density with a photoelectric colorimeter. Phase separation was found to decrease exponentially with time. However stability may be significantly affected by the inclusion of the dye. The most significant limitation of phase separation is that marked changes must occur within the emulsion before phase separation becomes evident (32).

1.2.2.2 Droplet size analysis

The methods of measuring particle sizes in emulsion systems have been amply reviewed by Groves & Freshwater (60) and Walstra et al (61). The techniques of microscopy, fluorescence microscopy, photo-micrography, Coulter counting and turbidimetry (60,61), electron microscopy, sedimentometry, and surfactant adsorption (60), have all been examined critically. In general it is concluded that the accurate determination of a complete range of sizes occurring in emulsions is extremely difficult. This was found to be particularly true for small droplets (diameter$<1\mu$m). Wide divergencies in the estimated numbers of these were obtained with different methods of size measurement.

Direct experimental measurements of droplet size are most frequently expressed as the population within various size ranges, for which the proper representation is a histogram or size frequency curve (1e,62a). Berkman (63) found that progressive changes in the size distribution of an emulsion could be followed as a measure of stability. However, Jellinek (64) considered it unlikely that emulsions prepared with different materials, or by different methods, would conform to similar types of size distribution. This point has been illustrated recently by Elworthy & Florence (65ab) who found that comparison between emulsions was difficult even when size distributions were of the same general form. Nevertheless, size frequency distributions are of considerable value since the maximum amount of information is conveyed.

Herdan (66) noted that many physical systems appeared to obey standard distribution forms, particularly the normal (Gaussian) or log-normal functions. Both forms have the advantage that they may be reduced, by a simple mathematical device, to yield straight line plots (67,68). The data may then be uniquely defined by only two parameters. Both types of distribution have been applied to size analysis in emulsion systems (60). The normal distribution can only give an approximate fit of the data, usually when the distribution is narrow, since the presence of droplets larger than twice the mean size predicts the occurrence of droplets with negative diameters! Rajagopal (69) re-examined the theoretical basis of the log-normal function for emulsions and affirmed its suitability for these systems. This view has been supported by experimental observations on liquid paraffin emulsions stabilized with potassium laurate (70a). Slight deviation from the log-normal distribution was reported by Rowe (58) and Hallworth & Carless (71) for a number of SDDS stabilized emulsions. Rehfeld (72) found that the log-normal function was fitted by the sizing data from freshly prepared dispersions of benzene in SDDS solution after emulsification down to an equilibrium size distribution.

Many empirical functions have been proposed in order to fit observed size distributions of emulsions (60,64,69) though these often lack the practical significance of the log-normal distribution.

For data which were significantly deviant from log-normal Rowe (58) suggested that the spread of sizes in a sample could be summarized by the "polydispersity ratio", a ratio of the mass median diameter to number median diameter (50% of the droplets by weight and number respectively have a value larger than the median). Such an expression has been used to follow changes in macromolecular stabilized emulsions (73).

Direct measurements of droplet size have been expressed in a kinetic fashion by a number of other methods, notably by the average droplet diameter which can be defined in a variety of ways. The number average diameters are the simplest to derive, the arithmetic, mean surface and mean volume diameters being the most useful. If the total surface area for a given volume of dispersed oil is required then the volume-surface mean diameter should be determined (1e,62). Sherman (62) has pointed out that the choice of mean diameter should be made in relation to the property of the emulsion being investigated. Mahrous & Lemberger (73) supplemented observations on number-size distributions by calculating the weight distribution (the weight of oil in the various size ranges). They stressed that excessive reliance on one size parameter may be misleading since volume or weight parameters are the most sensitive to small numbers of large droplets. Knoechel & Wurster (74) followed the coarsening of SDDS stabilized emulsions of long chain paraffin. The arithmetic mean, volume-surface and weight mean diameters were monitored over a period of 200 days (at 30 day intervals). Whilst the arithmetic mean diameter increased progressively with time, the volume-surface and weight means displayed an initial decrease followed by the expected increase. The apparent increase in subdivision of the emulsions was reported to be due to coarsening of submicron sized droplets into the visible range.

One of the most popular expressions of the degree of dispersion of an emulsion has been the specific interface (S), that is the interfacial area per unit weight or volume of dispersed phase. The parameter may be calculated as the area per unit weight from:

$$S = 6 / p_o d_{vs} \quad , \qquad 1.2$$

where p_o is the density of the dispersed phase and d_{vs} is the mean volume-surface diameter (75). Cooper (76) has examined the photomicrographs of a large number of paraffin oil/potassium oleate solution emulsions having different droplet size distributions. It was found that S was less sensitive to sampling errors and therefore superior to average diameters (arithmetic, surface or volume) in defining an emulsion. King & Mukherjee (75) established that after an initial rapid rate of coalescence the specific interface decreased at an approximately linear rate with time. A coefficient of stability was expressed as the reciprocal of this rate. A number of authors have since reported comparable changes in specific interface (74,77-79). Hill & Knight (80) have developed a theory of coalescence, for uncharged spheres of varying sizes, from which it was predicted that the reciprocal of total interfacial area would increase linearly with time. A number of emulsions stabilized with nonionic surfactants have been found to conform to this theory (65a). King (53) suggested that the fall in S was a more useful parameter than phase separation when comparing emulsions of moderate stability. However, specific interfaces which fell approximately exponentially with time have been recorded for cottonseed olive and mineral oils stabilized with gums (81). Further limitations of S arise because its calculation from d_{vs} which is insensitive to the presence of very small droplets though these certainly affect the actual interfacial area and emulsion properties (62a,82).

1.2.2.3 Adsorption of surfactant

A number of workers have calculated the total interfacial area of an emulsion from the analytical estimation of the amount of surfactant adsorbed by emulsion droplets. Independent information is required on the area of interface occupied by each surfactant molecule. From a knowledge of the total volume of oil dispersed the average droplet size may be calculated (82-84). The principal limitations of this technique are that no information can be obtained on the distribution about the mean size and that the degree of interfacial packing of surfactant assigned to a particular emulsion is subject to error (Section 1.3.3).

1.2.2.4 Droplet concentration

A useful technique for following changes in emulsion systems is that developed by Smith & Grinling (85), although the experimental modifications introduced by Cockton & Wynn (86) are normally applied. The procedure involves the accurate dilution of an emulsion in order that the number of droplets in a known volume can be counted microscopically. The results are usually expressed as the number of droplets into which unit volume of oil is subdivided (86), or as the droplet concentration (in g^{-1} or cm^{-3} of emulsion) (87bc,88). Van den Tempel (87abc,88) developed a kinetic theory of coalescence which enabled him to calculate the rate constant from a first order decay of droplet number with time. This approach has been adopted in a number of instances (65b,71,89ab,90-93). Elworthy & Florence (65b) found that rates calculated in this way were more suitable for the comparison of different systems than were size distributions. The sensitivity of this method has been stressed; a 10% change in interfacial area being comparable with a 27% decrease in droplet number (87b). However, in some instances a non-linear decrease in log droplet number has meant that the rate constants were difficult to obtain and of doubtful significance (71,91-93).

1.2.2.5 Other methods

The relative changes in emulsion systems may be deduced from other properties such as the creaming rate, electrical resistance or optical properties (turbidity, light reflectance or scattering) (52,60). These indirect observations provide only minimal information, for example, aggregation will markedly affect creaming rate or optical properties yet may go undetected in such studies.

The measurement of changes in rheological properties with time has been of considerable empirical value. It has been pointed out that such observations are of limited importance in understanding the mechanism of the instability processes because rheological properties depend upon various factors other than droplet size (43). Nevertheless, the sensitivity of rheological properties suggests that slight changes may be detected in the earliest stages of emulsion breakdown by these measurements (32,39).

Accelerated testing of emulsion systems is now a well established means of evaluating stability. The techniques available have been reviewed comprehensively by Groves (42) and Sherman (33). Although accelerated tests (reduced or elevated temperature and high speed centrifugation) have provided useful information for the comparison of emulsion formulations, extrapolation to predict the relative stabilities under normal storage conditions is of doubtful significance. The mechanism by which changes occur may be completely altered under abnormal stress. The most significant advances in the evaluation of stability through accelerated testing have been made by utilizing the ultra-centrifuge, as reviewed by Garrett (94). Observation of the sample during centrifugation has been achieved (82) so that separation of the emulsion can be followed. Many factors have been examined, such as the effect of emulsion age (83), temperature (95), dispersed phase volume (96), electrolyte (97) and the effect of a mixed surfactant film (98) on the ultra-centrifugal stability of Nujol emulsified in SDDS solution.

Emulsion composition was also shown to affect ultracentrifugal stability (99). The significance and limitations of centrifugation in the evaluation of emulsions has been discussed by Vold & Groot (43). These reports offer a considerable amount to the understanding of the processes involved in ultracentrifugal separation and the possibility of relating the observations to "free standing emulsions".

1.2.2.6 Coalescence at a plane interface

The coalescence of single oil or water droplets with the respective bulk phase at the oil-water (or surfactant solution) interface has been studied by numerous investigators in various disciplines. This work has been reviewed by several authors (100-103).

Stability can be assessed by measuring the rest-times, timed from arrival of droplets at the interface to their coalescence. This technique has been suggested for the preliminary investigation and prediction of emulsion stability (1c,50,52,102b). A small number of studies have been concerned with the application of single droplet stability to emulsion stability (104-110). It is generally accepted that the stability of elementary droplets at an interface will be different from emulsion stability, but a number of correlations between the two have been reported. Osipow et al (105) showed that the bulk stability of a tetradecane emulsion passed through a maximum in the region of the critical micelle concentration (cmc) of sodium alkyl sulphate stabilizers. The permanence of single oil droplets at the tetradecane-surfactant solution interface increased in accordance with bulk stability below the cmc. Interestingly, it has been reported elsewhere (104) that light petroleum or benzene droplets at an oil-aqueous solution interface may attain a maximum stability near to the cmc of potassium laurate or cetyl trimethyl ammonium bromide (CTAB) solutions. Ishida et al (109) found that the coalescence rate of single droplets reflected the stabilizing effect of different non-ionic surfactants in emulsions.

A parallel has been drawn between the known effect of an emulsifying agent in stabilizing emulsions of the phase in which it is least soluble, and the observed stabilities of single oil or water droplets (104). It was postulated that coalescence cannot occur until the interfacial film is displaced, and that this can be achieved most readily through film segments passing into, or being wetted by, the dispersed phase. Cockbain & McRoberts (104) also found that high droplet stability was not dependant upon a high interfacial viscosity. The converse appears to be true for single droplets stabilized by macromolecular agents. Correlations between droplet stability and film viscosity and/or thickness have been obtained using serum albumin, gum arabic, pectin (for petroleum ether droplets), and cellulose derivatives (for benzene) (107). Comparable behaviour has been reported for adsorbed films of gelatin with a number of oils (heptane, cyclohexane, benzene or cyclohexene) (108a), and egg albumin or polyvinyl alcohol films with benzene (108b). Similar correlations have been observed for the stability of emulsion systems in the presence of these agents (Section 1.2.3.2).

1.2.3 Maintenance of stability

1.2.3.1 The third component

As stated earlier (Section 1.1), the stability of an emulsion may be enhanced by the addition of a third substance. King (53) observed that in the absence of this component an o/w dispersion rapidly coalesced into separate phases. Cheesman & King (56) demonstrated that simple organic electrolytes can confer a low order of stability on certain emulsions (Section 1.2.3.2). However, in order to attain even a moderate degree of stability it is necessary to incorporate an emulsifying agent which is capable of forming an interfacial film around individual droplets. A wide range of substances have been found to be suitable for this purpose, including certain macromolecular agents (eg. gums, synthetic polymers and proteins) and finely divided solids, but by far the largest group of stabilizers in use are the so-called "amphipathic" surface active agents (1b,111a). The term amphipathic was introduced by Hartley (112) to describe molecules in which both hydrophilic and hydrophobic groups are present. Such molecules are strongly adsorbed or orientated at air-water (a-w) and oil-water (o-w) interfaces (Section 1.3.2).

The means by which a stabilizing material is effective in maintaining discrete droplets will depend upon the chemical nature of both the adsorbate and the adsorbent (37a). The stabilizer may:-

(i) Decrease the free energy of the system,

(ii) Form an interfacial barrier between droplets,

(iii) Affect the electrostatic charge on the droplets.

1.2.3.2 Stabilization of emulsions by surface active agents (Surfactants)

A. Decrease in free energy

The adsorption of surface active agents to the o-w interface causes a marked fall in the interfacial tension (Section 1.3.3). The resultant decrease in interfacial free energy within the system was, at one time, considered to be largely responsible for emulsion stabilization (1b). However, King (53) found that a low interfacial tension was not, in itself, a sufficient criterion for stability. It has also been observed that emulsions having the same interfacial free energy may exhibit widely differing stabilities (37a). As illustrated by Becher (113), even a small interfacial tension may represent considerable free energy and the resulting emulsion can be highly unstable through coalescence. Lawrence (118) even suggested that a low interfacial tension could be conducive to low emulsion stability because of the lesser tendency of droplets to retain a spherical shape. It is now generally understood that a marked lowering of interfacial tension is symptomatic of adsorption but cannot represent the totality of the stabilizing effect of a surface active agent. Stability is highly dependent on the formation of an interfacial film which can prevent coalescence.

B. The Interfacial Barrier

The interfacial film must be capable of withstanding the dynamic or static forces between droplets. In general, the stability of an emulsion has been related to the "strength" of the emulsifer film (53). It is now believed that the barrier represents a combination of steric, viscous and elastic properties which depends upon the emulsifying agent (37a). Stability will depend upon the ability of the film to slow the drainage of continuous phase from between droplets and its resistance to desorption, displacement, penetration or wetting by the dispersed phase.

(a) Steric stabilization and rigid films.

The presence of an emulsifying agent around droplets may present a physical barrier which enables the droplets to collide or lie in close proximity for appreciable time without coalescing. The earliest considerations of adsorbed films (114,115,116b), which were directed towards an explanation of emulsion type (o/w or w/o) and reversal of type (inversion), regarded the film as a purely mechanical barrier. The stabilization achieved by finely divided solids and some macromolecules is presumed to be due, at least in part, to rigidity or coherence creating a steric barrier (45). Becher (113) has suggested that any closely packed adsorbed film will give rise to some degree of steric stabilization. Nevertheless, it is doubtful whether surfactant films, particularly with ionic agents owe much of their stabilizing properties to mechanical effects (1b). This may not be entirely true in the case of mixed films (Section 1.2.5). The presence of a "solvation barrier" of loosely held water molecules has been proposed as a further barrier to coalescence (117a).

A valid objection to the desirability of a rigid interfacial film is that it may not be sufficiently adaptable to accommodate small defects or disturbances in the interfacial region (118). This opinion is supported by Elworthy <u>et al</u> (119b) who found that hexadecanol enhanced the stability of a nonionic (hexaoxyethylene glycol monohexadecyl ether) stabilized emulsion of chlorobenzene. However, hexadecanol alone gave rise to a rigid film and the emulsion was poorly stabilized.

(b) Viscous & Viscoelastic Films.

A viscous layer around the droplets may prevent thinning of the interfacial film and displacement of the adsorbed species during the collision or contact of two droplets (117a). Many macromolecular films doubtless exert their effect by means of a combination of viscous and mechanical properties (45,89a,120,121). The most important properties of the film are probably its permanence (desorption is not readily achieved) and coherence (45). Certain non-ionic surface active agents provide viscous and elastic films at o-w interfaces and have found use in w/o emulsions (38,122,123).

The experimental evidence linking the interfacial shear viscosity of adsorbed charged films with emulsion stability is in conflict. The results of Blakey & Lawrence (55) are often quoted in support of the view that an emulsion is not necessarily unstable if the film is not viscous. These authors found many instances where effective stabilizers, which gave a high viscosity at the a-w interface, possessed very low viscosity at the o-w interface. It was concluded that interfacial viscosity plays no part in the stabilization of o/w emulsions. However, Sherman (124) has pointed out that "stability" was assessed empirically as the volume of separated dispersed phase at a particular time, which does not necessarily reflect the true rate of coalescence. Carless & Hallworth (125,126) have determined interfacial viscosities for a wide variety of surface active agents at both a-w and o-w interfaces. A high interfacial viscosity was accompanied by marked emulsion stability for some systems but numerous others showed no such relationship.

Kitchener & Mussellwhite (45) subscribe to the opinion that interfacial viscosity is not a significant factor in emulsions stabilized by micromolecular surfactants in general. They argue firstly that a high interfacial viscosity is rarely encountered, except with macromolecular adsorbed films, and secondly that an adsorbed surfactant tends to immobilize the droplet surface and minimize surface flow when two droplets collide. Any distortion of the droplets during collision will result in stretching a "dilation" of the interface. The viscous resistance to this expansion within the film is termed the dilational viscosity (127,128). The contribution of this property to stability is unknown. Kanner & Glass (128) have made the general statement that stability will increase as the interfacial viscosity and yield value (plasticity) increase. Recently Sherman (124) has summarized the probable contribution of interfacial rheological properties towards stability. From a consideration of the total forces acting as an emulsion droplet, he concludes that, for a rigid film, the maximum compressive force the film can stand will determine stability. In a visco-elastic film there is a critical compressive force in excess of which the film will begin to rupture. If such a rupture is sufficient the adsorbed film is displaced from the contact region of the droplets and coalescence will occur. Sherman (124) also stresses that more detailed rheological studies are required, probably from more advanced techniques in the examination of films, in order to fully understand the coalescence mechanism.

The principal drawback to studies to date has been the difficulty in measuring the relevant properties directly. Firstly it is necessary to study film properties at an extended flat interface (129). Not only is it doubtful whether such results can be applied to films in sheared emulsions (62b), but limitations of the equipment available is also a problem (1b,45). Conflicting experimental results may have arisen because the surface and interfacial viscosities significant for emulsion stability may be an order of magnitude lower than that which is detectable (1b). Most workers have used an oscillatory type of instrument (123, 128) which may displace molecules from equilibrium, the stress developed then depending on the molecular rearrangements taking place (62b). Kitchener & Mussellwhite (45) have also stressed that much of the earlier experimental work may have been performed using impure materials. It is probable that even minute quantities of impurity can markedly influence the results obtained (125,126).

(c) The existence of lamellae, elastic properties.

As two droplets of a pure dispersed liquid approach they may distort because of the pressure between them. This distortion involves an increase in surface area and is opposed by the interfacial tension (130). The region of closest approach of the two small droplets is on the line of the two centres and coalescence will occur here immediately the intervening film has drained away. If two droplets approach closely in the presence of a surface active agent, the time required for coalescence is greatly extended. A flattening of opposite faces of the droplets may occur, thus producing a thin liquid film or lamella of the continuous medium. It has been suggested that a "stable" lamella may remain at equilibrium thickness between aggregated or creamed emulsion droplets (45), much as lamellae promote foam stability (117a,131).

In order to achieve a stable condition, in opposition to van der Waals forces of attraction between droplets, a "disjoining pressure" acting perpendicular to the plane of the interface, has been proposed (132). One consequence of attractive forces between droplets is that liquid lamellae are inherently unstable. As film thinning proceeds into the range of attractive forces, a sharp increase in attraction will result (see below). This leads to the concept of a critical thickness for the onset of film rupture. From the compression together of two paraffin droplets in a surfactant (10^{-2} mol dm^{-3} SDDS) medium van den Tempel (133) found evidence for a non-electrostatic "disjoining pressure" at very small separation distances. Sonntag & Netzel (134) found that the thickness for rupture was increased by the addition of electrolyte and that thickness varied with the oil used (eg. octane $<$ chlorobenzene $<$ cyclohexane).

For lamellae to exist there must be an element of surface elasticity, since a parallel liquid film cannot arise from attraction and interfacial forces only. Surface elasticity results from a non uniformity of interfacial tension which can only occur in the presence of an adsorbed surfactant (45). The extension of an interface causes a temporary increase in the interfacial tension as the new interface adsorbs more of the surface active species. This adsorption lag, known as the Marangoni effect (135), is difficult to quantify although it becomes more significant if the concentration of surface active agent is low. The Gibbs effect (136) arises within an expanding lamella, as between colliding oil droplets for example. Irrespective of the rate of adsorption a lamella cannot thin indefinitely without becoming depleted in surfactant. This again causes a rise in tension but, in contrast to the Marangoni effect it becomes more significant in very thin lamellae and with higher surfactant concentrations. The restoring effect is highly time dependant since the depletion is counteracted by adsorption from solution. However, if the lateral dimensions of the depleted element of film are in the order of its thickness, the equilibrium time for the film is very short compared with adsorptive transport (137). The dilational elasticity produces a healing mechanism tending to restore the monolayer and underlying liquid, thus promoting regular laminar thinning of the draining film (45).

More recently MacRitchie (138) proposed a third elastic restoring mechanism which could act as a barrier to coalescence. Unlike the coalescence of droplets of pure liquid, the coalescence of stabilized droplets may momentarily increase the chemical potential of adsorbed molecules in the interface. This increase provides the restoring mechanism, since a return to equilibrium may be achieved by desorption or an increase in interfacial area. It was argued that surfactants with a very low solubility in the dispersed phase would be less easily desorbed and more effective as stabilizers.

Florence & Rogers (37b) have proposed that many emulsion stabilizers do not act by maintaining thick liquid films between droplets but through the stability of thin films due to elasticity. It was suggested that the behaviour of this film, probably the rate of thinning, determines the probability of coalescence. Because of the complexities of real emulsions, model systems were recommended for further study. The simplest and most informative of these may prove to be thin films between two identical oil phases (as cited above), soap films and foams.

One of the principal problems in elucidating the significance of Gibbs elasticity has been the problem of its measurement. A few estimates have been made on films of slightly impure SDDS (137,139), sodium dodecyl sulphonate and CTAB (137). From the theoretical treatment of Gibbs elasticity van den Tempel (140) showed a qualitative agreement between elasticity and foam stability. Jones _et al_ (131) concluded that foam stability was highly dependent upon elasticity and/or electrical repulsion (see below) but that surface viscosity played only a minor role by slowing film drainage. A qualitative relation has also been observed between foam/emulsion stability and interfacial elasticity/viscosity (127). Elasticity has been shown to reach a maximum at an SDDS concentration below the cmc, and to be highly dependant on trace impurities (137,140).

C. Electrical stabilization

The possibility that electrical effects may be significant in stabilizing emulsions was recognized many years ago by Lewis (141). The origin of an electric charge in colloidal systems has been discussed by Alexander & Johnson (142). Charge was believed to arise in three ways, by adsorption, ionization or friction. In the case of o/w emulsions stabilized by anionic surfactants adsorption has been pictured (Sections 1.3.2 and 1.3.3) with the polar "head" groups penetrating through the interface into the aqueous phase. Ionization of these groups will surround the droplets with negative charge. In the absence of surfactant it has been observed that droplets of pure paraffinic oils carry a negative charge (117f,143). This has been attributed to adsorption (or desorption) in a more fundamental sense, that is preferential concentration of the hydroxyl ions from the aqueous phase to the interface (142). In the presence of trace amounts of non-ionized organic additive or ions this effect probably becomes negligible (117f). Equally possible is the existence of a frictional charge which, according to the empirical rule of Coehn (144), would tend to make the oil phase negative relative to the higher dielectric liquid (1b).

(a) Electrical double layer:

The concept of a "double layer" was introduced by Helmholtz (145). It was pointed out that if ions of one charge were closely bound to a particle surface, ions of opposite charge (counter ions) would line up parallel to them to form a double layer. Helmholtz theory depicted the double layer as two distinct and concentric shells of ions which predicts a sharp potential drop at the interface. Gouy (146) considered that the general mobility of ions would preclude such an arrangement. He proposed that the double layer was of a diffuse nature with the electric density of the outer ionic layer falling off exponentially with distance from the surface. Double layer theory was further modified by Stern(147) who combined the Helmholtz and Gouy models into a two-part double layer (Fig.1). The inner part, an attached layer of counter ions(Stern layer) was characterized by a sharp drop in potential across its thickness. The outer layer was analogous to the Gouy diffuse layer and exhibited a gradual fall in potential.

(b) Double layer repulsion:

The important consequence of a double layer in colloid or emulsion stability is that the repulsion which arises may prevent close approach of particles or droplets. The calculation of the repulsive effect between two double layers has been achieved in a semi-quantitative fashion by Derjaguin & Landau (148) and Verwey & Overbeek (149). The so-called DLVO theory is an evaluation of the net attractive (van der Waals) and repulsive (electrical) forces between particles. Thus the total interaction between two particles (VT) is:

$$VT = VA + VR , \qquad 1.3$$

where VA and VR are the attractive and repulsive forces respectively. Furthermore, according to Hamaker (150) the attractive forces (VA) are approximated by:-

$$VA = -A_H r \;/\; 12\,H , \qquad 1.4$$

where A_H is the Hamaker constant for the dispersed material, r is the particle radius and H is the separation distance. The repulsive interaction can be estimated† from

$$VR = \tfrac{1}{2}\,\varepsilon\, r\, \Psi_o^2 \;\ln\, (1 + \exp^{-K^1 H}), \qquad 1.5$$

where ε is the dielectric constant of the medium, r is the particle radius, Ψ_o is the surface potential, K^1 is the reciprocal of effective double layer thickness (45) and H is the interparticulate distance. The summation (Equation 1.3)at increasing distances gives rise to the total interaction energy curve which may be of three general types as illustrated in Figure 2.

Two extremes occur when VR$\gg$ VA (Curve A) and when VA$\gg$VR (Curve C), conditions which lead to complete and indefinite de-aggregation and rapid aggregation respectively. Curve B shows a high potential energy barrier which, if it exceeds the mean thermal energy (kT) of particles, will prevent closer approach into the region of strong attraction. At considerably longer distances ($>$10nm) the attractive forces, which fall off more gradually than repulsion, may give rise to loose flocculation in the "secondary minimum".

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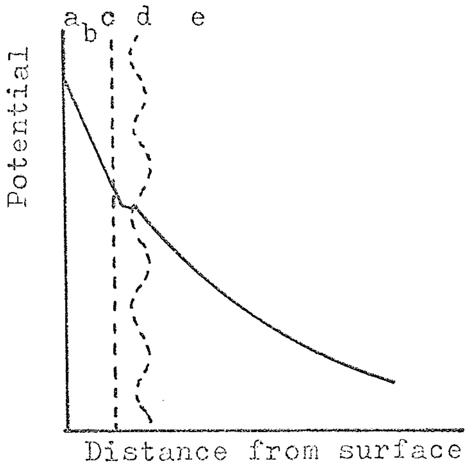
† Footnote : It is generally considered that this formula can be used for most practical systems although it is strictly valid only for spheres with low Ψ_o (<25mV) and where $K^1 r \gg 1$ and $H \gg 1/K^1$.

FIGURE 1

The decay of potential with distance from a charged surface (according to the Stern model of an electrical double layer).

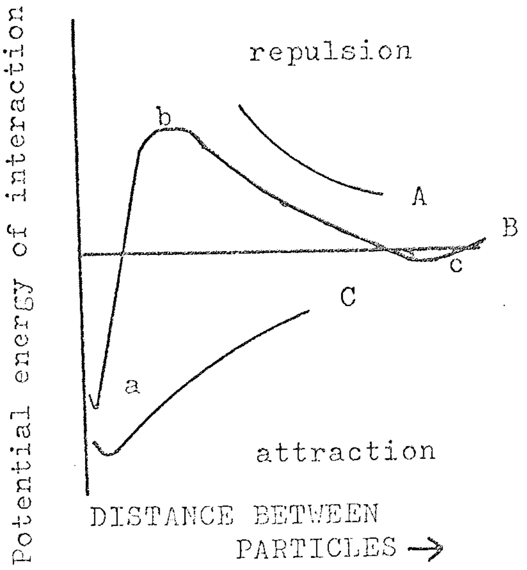


KEY

a	Particle surface
b	Stern layer
c	Stern plane
d	Plane of shear
e	Diffuse layer

FIGURE 2

Potential energy (V_T) curves for the interaction of two particles



KEY

A	Repulsion $\gg$ Attraction
B	curve showing primary minimum (a), energy barrier (b), secondary minimum (c).
C	Attraction $\gg$ Repulsion

D. Electrical theory applied to emulsions.

(a) Double layer in emulsions.

The majority of the theoretical work on double layers has been concerned with solid-liquid interfaces. Verwey (151) pointed out that a liquid-liquid system was a specialized case in which two diffuse layers could exist, one on each side of the interface. It was suggested that the form of the charge distribution was made more like that of the solid-liquid model by the presence of surface active ions. Van den Tempel (87a) has examined the electrical double layer at the o-w interface in more detail. In the absence of surfactant the potential, though significant at both sides of the interface, was smaller on the aqueous side. For a non-conducting oil stabilized by an ionic soap the potential at the aqueous side of the interface was dependant only on the amount of ions adsorbed and electrolyte concentration in the aqueous medium (a higher concentration decreased double layer thickness). The capacity of the diffuse layer in the oil and its contribution to the total interaction energy were negligible under these conditions.

The overall double layer repulsion has been estimated for stabilized liquid dispersions, by using realistic values for r, A_{II}, and K^{1} (16, 149). These curves, and that obtained using a paraffin oil emulsion stabilized by bovine serum albumin (89b), were of the general type (Curve B, Figure 2). However, further problems do arise when applying DLVO theory to o-w emulsions. If water is slightly soluble in the oil (eg benzene) the net potential may be reduced because of dissolution of hydrated counter ions in the oil (117b). Even more significant is the apparent lack of agreement on the correct value of the Hamaker constant (Equation 1.4) since the interaction curve, and particularly the significance of the secondary minimum (see below), depends on its magnitude. The presence of solvated layers or adsorbed films may modify A_{II} although these probably need to be of considerable thickness relative to droplet size. The likely effect of solvation layers has been calculated and reductions in interactions of up to 5-50 times were reported (152). The flattening of the faces of approaching droplets gives rise to an increased repulsion potential the magnitude of which is unknown (45). The approach of droplets adds a further problem because inter-ionic repulsion may cause lateral displacement of the adsorbed ions around the droplet surface, thus making the prediction of overlapping double layer repulsion impossible. Robinson (153) suggested that such a displacement might be reduced or prevented by a condensed monomolecular film which could not be compressed so easily. The effect should also be less for small droplets (117a). Here again, the importance of a distribution of droplet sizes on the overall interaction is not known. Greenwald (48) considered that the ionic displacement was the most important factor in causing problems in relating DLVO theory to emulsion stability.

Further difficulties arise in attributing an appropriate value to ψ_0. It has generally been shown that zeta potential (Z) can be used with little error (1b,45) but the calculation of this value from electrophoretic mobility (Section 3.4) also requires that certain approximations be made. Finally, DLVO theory assumes that the surface potential remains constant during the approach of two droplets, which implies rapid desorption of surfactant as the particles interact. Ho <u>et al</u> (153) have shown that if slow desorption occurs the surface charge would remain essentially constant during droplet approach and the energy barrier could be much greater than that predicted.

(b) Electrical charge and emulsion stability.

The significance of DLVO theory and the role of charge in determining emulsion stability has been discussed by a number of authors

(1b,45,48,117b,149).

The stability of oil hydrosols (53,56,154) and oil dispersions in electrolyte solution (56) has been attributed to double layer repulsion between the droplets. However, Limburg (155) found no relationship between the mobility of droplets in an electric field (measured by a moving boundary technique) and emulsion stability, whereas such a relationship was evident with oil-hydrosols. It was reasoned that stability must be due to the protective film of emulsifying agent. From the microelectrophoretic examination of a range of emulsions King & Wrczesinski (154) decided that there was no relation between stability to coalescence and electric charge on the droplets. After addition of electrolyte the emulsions showed an increased tendency to aggregate and cream, but only those electrolytes which could precipitate the emulsifier affected the coalescence rate. Recent observations give considerable support to these earlier findings. In a review on the stabilization of emulsions by non-ionic surfactants Florence & Rogers (37a) make the general statement that the stability of many dispersions cannot be explained on the basis of VT. Hallworth & Carless (71,91) found that electrical charge could not explain the observed differences in stability of a range of hydrocarbon emulsions.

It has been emphasized that the aggregation of droplets does not necessarily lead to coalescence because of the further presence of an adsorbed film. The DLVO theory has been considered to provide a reasonable description of the electrostatic barrier towards aggregation. Lawrence & Mills (79) measured the fall in droplet number with time for dilute (1% $^{v}/_{v}$) o/w dispersion of Nujol or ditolyl within which creaming was prevented. In the absence of any stabilizer the kinetics of coalescence indicated a moderate energy barrier when analysed in terms of the Smoluchowski theory of coagulation (Section 5.3.4). This was accounted for by the presence of a residual negative charge on the oil droplets. In the presence of adsorbed surfactant (sodium oleate) a far greater barrier to coalescence was indicated. Van den Tempel (87c) found that the kinetics of aggregation followed the Smoluchowski theory of rapid coagulation for emulsions moderately stabilized by ionic surfactants though the observed rates were unexpectedly high. The aggregating effect of different concentrations of added electrolyte was in close agreement with that predicted from double layer theory.

The role of electrical forces in determining the overall stability of emulsions stabilized by polyoxyethylene ethers has been discussed at some length (65abc). It was concluded that electrical forces made a definite contribution to stability if the film was neither mobile nor readily desorbed. As early as 1914 it was suggested that a stable emulsion could be maintained by a zeta potential in excess of 30mV (156). Verwey & Overbeek (149) predicted that the maximum in the potential energy curve (Figure 2) would have to be about 15 or 25kT for moderate and good stability respectively. This compares well with the estimate of 10-20kT (corresponding to $Z \simeq 50-100$mV) necessary to prevent aggregation of colloidal particles (157). More recently Riddick (158) suggested that a Z of 30-40mV would give moderate stability of solid particles but a value as high as 80-100mV would be required for very high stability. The corresponding values for emulsions are believed to be somewhat higher, about 50 and over 100mV respectively (113,158). However, Z as high as 70mV may be unable to stabilize droplets if the surfactant film is relatively mobile (65c).

According to Riegelman (159) a relatively low concentration of ionic surfactant will provide a thick electrical double layer leading to complete deaggregation. There is evidence to suggest that under these conditions droplets may aggregate in the secondary minimum. The special feature of this behaviour is that the particles remain separated by fairly thick (>20nm) lamellae (45). The significance of the secondary minimum in emulsions is not certain, particularly because of doubt concerning the Hamaker constant(1b). However the effect is probably negligible for droplets of diameter 0.1µm, but appreciable for those above 10µm (45). There is some evidence for this phenomenon in dilute emulsions. The aggregation of petroleum ether (1%) emulsions (stabilized by albumin in the presence of electrolyte) attained a readily reversible equilibrium in the region of 20mV. This indicated aggregation in the secondary minimum in accordance with DLVO theory. A similar reversible aggregation has been observed in highly dilute emulsions (10^{-3} to 10^{-4}%) of liquid paraffin or olive oil (160). When two macroscopic paraffin droplets stabilized by 10^{-2} mol dm^{-3} SDDS were forced together an intervening water film about 10-20nm thick was maintained (133). The droplets were believed to be in the secondary minimum which became thinner with an increase in electrolyte concentration.

The droplets in a creamed emulsion will be largely aggregated though collisions will still occur by Brownian motion. The lamella thickness may be reduced due to overlapping double layers (159) and increased aggregation due to the distribution of sizes (88). As the concentration of surfactant (or added electrolyte) is increased the double layer becomes thinner and the energy barrier reduced (87a). At high ionic strength the lamellae become very thin and depend for stability upon the steric hindrance of film molecules (45).

1.2.4 The effect of oil phase on stability

Robinson (3) has reviewed some of the physical and chemical properties which may influence the stability of an emulsion. In addition to the physical properties of the adsorbed film, the chemical nature and viscosity of the dispersed phase and the interfacial tension were all listed. Whilst many of the factors which influence emulsion stability have been considered in detail the relevance of the nature of dispersed phase has received little attention. King (53) observed that marked differences in stability resulted from emulsification of a range of oils and their mixtures in sodium oleate solution. The density of the internal phase appeared to be important in determining stability whilst internal phase viscosity appeared to bear no relation to either bulk viscosity (η) or stability. However the chemical nature of the oil was also considered, for example, a high polarity seemed to contribute to the poor stability of nitrobenzene emulsions.

Toms (161) studied the effect of a number of dispersed phases on η for a range soap stabilized emulsions. It was concluded that the influence of dispersed phase depended upon its interaction with the emulsifier film. Shotton & White (162ab) further observed the influence of the dispersed phase on film structure and the stability of emulsions. Acacia stabilized dispersions of paraffin oils (heptane and light liquid paraffin) were significantly more stable than those of benzene. Cyclohexane emulsions were of intermediate stability. These differences were attributed to a variation in the thickness of the interfacial film with the type of oil dispersed. The poor stability of benzene emulsions as compared with those of liquid paraffin, with potassium laurate as the stabilizer, has also been reported (70). The dispersed phase has been shown to influence stability in the presence of non-ionic surfactants (polyoxyethylene glycol hexadecyl ethers) (37a). Differences in adsorption at polar and non-polar o-w interfaces were believed to explain the low stability of anisole or chlorobenzene emulsions in relation to those of hexadecane.

In a review on o/w emulsion stability, and excluding oils of high polarity, Garrett (41) stated a popularly held view, that the nature of the oil is of negligible practical interest in all aspects of emulsion stability. Bernstein et al (163) have shown that the initial coalescence rates (<3 hours) of highly dilute emulsions (dioctyl or dibutyl phthalate, ditolyl, hexadecane), in low concentrations of SDDS, are independant of the oil phase. However there is some evidence that the nature of the oil phase can be significant irrespective of oil polarity. Groot (164) for example, found that emulsions of Skellysolve C (largely heptane), stabilized with SDDS, were considerably less stable than those containing liquid paraffin. Similarly, Hallworth & Carless (71) showed that emulsions of a number of paraffinic oils stabilized with SDDS or sodium hexadecyl sulphate (SHDS) exhibited a marked increase in stability with increasing paraffin chain length. Stability was found to increase in the order chlorobenzene < hexane $\simeq$ light petroleum (60-80^0) < light petroleum (120-160^0) < light liquid paraffin. It was proposed that when the paraffin chain length of the oil molecules was at least as long as those of the alkyl sulphate, maximum van der Waals interaction could occur and a more coherent film would result. Furthermore the stability of light petroleum emulsions was considerably enhanced by the addition of trace amounts of purified light liquid paraffin. The possible reasons for this phenomenon were examined and the concentration of long chain component at the interface, in a manner analogous to the adsorption of long chain alcohols (Sections 1.2.5 and 1.3.3.4), was considered to be the most likely explanation. Higuchi & Misra (49) previously reported the stabilizing effect of hexadecane and Nujol on dilute carbon tetrachloride emulsions stabilized with non-ionic emulsifiers. This observation provided the basis of molecular diffusion theory (Section 1.2.1).

Interestingly, the formation of microemulsions is also highly dependant on the nature of the dispersed oil (165,166). The stability of such systems depends on the formation of a mixed surfactant film (Section 1.2.5), but penetration by the oil molecules is necessary to allow for the high curvature of the small droplets (165). Prince (166) has reviewed the results for a number of emulsions prepared using octadecane, kerosene and Nujol in the presence of alkyl sulphates. The latter oil did not form microemulsions because of the unsuitable partition of the stabilizing alcohol (octadecanol). Lin et al (167) observed wide differences in the rate of oil separation from a number of dispersions (eg. isopropyl myristate, octyl alcohol) emulsified by mixed non-ionic surfactants.

The concept of "required-HLB" (critical-HLB) for a particular oil highlights the dependence of stability on the nature of the dispersed phase. The chemical nature of the continuous and dispersed phases and emulsifier all influence HLB. Each oil phase can be ascribed a value of HLB at which optimum stability will be obtained (1f,62a,168). Consequently, not all dispersed phases will be equally stable with a given emulsifier. Griffin (168) calculated the required-HLB for several oil mixtures as the volume fraction average of the respective required-HLB values. Gorman & Hall (169) suggested that the dielectric constant of the oil phase correlated well with required-HLB. Lo et al (170) have measured critical-HLB for a number of oils and oil mixtures. The values increased with increasing dielectric constant for the compounds hexane, cyclohexane and benzene but for the aliphatic hydrocarbons (C_6 - C_{14}) required-HLB was related inversely to dielectric constant.

The required-HLB for mixed oils has been found to deviate significantly from the additivity rule (170,171). The advantages of phase inversion temperature (PIT) over HLB in the selection of suitable non-ionic emulsifiers has been emphasized (172a). The effect of oil type and oil mixtures on the PIT of polyoxyethylene nonyl phenyl ethers has been investigated (172b). Phase inversion temperatures for heptane increased in emulsions with hydrocarbon additives in the order benzene < m-xylene < cyclohexane < liquid paraffin at all volume fractions of additive.

Vold & Mittal (99) have reported that the nature of the oil phase can influence the ultracentrifugal stability of emulsions. The rate of separation of oil from olive oil and nujol emulsions was found to be significantly different for a number of surfactants (SDDS, Cetyl pyridinium chloride, polyoxyethylene octyl phenylether, polyoxyethylene sorbitan monolaurate). It was concluded that "less quantitative concepts" such as the chemical nature of the oil and geometric fit between surfactant molecules, in addition to physical characteristics (eg. viscosity, interfacial tension), were responsible for the observed differences in stability. More recently Rehfeld (173) has measured the centrifugal stabilities of paraffin hydrocarbon emulsions (C_6 - C_{17}), benzene, and various alkyl benzenes in SDDS solution by following the volume of creamleft after a particular time of centrifuging. The emulsion stability appeared to be inversely correlated with the tendency of the oil to spread on the aqueous surfactant solution.

1.2.5 Mixed films and stability

Schulman & Rideal (174) have shown that the penetration of an insoluble surface monolayer (eg. cholesterol, cetyl alcohol (hexadecanol)) by a water soluble surfactant can occur in spread films (Section 1.3.2.1). It was considered essential that the non-polar portions of both molecules could interact strongly; the resultant penetration was detected by a sharp increase in surface pressure. It was postulated that in certain circumstances a definite stoichiometric complex of dissimilar molecules could occur. From a study of emulsion stability Schulman & Cockbain (175ab) suggested that a corresponding intermolecular complex could form at the oil-water interface. By using an oil soluble and a water soluble adsorbate they obtained increased emulsion stability, presumably as a result of a more densely packed adsorbed film. An extensive range of emulsifying agents were used to prepare Nujol emulsions and stability was measured as the time required for phase separation to become visible. Stable o/w emulsions were formed when the mixed film was of a liquid condensed type with a high electric charge and low interfacial tension (175a). For stable w/o emulsions a highly condensed and electrically neutral film was considered necessary (175b).

The experimental techniques used in the above study have been criticized on two main points. Firstly, stability was assessed in a manner which is subject to considerable error, particularly since mixed systems with lower interfacial tensions may give a much finer dispersion of the oil (104). Secondly, it has been suggested that the excess of surface active components in some of the systems could cause structure to develop in the continuous phase (176,177).

Subsequent investigations have not definitely established the fundamental basis of interfacial complex formation. Van den Tempel (88) observed no enhancement of stability in paraffin emulsions when cholesterol was used with SDDS or hexadecanol with sodium diethyl hexyl sulphosuccinate (Aerosol OT). However, it is now well established that "mixed" emulsifiers can improve emulsion stability (91,98, 178). Cockbain & McRoberts(104) obtained enhanced stability of single paraffin droplets, but not of benzene droplets, at a plane oil-potassium laurate solution interface, when cholesterol was added to the oil phase. It appeared (from interfacial tension measurements) that cholesterol was co-adsorbed well from paraffin oil but poorly from benzene.

Complexes of lauryl alcohol (dodecanol) in 1:1 and 1:2 mole ratios with SDDS have been found in aqueous solution (179). Corresponding behaviour has been postulated for the hexadecanol + sodium stearate system (180) and SDDS with stearyl alcohol (octadecanol) (126) or hexadecanol (181). Others prefer to regard the interface as a mixed film with the alcohol filling spaces between surfactant molecules (98, 119b). At high concentrations of surfactant the area per adsorbed molecule may be between 0.25 - 0.70nm^2 (Sections 1.3.2.2 and 1.3.3.2) so that it is often sterically possible to fit in an equal number of alcohol molecules. However, stable emulsions have been produced at areas per molecule at least as large as 0.50nm^2 (1b,114,199b) and areas up to 1.60nm^2 have been reported for benzene stabilized by sodium oleate (182). These results suggest that the film need not, after all, be in a condensed form.

The formation of microemulsions further illustrates the dependance of surfactant film interaction upon the surfactants and bulk phases (165). In benzene emulsions the alkyl alcohols with more than ten carbon atoms (i.e. $> C_{10}$) in the chain formed highly condensed or rigid films with potassium oleate. Cholesterol and hexadecanol exhibited similar behaviour with alkyl sulphate surfactants. If an alkane (C_7 - C_{18}) was used as the oil phase then hexadecanol combined in less condensed films in which all three hydrocarbon components (oil molecules and alkyl groups of both surfactants) could interact.

One aspect of emulsion stabilization which has been the subject of much recent discussion is that stability is promoted by the formation of a liquid crystalline phase at the o-w interface. Friberg and others (183abc) have shown that the presence of such a phase in the ternary system of two non-ionic emulsifiers with oil and water can markedly affect emulsion properties and stability. Similar observations have been made by Marland & Mulley (184) in a phase rule study of a dodecane/water system containing a non-ionic surfactant and dodecanol. As early as 1952 it was suggested that the complex between ionic surfactants and aliphatic alcohols, which gave the most efficient stabilization against coalescence, could be of the liquid crystal type (118). It is now generally supposed that liquid crystal formation almost certainly occurs in systems containing a surfactant and an alcohol in conjunction with oil and water phases; however, its incidence will depend upon the nature (eg. hydrocarbon chain length and solubility in the two phases) and concentration of the surfactant and alcohol (185).

1.3 STRUCTURE OF THE PHASE BOUNDARY

1.3.1 The oil-water interface

The classical picture of a liquid-liquid interface has been depicted by Becher (1a) for example. At a molecular level the net forces within the interface are somewhat different from those in the air-liquid surface. Nevertheless, the magnitude of the van der Waals forces of attraction between dissimilar molecules at the interface is likely to be different from that in the bulk of either of the liquids. An imbalance of forces exists giving rise to an interfacial tension analogous to the tension in the surface of a liquid.

Whilst most of the forces are confined to adjacent unimolecular layers of the two liquids it seems certain that molecules somewhat further from the interface are influenced to some degree and these may be considered as part of the interfacial region (186,187). The extent of this region is widely believed to be of only a few molecules thickness but it could be much more (187,188). Since surface layers lend themselves poorly to direct physical investigation the measurement of surface layer thickness is difficult. However, it is likely that the layer thickness in water does depend on the nature of the other phase (189).

Good (190) has considered the surface orientation in strongly hydrogen-bonded liquids, particularly that of water in contact with air or non-polar liquid. He suggested an orientation of oxygen atoms to the interface with both hydrogen atoms towards the bulk water, and extending over several molecular layers. It has also been reported that this arrangement occurs more strongly at hydrocarbon interfaces than at the air-water surface (191). This proposed orientation is in contrast to the earlier opinion (116a) which supported the opposite configuration.

The strong orientation of organic molecules in which a polar group can be presented to the water surface or interface is predictable (116a). For the alignment of non-polar organic molecules (eg. alkanes) at the liquid interface it appears likely that single molecules favour an orientation parallel to a water surface (192). However, in the condensed state it is probable that an angular or vertical orientation is assumed (191,193). Ohki & Fukuda (193) found that the latter orientation, permitting the hydrocarbon chains to act along their long axes, was energetically more favourable than parallel or random positioning. In contrast a number of authors (194,195) are in favour of a more parallel orientation, particularly for the short chain alkanes ($< C_9$).

The various forces which operate at an interface have been described. The cohesion between like molecules and adhesion across the interface may be defined as follows (1a,62a). If a cylinder of liquid with unit cross sectional area is split laterally into two units the work required is defined as the work of cohesion (WC) and:-

$$WC = 2\gamma_2 , \qquad 1.6$$

where γ_2 is the surface tension of the liquid. Similarly, if two systems are in contact these may be separated to create two surfaces and the work required is defined as the work of adhesion (WA) given by the following equation:-

$$WA = \gamma_1 + \gamma_2 - \gamma_{12} , \quad 1.7$$

where γ_1 and γ_2 are the tensions of the surfaces formed and γ_{12} is the interfacial tension between the two liquids.

When a drop of liquid 1 is placed upon a liquid substrate 2, phase 1 may remain as a lens or spread across the surface. In order to quantify this phenomenon Harkins (196a) introduced the concept of spreading coefficient, defined as:-

$$s = WA - WC \quad , \qquad 1.8a$$

ie. $$s = \gamma_2 - \gamma_1 - \gamma_{12} \quad , \qquad 1.8b$$

where the tensions γ_1, γ_2 and γ_{12} are measured as mutually saturated phases. Thus if WA>WC the coefficient s is positive and spreading will occur, and conversely if WA<WC s will be negative and spreading will not occur. This concept has been carried still further to classify liquid-liquid interfaces by the estimation of "critical tension". Shafrin & Zisman (197) have argued that alkanes below nonane spread spontaneously on a water surface (S>0) but from nonane upwards alkanes are non spreading; thus the critical tension γc was found to be between those of octane-water and nonane-water (21.9mN m^{-1}). This value, although constant for saturated branched or cyclic hydrocarbons was higher for unsaturated compounds, presumably as a result of increased liquid-liquid adhesion.

1.3.2 Interfacial films

1.3.2.1 Early work

The possibility of molecular orientation in films at an interface was described by Hardy (198). It was observed that film forming molecules consist of hydrophilic and hydrophobic portions which should be directed into and away from the aqueous phase respectively. This hypothesis was further elaborated by Harkins (116b) who suggested the energetic favourability of adsorption and orientation at interfaces. Much of the stimulus for the study of adsorption has come from the early investigation of insoluble monolayers spread onto surfaces (117c,196b,199a,200) which exhibit similar behaviour to adsorbed films (117c,196b,199b).

The first physical model of an interfacial film was provided by Langmuir (201ab). A range of long chain fatty acids and alcohols were spread at the air-water surface and compressed by means of a movable horizontal barrier. Compression resulted in a minimum area per molecule of 0.21nm^2 irrespective of chain length, showing that the different molecules were elongated and orientated identically at a steep angle with respect to the surface. Further studies (199a) have shown that the hydrophobic chains must be flexible and may lie flat on the surface at high areas per molecule.

By recording the force exerted by the film in resisting compression Langmuir (201ab) constructed force vs. area curves which have since been used to classify monomolecular films according to their behaviour. Pursuing a two dimensional analogy to bulk matter, films have been described as of gaseous, liquid or solid types. The interpretation of monolayer behaviour is based upon the combined analysis of the van der Waals attraction between hydrophobic groups and the polar interaction between "head" groups (201b). However Adam (199a) and Harkins (196b) have indicated the possibility of hydrogen bonding of polar groups with water, showing that interaction with other film forming molecules or water could occur.

1.3.2.2 Physical states of films

The states which may be ascribed to films at interfaces have been discussed fully by Harkins (196b) and Adamson (200) and only a brief summary will be presented here.

(i) Gaseous films.

A gaseous film is invariably formed at areas per molecule which are considerably greater than the molecular cross-section. There are no predominant intermolecular forces between the film forming molecules.

(ii) Liquid films.

In general liquid films are coherent in that there is some degree of interaction between the molecules present. The limiting area per molecule is significantly larger than the molecular cross-section indicating a looseness or disorganization in the interfacial packing. Liquid films may exhibit two distinct forms of force-area curve. Liquid expanded films (201b) approach a limiting area per molecule of about $0.50\mathrm{nm}^2$ for straight chain molecules. Highly compressible homogeneous films are formed but on compression a sharp transition into an "intermediate" type film occurs. This phase may consist of small islands of condensed liquid in equilibrium with the expanded liquid film. Further compression results in a transition to a liquid-condensed type film consisting of closely packed polar "heads" which rearrange on compression as water molecules are squeezed out of the film. The state is characterized by a linear force-area region of low compressibility. The limiting area per molecule may be as low as $0.25\mathrm{nm}^2$. The structure of liquid condensed films has been considered by Alexander (202).

(iii) Solid films.

Materials such as long chain fatty acids and alcohols on water exhibit quite linear force-area relations of low compressibility. The limiting area to which these materials may be compressed approximates to that of vertically packed hydrocarbon chains.

1.3.2.3 Surface Equations of state

Since differences in film properties are characterized by surface pressure (π)-area (A) behaviour further analogy can be drawn with bulk systems. The equation for the π-A relationship may be termed the "surface equation of state", as compared with the pressure-volume relationship of a gas (117c). Here there is a potentially simple method for identifying the nature of the film (196b).

The simpiest molecular equation of state is that for an ideal gas:-

$$PV = RT \qquad , \qquad 1.9a$$

where P is the pressure of the gas per unit area, V is the volume per mole of gas, R is the gas constant and T the absolute temperature. The two dimensional analogue of this equation may be written, by inference or derivation (203a), as

$$\pi A = kT \qquad , \qquad 1.9b$$

where π is the film pressure allowing kinetic movement in two dimensions and k is Boltzmann's constant. This relation assumes that the area of each film molecule is negligibly small compared with A and that there is no interaction (cohesion or repulsion) in the film. Consequently it is only obeyed as $\pi \rightarrow 0$ (i.e. $A \rightarrow \infty$). A great many attempts have been made to derive a more general equation for "gaseous" films. For more concentrated monolayers, for example, Langmuir (201b) corrected for the physical size of the film molecule to obtain

$$\pi (A-Ao) = kT \qquad 1.9c$$

where Ao is the area occupied by the molecule. This equation is often obeyed for neutral films at the oil-water interface, where inter-chain cohesion may be neglected (117c,204a).

When lateral interactions become significant the effective surface pressure becomes

$$\Pi = \Pi a + \Pi b \qquad 1.10a$$

where Πa arises from cohesion and Πb is the kinetic pressure. A further complication arises when ionized film molecules are considered (205) since the electrical repulsion in the monolayer gives rise to a repulsion pressure (Πr) and

$$\Pi = \Pi a + \Pi b + \Pi r \qquad 1.10b$$

The behaviour of ionized monolayers at an o-w interface has been studied in some detail since there is little film coherence (Πa). The Gouy theory of diffuse double layer repulsion (Section 1.2.3.2) has been applied in order to estimate the magnitude of Πr (117c,203b,205). Substitution into Equation 1.10b gives the general equation of state which, in its simplest form for completely ionized films at the o-w interface (203b) predicts that

$$\Pi = \frac{kT}{A-Ao} = \frac{2kT}{A} \qquad 1.11$$

The general equation has been modified by introducing a coherence term for films at the a-w interface (206) and a factor for ionic films in the absence of salt (204b,207). However, disagreement with the equation has frequently been recorded for spread and adsorbed films at both air- and oil-water interfaces (203b) (Section 1.3.3.2) at all but extremely low pressures. This is no doubt due to the inadequacies of the simple electrical model upon which the validity of Equation 1.11 depends.

In the liquid-expanded state the situation is further complicated by cohesive forces between the molecules making up the film. The correction for van der Waals attraction is often assumed to take the form of Equation 1.9c (201b) but the relation assumes that cohesion will remain invariant over a wide range of areas (200) and agreement is often poor for surface films on liquids (196b).

The intermediate and condensed films can be viewed as "semi-solid" in nature with more or less water between the polar head group. The π-A plots are almost linear and as such can be identified and characterized easily (196b,200).

1.3.3 Studies on adsorbed films

In order to characterize an interfacial film it is necessary to obtain both the relationship between the adsorption and bulk phase concentration and the state of the adsorbate in the interface. Surfactant films which are adsorbed from solution cannot be investigated by compression studies since any compression of the soluble components will result in desorption from the interface. The properties of adsorbed films are generally deduced from interfacial tension studies and Gibbs' equation.

1.3.3.1 Gibbs' adsorption equation

A. Derivation

If the consideration of intermolecular forces at an interface is extended to solutions it has been argued that those molecules for which the interaction energy is lowest will tend to accumulate in the interface (Section 1.3.2.1). Thus the free energy of the system will attain a minimum value at adsorption (or desorption) equilibrium. The Gibbs adsorption equation (208) is a thermodynamic expression which relates the interfacial concentration of an adsorbate to its bulk activity or fugacity and the interfacial tension (γ). Thus in liquid-liquid systems (where γ is readily measured) the equation may be used to determine the interfacial concentration of an adsorbate.

In its strictest form the Gibbs equation is necessarily thermodynamically correct and may be written as

$$A' d\gamma + n_i \, d\mu_i = 0 , \tag{1.12}$$

at constant temperature, where A' is the surface area, γ is the surface or interfacial tension, n_i is the excess number of molecules of the i th component and μ_i is the surface chemical potential of the adsorbed species (117d). However all surface or interfacial species must be included in the summation term and it becomes necessary to make extra-thermodynamic assumptions to obtain a useful expression.

The derived Gibbs equation takes the form

$$\Gamma = \frac{1}{RT} \cdot \frac{d\gamma}{d \ln a} \qquad 1.13a$$

(where R is the gas constant, T is the absolute temperature and a is the mean activity of the solute) for non-electrolytes or uni-valent electrolytes in the presence of a large and constant concentration of common electrolyte. For the adsorption of uni-valent electrolyte from a simple solution the derived equation becomes

$$\Gamma = \frac{1}{2RT} \cdot \frac{d\gamma}{d \ln a} \qquad 1.13b$$

A more comprehensive account of the derivation of Gibbs' adsorption equation can be found in Appendix 1.

The derivation of the equation has been criticised on the assumptions involved (209). The model proposed for the interfacial region has been questioned on the grounds that it does not correspond to the physical picture of an interfacial layer (210). In contrast Scatchard (211) re-examined the original derivation and found it to be valid.

B. Experimental verification of the derived equations.

(a) Air-Water Interface.

A considerable amount of experimental work has been directed towards the verification of the adsorption equation. McBain and colleagues (212ab) found that by skimming off a thin surface layer (approximately 0.05mm) of solution for analysis reproducible concentration measurements could be obtained. Good agreement with Equation 1.13a was reported for a number of substances including phenol, toluidine and hexanoic acid (212a). However, the method involved considerable mechanical difficulties and an alternative technique was developed (212bc). A small depth of surface (≃ 3mm) was compressed and the consequent increase in bulk concentration was measured interferometrically; results obtained using hydrocinnamic or lauryl sulphonic acid solutions were again in good agreement with Equation 1.13a . The molecular areas of spread monolayers of sparingly soluble substances such as fatty acids (117d,199) have been found to be in excellent agreement with those from Equation 1.13a for the same substances.

The adsorption of SDDS to the air-water surface has been measured by Wilson et al (213). A volume of foam was generated from the surfactant solution and the change in bulk concentration determined by analysis. From the mean bubble size in the foam, and hence the total surface area, an estimate of the area per adsorbed molecule was obtained. Nillson (214) measured the adsorption of tritium-labelled SDDS by measuring the particle emission from the air-solution surface in the presence of added electrolyte. Both these authors obtained results which were comparable with those from the Gibbs equations.

A number of other workers have used a radioactive labelling technique though there is some contradiction in the findings. However, reviewers of the topic have concluded that an overall improvement in the technique has led to increasing agreement with the theory (11b, 117d).

The estimation of surface excess from the surface potential of SDDS solution has also corroborated the validity of Equation 1.13b or the alternative form 1.13a when excess electrolyte (sodium chloride) was present (215).

(b) Oil-Water Interface.

Adam (199b) reported an ingenious technique to measure the amount of adsorption on hydrocarbon droplets of known total area. The droplets were passed through surfactant solution to allow saturated adsorption to occur and then discharged into a separate chamber. This method was similar in principle to that of Wilson (213) described above. However, the measured adsorption was several times greater than that predicted by the Gibbs equation (Equation 1.13a). Nevertheless Davies (216) has shown that sparingly soluble films of CTAB spread at petroleum ether-water interfaces conform to Equation 1.13a in the presence of inorganic electrolyte.

Cockbain (84) has measured the adsorption of SDDS at a decane-solution interface in the presence of excess electrolyte using Equation 1.13a . In addition a single decane emulsion (20% $^v/v$) was prepared and divided into aliquots. These were diluted with SDDS solutions at different concentrations and divided into two groups. To one group an excess of sodium chloride was added. After creaming the sera of all the emulsions were analysed for SDDS content. The total area of the interface was computed for those emulsions containing excess electrolyte. This area was used to calculate the adsorption in the remaining group. The results obtained amply demonstrated the need for the factor 2 in equation 1.13b for the calculation of SDDS adsorption in the absence of excess electrolyte. A comparision of the emulsion technique and Gibbs equation has shown agreement at the toluene-SDDS solution interface (217). Haydon and Phillips (218) have investigated the adsorption of SDDS and dodecyl trimethyl ammonium bromide (DTAB) at a petroleum ether interface in the absence of excess electrolyte. Adsorption was measured independently from surface potential studies. When DTAB was used results were in accordance with Equation 1.13b . Provided the water was highly purified, the adsorption of SDDS was predicted by the same equation across the concentration range 1.6x 10^{-4} mol dm^{-3} to the critical micelle concentration. However, using singly distilled water it appeared that trace impurities could provide a swamping excess of electrolyte at concentrations of surfactant below about 3 x 10^{-4} mol dm^{-3}

and adsorption was then predicted by Equation 1.13a .

1.3.3.2 Adsorbed films of alkyl sulphates

As a general rule adsorbed films of pure soluble surfactants are of the gaseous or expanded types. However, ideal behaviour is only possible at extremely low concentrations; otherwise corrections are necessary for the area occupied by the adsorbed molecules and any lateral interactions between them (199b) (Section 1.3.2.3). The existence of an ideal region for alkyl sulphates at air- and oil-water interfaces has been investigated only recently (219). In the presence of excess electrolyte extremely low concentrations of sodium decyl sulphate (SDS) and SDDS were shown to give ideally gaseous films. Subsequently, the thermodynamics of adsorption in this region has been discussed (220ab). Self interaction of surfactant molecules was presumed to account for non ideality arising at a range of alkane-water interfaces at concentrations of SDDS in excess of 10^{-6} mol dm^{-3} (220b). The same effects were found at the air-water interface with SDDS concentrations above about 10^{-4} mol dm^{-3} (220a). Marked deviations from ideality have been reported elsewhere for adsorbed films of SDDS at air-water interfaces with surfactant concentrations above 10^{-3} mol dm^{-3} (221,222).

The equation of state describing the behaviour of SDDS films in non-ideal regions has been the subject of much conjecture. A general empirical equation of the form:-

$$\Pi\,(A - A_o) \;=\; n\,KT \quad , \qquad 1.14$$

where n is a constant, has often been applied to observed data. Various values have been assigned to n for adsorbed films at the air-water interface in the absence of electrolyte. For example, Brady (221) reported that n=2 over the concentration range 1.6 x10^{-3} to 10^{-2} mol dm^{-3}. Over a similar concentration range Pethica (222) found that n=1.2. The latter author also found Equation 1.11 to be inadequate for adsorbed alkyl sulphate ions. Cassie & Palmer (223) have suggested that Equation 1.14 (n=1.5) should apply to ionized films at oil-water interfaces in the absence of excess electrolyte. However, Cockbain (84) obtained results for the adsorption of SDDS, at the decane-water interface, which were not fitted by any simple form of Equation 1.14 at concentrations above 10^{-4} mol dm^{-3}. There was also poor agreement with the general equation of state for charged films (Equation 1.11) though correlation was improved if excess sodium chloride was included. Equations of state for adsorption at the o-w interface have been discussed by Ghosh & Kundu (224). Even modified forms of Equation 1.1. did not correlate with measured data for ionized (dodecyl trimethyl ammonium bromide (DTAB))films. Observations at the petroleum ether-water interface support these views (218). The adsorption of DTAB at concentrations up to the cmc was described by Equation 1.11 but the correlation with adsorbed SDDS was poor above 1.6 x 10^{-4} mol dm^{-3}. The conclusion has been drawn that the assumptions involved in deriving Equation 1.11 (Section 1.3.2.2) are not valid for alkyl sulphate films (84,203b,222).

Several authors have reported an apparently linear region in plots of surface or interfacial tension vs. concentration for surfactants just below the cmc. Such behaviour, which implies a constant adsorption of surfactant by Gibbs equation, has been found for numerous non-ionic (225) and anionic surfactants, including alkyl sulphates (226,227) at the air-water interface. Van den Tempel (87a) reported evidence for this phenomenon at the oil (50% monochlorbenzene + paraffin oil)-water interface for a number of surfactants. Van voorst Vader (228ab) inspected alkyl sulphate adsorption over the relevant concentration range at a number of oil-water interfaces including heptane, petroleum spirit and benzene. It was found that adsorption became independant of concentration over what was termed a "saturated adsorption region". The degree of saturated adsorption appeared to be dependent upon the polar group of the surfactant and its interaction with other polar groups in the interface. A striking comparison was drawn with the properties of liquid condensed monolayers, suggesting that similar intermolecular attraction forces were responsible for both phenomena (228a). More recently a saturated adsorption region has been reported to occur at SDDS concentrations above 10^{-4} mol dm^{-3} and SDS concentrations above 5×10^{-4} mol dm^{-3} at interfaces with alkane (229). However, direct measurements of SDDS adsorption (213,214) have not supported these findings.

The Gibbs equation does not facilitate the estimation of surfactant adsorption at still higher concentrations (ie. above the cmc) owing to the discontinuity in surface or interfacial tension measurements (45, 111b). It has been assumed that the near constancy of these tensions as the concentration is raised indicates that there is no significant adsorption increase. The excess surfactant ions are presumed to form micelles, the interfacial adsorption of which is opposed sterically and by the polar nature of the micelle exterior (1c). Nillson (214) found that adsorption of tritiated SDDS from solution to the air-water surface reached a constant surface excess as the concentration was increased past the cmc. Similarly Wilson <u>et al</u> (213) showed that adsorption of SDDS onto foams reached a constant value at the cmc. The limiting area per molecule of adsorbed ion was 0.40 nm^2 $molecule^{-1}$ suggesting that expanded films persisted above the critical concentration, a conclusion also reached by Brady (221). Despite these findings the possibility of micellar or polymolecular surfactant adsorption at interfaces cannot be discounted entirely. A number of estimates of surface excess using the radio-tracer technique (admittedly a rather unreliable device at high isotope concentrations) have suggested that the surface excess continues to rise above that for a monomolecular film (111b). Microtome studies have also given some suggestion that polymolecular adsorption can occur with dodecyl sulphonic acid (212b). In emulsions, polymolecular adsorption has been proposed to explain the increased aggregation of light petroleum and, more noticeably, benzene dispersions at concentrations of surfactant (eg. potassium laurate, SDDS, CTAB) above the cmc (230). Disaggregation at still higher concentrations was attributed to a higher degree of polymolecular adsorption or to the adsorption of micelles. The concept of polymolecular and micellar adsorption has been questioned by Becher (1c) and Higuchi et al (231). Such an adsorption of pure surfactants is considered to be highly improbable. However in mixed or impure surfactant systems, which are capable of forming more condensed films, models for micellar (159) and polymolecular (70b,232) adsorption have been proposed at high surfactant concentrations. In the case of a high concentration of alkyl sulphate, where a mixed film may arise from incomplete sulphation of aliphatic alcohol during manufacture or through interfacial hydrolysis back to the alcohol, the possibility of a multimolecular adsorbed film cannot therefore be dismissed.

1.3.3.3 The influence of oil phase

Alexander and Teorell (233) obtained Π-A relationships for lecithin and sodium hexadecyl sulphate (SHDS) at the benzene-water interface, which indicated that cohesive interactions between hydrocarbon chains of the surfactants was considerably reduced in an oil medium (i.e. Π_a eliminated from Equation 1.10b). In support of this observation Adam (199b) found that materials which gave liquid type films at the air-water surface often formed more expanded films at an oil-water interface. It was proposed that the lateral interactions of the surfactant hydrophobic groups could be satisfied individually by oil molecules and that the motions of the latter would enhance movement of the adsorbed molecules, both processes making the film more gaseous.

In contrast Hutchinson (234ab) investigated a number of fatty acids and alcohols which developed Π-A curves with a transition point and shape characteristic of a more condensed film at oil-water interface than on water alone. It was also suggested that the lateral attraction between surfactant "tails" and oil molecules may be considerable. However, in subsequent studies Hutchinson (234c) showed that adsorbed films from an impure SDDS solution $(1 \times 10^{-4}$ to 7×10^{-3} mol dm$^{-3})$ were all gaseous at the oil (cyclohexane, benzene, chlorobenzene or nitrobenzene)-water interface. Nevertheless large variations in the Π-A product indicated a considerable deviation from ideal behaviour. The nature of the oil was observed to exert considerable effect on the properties of the film obtained. Thus, films at the nitrobenzene-water interface were more condensed than at the water surface, chlorobenzene did not alter the film significantly whilst benzene and cyclohexane-water interfaces gave more expanded films.

The supposition that adsorbed films become more expanded at oil-water interfaces is further supported by the measured limiting areas per molecule as the concentration approaches the critical micelle concentration. Values obtained for SDDS at the air-water interface lie between 0.35nm^2 and 0.50nm^2 per molecule (213,214,221,228a,235-237). The areas obtained for oil-water interfaces show some dependence on the oil phase but are normally increased. Cockbain (84) found a limiting area per molecule of 0.48nm^2 at the decane-water interface. This value has also been obtained for the petroleum ether-water interface (218). Rehfeldt (237) found that the limiting area for surface adsorption ($0.44nm^2$) was increased only slightly by alkanes (e.g. hexane $0.45nm^2$: decane $0.49nm^2$), somewhat more by unsaturated hydrocarbons (hexene $0.57nm^2$) and considerably increased by benzene ($0.65nm^2$).

Recent studies on the thermodynamics of oil-water interfaces (219,220b,238) have shown that adsorption behaviour and film properties depend on the nature of the oil phase. The effect of the chain length of normal hydrocarbon oil on SDDS adsorption has been investigated (229). The nature of the oil was found to affect adsorption in a limited concentration range above the ideal adsorption region but below the saturated adsorption region. It was concluded that the different oils must affect the degree of self interaction of the surfactant molecules. Similar results have been obtained from a study of the nature of adsorbed quaternary ammonium salts at alkane-water interfaces (239). The nature of the oil was found to influence adsorption at all concentrations below the critical micelle concentration, the films becoming more expanded with an increase in alkane chain length. The relative effect of chain length of the oil on surface excess was dependant upon the bulk concentration. For example, an increase in the bulk concentration of dodecyl-dimethyl-ethyl ammonium chloride showed an increased tendency to adsorb onto longer chain length alkanes. Interactions of oil molecules with both hydrophilic and hydrophobic surfactant groups were considered. It was suggested that at higher concentrations a more vertical orientation of surfactant molecules improved the interaction with longer chain hydrocarbons. Van voorst Vader (228a) examined a more diverse range of oils and has shown that the oil phase can affect the nature of the film in the saturated adsorption region if the oil molecules contain a polar group. Recently, Buscall & Davis (240) have re-measured the adsorption of surfactant at various alkane-aqueous SDDS solution interfaces. The results obtained using highly purified oils (hexane, octane, decane, dodecane and hexadecane) did not indicate any dependence of adsorption upon alkane chain length. It was suggested that the effects found by previous workers were due to impurities in the oil phase rather than any specific interaction between alkane and surfactant molecules.

Although little information is available regarding adsorption above the critical micelle concentration, it is perhaps significant that Cockbain (230) observed marked differences in the aggregation behaviour of benzene and light petroleum emulsions.

1.3.3.4 Interactions in mixed films

Mixed films, both spread and adsorbed, are formed by substances which are capable of separate monolayer existence. Just as for simple films, much of the understanding of the nature of mixed films has been as a direct result of studies on spread monolayers at air-water surfaces. Thus it has been shown that the behavior of mixed films may range between an essentially ideal "solution", as with similar long chain fatty acids, to apparent stoichiometric complex formation (241-243). The extent of molecular association has been found to depend upon mutual interaction of the polar and hydrophobic portions of the interacting species. Davies and Rideal (117e) have considered the probable polar interactions, as with an ionic + non-ionic surfactant mixture, concluding that the shielding of charged ionic "heads" by non-ionic polar groups is probably more important than interactions (eg. hydrogen bonding) between the two. This conclusion was reached by Goodrich (244) who suggested that complexing could occur if the hydrophobic portions were sufficiently symmetrical to permit close packing. Dervichian (245) has also suggested that hydrocarbon chain interactions are prevalent since no complexing was found to occur between straight hydrocarbon chains of less than 8C atoms. More recently Lucassen-Reynders (246a) has pointed out that any assessment of interactions in spread or adsorbed films must also take into account the presence of substrate or solvent molecules, a factor not previously considered. By using the thermodynamic convention of a surface phase (Appendix I), in contrast to the surface plane used by Goodrich (244), an approximate measure of the interaction of surfactant and solvent could be obtained. For example the investigation of adsorbed surface films of lauric acid + Na laurate (246b) indicated the formation of a stoichiometric complex; comparison of Π-A curves for the pure and mixed films revealed a degree of surfactant-solvent interaction consistent with the theory.

Of further significance is the observation that spread monolayers could be "penetrated" by soluble surface active constituents of the liquid substrate, resulting in a marked increase in surface pressure (174). The extent of penetration and molecular association in the mixed film was shown to depend upon mutual interactions of both polar and hydrophobic moieties of interacting molecules. Subsequent investigations into the penetration of alkanol monolayers by alkyl sulphates have been performed by numerous authors. Schulman & Stenhagen (247) suggested that sodium hexadecyl sulphate (SHDS) penetrated and complexed with cholesterol or hexadecanol for example. Goddard & Schulman (248a) found that SHDS penetrated a number of long chain alcohol, acid and amine monolayers. In some cases a stable 1:1 complex was formed. It is now well established that SHDS penetrates readily into cholesterol (248a,249a) and hexadecanol (248b,249b) but no complex was indicated in these cases. A similar observation was made by Fowkes (250) for insoluble mixed films of SHDS and hexadecanol on a sodium chloride solution substrate. A transition in the film, to one of considerably closer packing, occured at an approximate 50% mole fraction mixture but this was attributed to a molecular rearrangement of sulphate molecules rather than the separation of a definite complex.

Whilst a considerable amount of information is available directly from studies on monolayers spread at air-water surfaces, comparatively little work is reported regarding adsorbed mixed films. Hutchinson (234d) has investigated the adsorption of an SDDS-octyl alcohol film from aqueous solution by means of a modified version of the Gibbs equation. The results obtained, although only approximate, showed no indication of either complex formation or enhanced SDDS adsorption in the presence of alcohol. However, even at relatively low concentrations of alcohol its concentration in the film was appreciable. On the other hand the surface tension measurements of Harva (251ab) have indicated that sodium laurate may form stoichiometric complexes with C_6, C_7, C_8 and C_{10} alcohols at higher concentrations.

The direct measurement of adsorption in mixed systems has been achieved by tritium labelling of one or both components (214). At a constant concentration of SDDS (10^{-3}mol dm^{-3}) and a range of concentrations of dodecanol it was found that strong adsorption of the alcohol occurred, reaching at least 50% of the film even at high dilution. Above the cmc the alcohol was removed from the interface, presumably becoming incorporated into mixed micelles.

Cockbain & McMullen (252) found no evidence in interfacial pressure estimates to suggest any interaction at benzene- or decane-water interfaces. Amongst the materials examined were SDDS or potassium laurate with octadecanol or cholesterol. On the same basis Kanellopoulos & Owen (253) could detect no interaction of SDDS at interfaces between surfactant solution and silicone fluid into which decanol, dodecanol or hexadecanol was dissolved. In both these studies the alcohols were strongly adsorbed at the interface.

In general then, the properties of mixed films and solutions are markedly different from those of surfactant alone irrespective of whether a definite complex is formed. The alcohol is strongly co-adsorbed and an increased condensation of the film is generally accepted. Surfactant films may be transformed to liquid condensed (175a) or rigid films (125, 119b)by the presence of a long chain alcohol. Surfactant films may give rise to a liquid crystal phase at the interface (Section 1.2.5). The particular interactions and hence the nature of adsorbed films of mixed systems may depend upon the concentration and chemical configuration of the surfactants but also upon the nature of the two bulk phases.

2

MATERIALS

2.1 WATER

All water was twice-distilled using an all glass apparatus comprising of two stills (Fisons "Loughborough", $4 dm^3$ per hour output) connected in series. The first $1 dm^3$ or more of distillate was discarded from each batch and the remainder was collected in glass aspirators ($10 dm^3$) which were stoppered when full. The water was stored overnight before each batch was monitored for its conductivity (specific conductance) and surface tension. These measurements were taken at $25 \pm 0.1°C$ by the methods described in Sections 2.2.2 and 3.1 respectively.

For all water samples used the conductivity did not exceed $1.2 \times 10^{-6} \Omega^{-1} cm^{-1}$ and the surface tension was 71.8 to 72.6 $mN\ m^{-1}$.

2.2 SURFACTANT

2.2.1 Choice of surfactant

Sodium alkyl sulphates were chosen as suitable agents for this study. The generic formula of the group can be written as

$$R\ (OSO_3^-\ \ Na^+)$$

in which R is a saturated aliphatic group with a straight or branched chain. This hydrophobic group must be sufficiently large to make the surface active anion appreciably amphipathic, which usually requires at least twelve carbon atoms, though shorter chain length agents are used in certain instances (111c). Not only are these compounds relatively cheap and readily available, but they can be prepared in homogeneous form and their composition may be routinely determined. Consequently there is more information available pertaining to their properties at interfaces than about any other class of anionic surfactant.

The most serious disadvantage of the group is their chemical instability; in particular, they tend to hydrolyse to free alcohol in aqueous media.

2.2.2 Characterization

The purity of a number of alkyl sulphates (listed in Table 2-1) was checked by measurement of critical micelle concentration (cmc) from conductimetric and surface tension measurements and by hydrolysis of the sulphate to the free alcohol which was then analysed by gas-liquid chromatography (GLC).

2.2.2.1 Gas-liquid chromatography

Approximately 10^{-3}kg of surfactant was refluxed for four hours with $30cm^3$ of water and $10cm^3$ of hydrochloric acid. The mixture was allowed to cool and the free alcohols were separated by shaking with three separate aliquots ($20cm^3$) of solvent ether. The ether was evaporated and a solution was prepared of approximately $10kg\ m^{-3}$ (0.01 $g\ cm^{-3}$) free alcohol in heptane.

The alcohols were chromatographed using a Perkin-Elmer F11 instrument with a flame ionization detector. Nitrogen was used as the carrier gas at a flow rate of $10^{-6}\ m^3\ s^{-1}$ ($1\ cm^3\ s^{-1}$). An Antarox CO-990 column was used (8 % Antarox in 80-100 mesh chromasorb W (AW-DMCS), obtained from Perkin-Elmer Ltd). At an operating temperature of 184°C this column was found to give adequate separation of C_8 and higher alcohols without perceptible "tailing" of the analysis peaks.

Pure standards of decanol, dodecanol and tetradecanol (Section 2.4) were used to find retention times and a mixture of equimolecular proportions of these alcohols ($0.1\ mol\ dm^{-3}$ in heptane) was employed to test the relationship between alcohol chain length and detector response (measured as peak area). The area relationships obtained using the standard mixture (see Table 2-2) were found to be linear within experimental limits. The analytical results for the range of surfactant samples are given in Table 2-2.

2.2.2.2 Critical micelle concentration

A stock solution of each surfactant (10^{-1} mol dm^{-3}) was prepared using doubly distilled water and $100cm^3$ of a wide range of dilutions were made up in volumetric flasks. These were immersed in a water bath at 25 ± 0.05°C for thirty minutes to allow the solutions to come to temperature.

The conductance (G) and surface tension (γ) of each solution was measured in a double walled beaker maintained at 25 ± 0.1°C by pumped flow from a water bath (see Section 3.1.4).

Conductivity ($K = Gb$) was determined using a Mullard conductivity cell, whose cell constant (b) was found to be 1.34, connected to a conductivity bridge (Wayne Kerr Universal Bridge, B221). Surface tensions were measured using the Wilhelmy Plate technique described elsewhere (Section 3.1).

The cmc was estimated from the sharp inflection in plots of conductivity or equivalent conductivity vs. square root of concentration (254,255) and surface tension vs. concentration (251 ab). A minimum in surface tension vs. concentration curves made the estimation of cmc more difficult. Previous workers (214,251ab,256-258) have proposed that such a minimum can arise from the presence of surface active impurities such as the free unsulphated alcohol.

A sample of 0.1kg of SDDS-A was recrystallized from a 50% $^v/v$ ethanol-water mixture. The surfactant was extracted with heptane for twenty to forty hours in a Soxhlet apparatus. Before use the Soxhlet was soaked overnight in chromic acid, rinsed thoroughly with water followed by acetone, dried and rewashed in solvent (heptane). The 20 hour extraction was performed using a conventional extraction thimble which had been subjected to 5 hours of heptane extraction. This was substituted in the longer extraction process where a glass wool packing was inserted into the Soxhlet prior to cleaning. The surfactant samples were washed with fresh solvent and dried under vacuum.

The cmc values obtained for all samples are listed in Table 2-2.

Table 2-1.

Alkyl sulphate samples and their sources.

Sample	Source	Grade
Sodium decyl sulphate $C_{10}H_{21}(OSO_3^-Na^+)$		
SDS-A	Eastman-Kodak	Reagent
Sodium dodecyl sulphate $C_{12}H_{25}(OSO_3^-Na^+)$		
SDDS-A	British Drug Houses	Specially pure
SDDS-B	Eastman-Kodak	Reagent
SDDS-C	Marchon Products	Specially purified*
SDDS-D	As SDDS-A	Soxhlet 20 hour
SDDS-E	As SDDS-A	Soxhlet 40 hour

NOTES

* Sample kindly supplied by Dr. B.W. Barry, School of Pharmacy, Portsmouth Polytechnic, Portsmouth, Hants.

Table 2-2.

Characterization of surfactants.

SAMPLE	cmc (mmol dm^{-3})			GLC (%)			
	(a)	(b)	(c)	C_{10}	C_{12}	C_{14}	Others
SDS-A	34.0	26.6	3.6	99.5	(n)	(n)	C_8 0.5
SDDS-A	8.12	7.50	2.8	0.8	99.2	(n)	(n)
SDDS-B	2.50	2.25	4.3	0.5	70.5	29.1	C_8 0.3
SDDS-C	8.15	7.00	4.5	0.6	99.0	0.4	(n)
SDDS-D	8.07	6.90	3.5	-	-	-	-
SDDS-E	8.00	7.32	1.3	-	-	-	-
Standard	-	-	-	32.29	34.86	32.85	-

NOTES

a conductivity method

b surface tension method

c depth of surface tension minimum (mN m^{-1})

n none detectable

2.2.2.3 Discussion; Selection of suitable samples

Homologue impurities (as detected by GLC) may be present in the original surfactant as either sulphate or free alcohol. The high contamination of sample SDDS-B has been verified independently (Appendix II). All other samples were of 99% purity or better with respect to homologues.

The discrepancy between cmc measurements for the two techniques employed can be explained partly by the dependence of cmc on the property being measured (111,237,254) and partly through the difficulty in judging the inflection point of the surface tension plots (Figure 4). With the exception of sample SDDS-B the cmc values measured by conductivity compare favourably with the literature values for purified samples (sodium decyl sulphate 33.0 mmol dm^{-3} and sodium dodecyl sulphate 8.10 mmol dm^{-3})(237,253,255,259). Since the homologue impurity is known to be low in these samples the slight lowering of cmc is probably due to the presence of free alcohol (251b,260). This suggestion is supported by the presence of the surface tension minimum. Comparison with the results of Miles & Shedlovsky (256) indicates that a minimum of 2 to 3 mN m^{-1} might be expected from about 0.1% of dodecanol in sodium dodecyl sulphate. Several workers have succeeded in removing such minima by Soxhlet extraction (256,261). In this work however, extraction for up to 100 hours failed to remove the minimum completely, in agreement with other observations (214,258).

Samples of SDS-A, SDDS-A and SDDS-E were selected as suitable agents for this study. The GLC, surface tension vs. concentration and equivalent conductivity vs. concentration curves for these materials are given in Figures 3 to 5. Each surfactant sample was divided into small portions (<0.05kg) which were stored under nitrogen in tightly sealed bottles. Surface tension vs. concentration curves were re-measured frequently after the bottles were opened.

FIGURE 3

TYPICAL TRACES FROM GLC ANALYSIS

Notes :

For experimental details and results see Section 2.2.2.
Each curve obtained by injecting 2×10^{-6} dm^{-3} sample onto column.

Traces shown for SDDS-A (curves A&B) or SDS-A (curves D&C) measured at sensitivity setting 10×10^{2} (curves A&D) or 20×10^{2} (curves B&C).

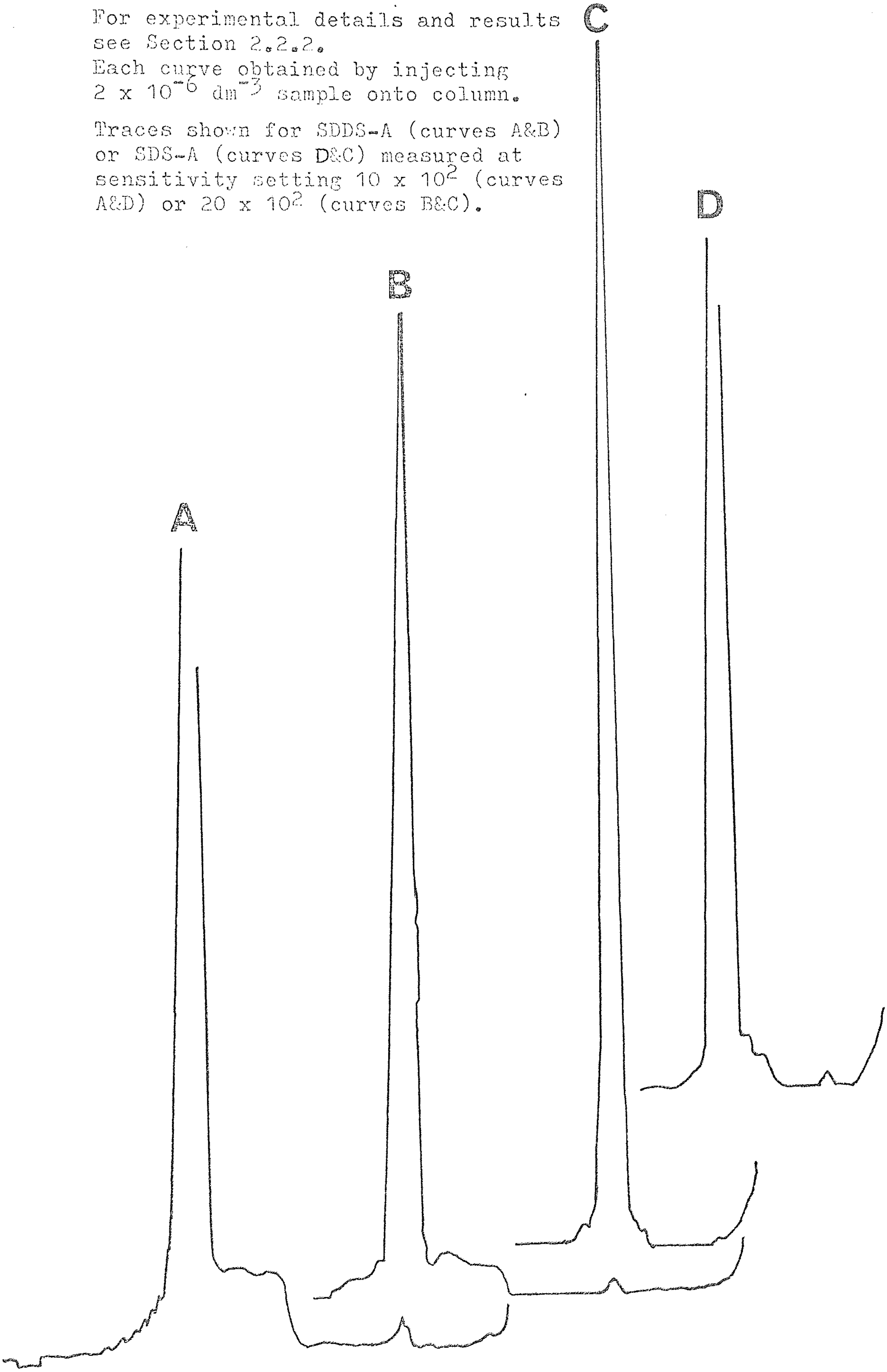


FIGURE 4

Measurement of critical micelle concentration from plots of interfacial tension versus logarithm of surfactant concentration.

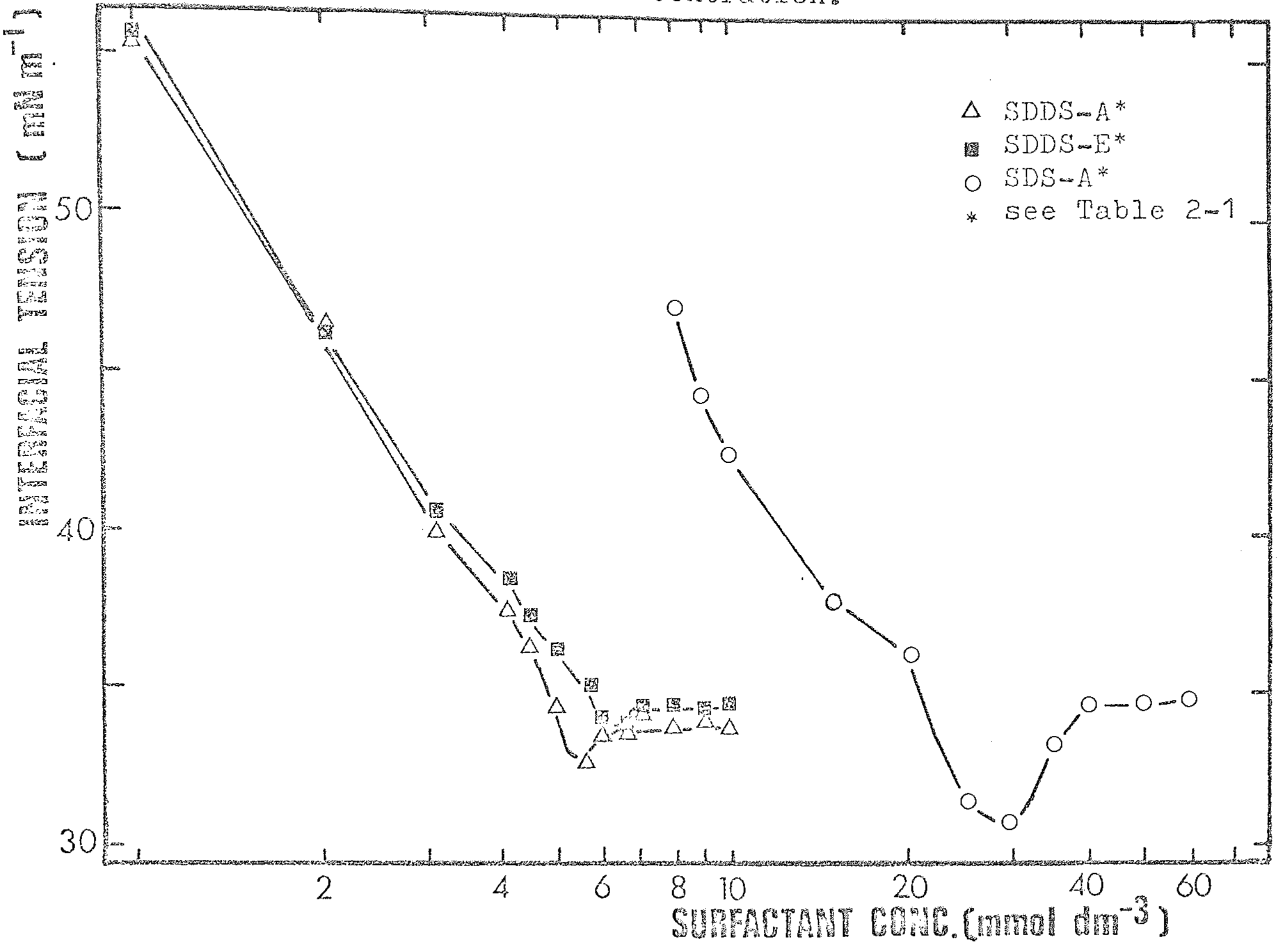
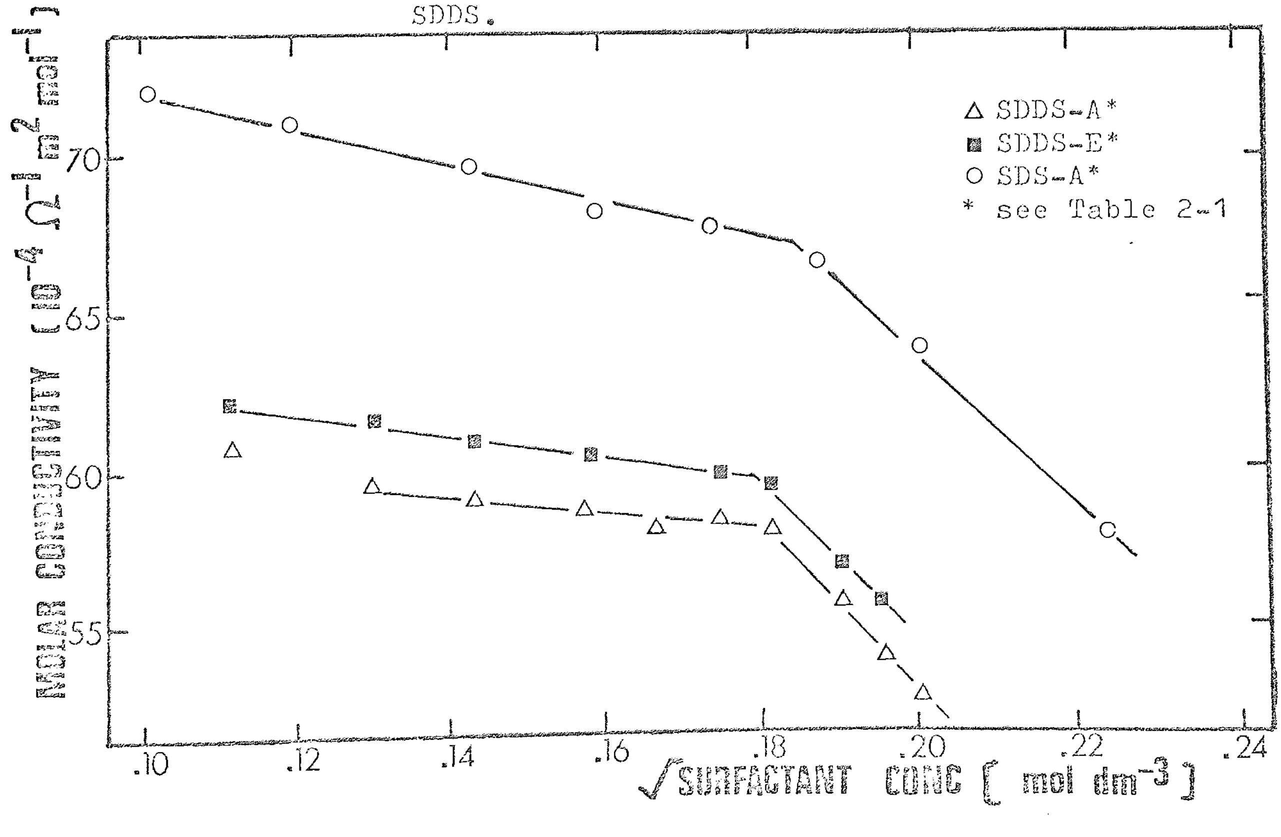


FIGURE 5

Measurement of critical micelle concentration from plots of molar conductivity versus square root of surfactant concentration ($\sqrt{c}$) for SDS and $2\sqrt{c}$ for SDDS.



2.3 OIL PHASE

2.3.1 Hydrocarbons

The hydrocarbons used, their suppliers and specified grades are given in Table 2-3.

The refractive indices, measured at the average D-line of sodium (589.3 nm), are compared with the literature values. Each refractive index (n_D^{25}) was measured twice using a standard model Abbe 60 refractometer (Bellingham & Stanley Ltd) in which the prisms and sample were maintained at 25± 0.1°C.

Surface (γ) and interfacial (γ_{ow}) tensions were measured using the Wilhelmy plate technique (Section 3.1).

2.3.2 Purified hydrocarbons

Refined samples of hexane, hexadecane and benzene were prepared. Each alkane was shaken repeatedly with fuming sulphuric acid (oleum) until the acid did not not become discoloured within five minutes. The oil phase was then washed with aqueous sodium carbonate (four times) and water (ten times). Hexane was distilled twice and the middle fraction (about 80% was collected each time.) Hexadecane was recrystallized four times without solvent. About ten per cent of unfrozen liquid was discarded each time.

Benzene (500cm^3) was recrystallized twice without solvent, about 20cm^3 was discarded on each occasion. The remaining benzene was stored over sulphuric acid for 24 hours. The sample was then washed with aqueous sodium carbonate and water, then distilled twice (as above). Finally the crystallization process was performed twice more.

The measured properties of these solvents are included in Table 2-3.

Table 2-3 Sources and grades of hydrocarbon oils; refractive index, surface tension and oil-water interfacial tension (at 25 ± 0.1°C) as compared with literature values (Reference 271 unless stated).

Hydrocarbon	Supplier and Grade	Refractive Index(n_D^{25}) measured	Refractive Index(n_D^{25}) literature	Surface Tension(mN m^{-1}) measured	Surface Tension(mN m^{-1}) literature	Interfacial Tension(mN m^{-1}) measured	Interfacial Tension(mN m^{-1}) literature
Hexane	BDH^{a}	1.375	1.372	18.5	17.9	50.4	50.4 (195)
Heptane	BDH^{b}	1.388	1.385	19.6	19.8	50.8	-
Octane	BDH^{c}	1.397	1.395	21.0	21.1	50.5	51.2 (195)
Nonane	BDH^{cd}	1.406	1.403	22.1	22.4	51.6	51.5 (195)
Decane	BDH^{e}	1.413	1.409	23.3	23.4	51.4	51.7(173,237)
Undecane	HW^{e}	1.419	-	23.5	-	51.4	52.1(173,195)
Dodecane	BDH^{a}	1.420	1.419	24.6	24.9	52.5	52.5 (195)
Tridecane	F ^{f}	1.420	-	25.0	-	52.5	-
Tetradecane	BDH^{a}	1.432	-	25.3	26.4(266)	52.9	52.9 (195)
Hexadecane	BDH^{a}	1.434	-	27.2	27.2(266)	53.0	53.3 (173)
Cyclopentane	BDH^{a}	1.400	1.404	21.6	21.8	45.0	-
Cyclohexane	BDH^{e}	1.430	1.423	24.6	24.4	46.6	49.6 (237)
Oct-1-ene	BDH^{e}	1.411	1.406	21.0	21.3	48.8	43.7 (237)
Dec-1-ene	BDH^{e}	1.422	1.419	22.9	23.5	48.2	-
Cyclohexene	BDH^{a}	1.446	1.444	26.1	25.9	41.0	43.5 (257)
Benzene	BDH^{d}	1.498	1.498	28.0	28.2	34.6	34.4 (257)
Toluene	BDH^{g}	1.496	1.494	29.4	27.9	38.1	35.2 (173)
o-Xylene	BDH^{a}	1.504	1.503	29.8	29.5	36.4	-
m-Xylene	BDH^{a}	1.494	1.495	28.0	28.1	-	-
p-Xylene	BDH^{b}	1.496	1.494	27.5	27.8	-	-

Table 2-3 Continued.

Hydrocarbon	Supplier and Grade	Refractive Index(n_D^{25})		Surface Tension(mN m^{-1})		Interfacial Tension(mN)	
		measured	literature	measured	literature	measured	literature
Liquid Paraffin							
Light (LLP)	BDH^e	-	-	28.2	-	56.6	-
Heavy (HLP)	BDH^e	-	-	29.4	-	58.1	-
Hexane-P	Purified	1.374	-	18.4	-	50.4	-
Hexadecane-P	Purified	1.435	-	27.2	-	53.0	-
Benzene-P	Purified	1.500	-	27.9	-	34.6	-

NOTES

BDH	British Drug Houses	a	GLC analysis	99%	d	Special for spectroscopy
HW	Hopkin and Williams	b	GLC analysis	99.5%	e	Laboratory Reagent
F	Fluka	c	GLC analysis	98.5%	f	Puriss
					g	Analar Reagent

2.4 ALCOHOLS

The alkanols propanol, butanol, pentanol and hexanol (C_3 to C_6) were supplied by BDH Chemicals Ltd as "laboratory reagent" grade. The C_8, C_{10}, C_{12} and C_{16} alcohols were "specially pure" (not less than 99%) from the same supplier. The tetradecanol (myristyl alcohol) was a "pure" sample obtained from Koch-Light Laboratories. The C_8, C_{10}, C_{12} and C_{14} alkanols all gave single peaks by GLC at high sensitivities (Section 2.2.2.1). All alcohols were used without further purification.

2.5 MISCELLANEOUS REAGENTS

Hydrochloric acid, sulphuric acid, potassium chloride and sodium carbonate were all "Analar" reagents supplied by BDH Chemicals Ltd.

Fuming sulphuric acid (oleum) and acetone were "laboratory reagent" grade from Fisons. Potassium dichromate was "technical" grade from the same supplier.

Solvent ether was obtained from May & Baker Ltd.

Carbon tetrachloride was a "spectrosol" sample from Hopkin & Williams Ltd.

All reagents were used as supplied.

3

METHODS

3.1 SURFACE AND INTERFACIAL TENSION

3.1.1 Principle of measurement

Surface and interfacial tensions were determined by a modified Wilhelmy plate technique (262). This and other methods of measuring tensions have been reviewed by a number of authors (1d,62a,200b). The suitability of the plate method for measuring the surface and interfacial tensions of surfactant solutions has also been evaluated (263-265).

The force (F) acting on a wetted plate whose lower edge is hanging in, and parallel to, the plane of surface of a liquid(or an interface) is given by

$$F = \Delta mg = 2(L + L^1)\gamma , \qquad 3.1$$

where Δm is the apparent increase in weight of the plate, g is acceleration due to gravity, L and L^1 are the length and thickness of the plate respectively and γ is the surface (or interfacial) tension.

3.1.2 The Wilhelmy Plate

The plates were cut from a precision strip of polished platinum (Johnson & Matthey Ltd). A hook of platinum wire (3.3×10^{-2} cm diameter, from the same supplier) was welded onto the upper edge of each plate. The plates were roughened slightly to enhance wetting by water (266) and the dimensions were measured microscopically. Before each tension measurement the platinum plate was cleaned by heating to red heat for 30s in a hot bunsen flame, then used immediately it had cooled (267).

3.1.3 The balance

The most elegant application of the Wilhelmy technique is in conjunction with an electrical balance (268,269).

In this study a micro-force balance (CI Electronics Ltd., MK 2B) was found to be highly suited to the routine measurement of surface or interfacial tensions. The instrument comprises two separate parts, a weighing compartment containing the balance head; and an electrical control cabinet (Plate 1). The balance employed was fitted with a vacuum head unit (as shown) mounted independently on a perspex plate. This arrangement was clamped firmly in position on a wide-based retort stand. Beneath the balance head was a platform which could be raised or lowered by a rack and pinion bolted onto the base of the stand.

The balance arm is maintained in continuous balance, enabling routine measurements to be made in the plane of a surface. Because a change in weight is detected by a light sensitive servo in the balance head this part of the instrument was covered in order to eliminate changes in background light during operation. A weight proportional current operates an indicating meter on the control cabinet and the weight is read directly. A potentiometric pen recorder was connected in series with the indicating meter in order to improve sensitivity, facilitate the measurement of equilibrium tension values and to follow surface ageing.

3.1.4 Calibration

The cleaned Wilhelmy plate was hung from the beam of the electrical balance by means of a thin wire. This arrangement was counter-balanced in air by a weighing pan and weights hung from the other balance arm. Fine adjustments of the zero were achieved for three of the five ranges available (corresponding to full scale balance readings of 10^2mg, 10mg and 2.5mg) by operation of the zero-adjust switches on the control cabinet. These ranges were then calibrated using standard weights (CI Electronics Ltd) of 10^2mg, 10mg and 2.0mg.

The location and mounting of the instrument prevented calibration of the remaining ranges (2.5×10^{-1}mg and 2.5×10^{-2}mg).

For the measurement of interfacial tensions the procedure was repeated with the plate immersed in the particular oil phase.

3.1.5 Operation

The Wilhelmy plate was removed, cleaned and returned to the balance arm. The zero value was re-checked.

Twenty-five cm^3 of test liquid (previously brought to $25^{\circ}C$) was placed in a double wall thermostatted beaker(Figure 6) maintained at $25 \pm 0.1^{\circ}C$ by pumped flow from a water bath (Townson & Mercer, Standard Bridge Control Thermostat Bath, E270). The beaker was positioned in a recess on the platform and raised to just below the plate, whereupon the reflected image of the plate indicated whether or not its edge was parallel with the liquid surface. The water pump was switched off, to reduce vibration, and the beaker was raised until the plate came into the plane of the surface.

For interfacial tensions the same procedure was performed, then sufficient of the less dense liquid was pipetted carefully onto the surface to completely immerse the plate.

The increase in weight on the balance arm was read directly from the indicating meter and chart recorder. All measurements were taken as the average of a set of at least three readings and the balance calibration was checked after each set.

3.1.6 End Correction

In some cases, particularly with fairly thick plates, the effective perimeter is not a simple sum of $2(L + L^1)$ because of the perturbation of the liquid meniscus at the corners of the plate (200b,270).

The "end correction" e was determined by measuring the surface tension of benzene and carbon tetrachloride using three plates of lengths (l) 0.506cm, 1.008cm and 1.494cm. All the plates were of thickness (L^1) 0.033cm and height 1.000cm. In order to obtain the force acting on the plate (F) for benzene with the largest plate a tare was added to the counter balance pan. From a graph of F vs. L at constant thickness (it is also assumed that e is constant for plates of these lengths) the gradient has a value 2γ. The surface tension values obtained for benzene (28.0 mN m^{-1}) and carbon tetrachloride (26.2 mN m^{-1}) compared favourably with literature values (28.18 and 26.15 mN m^{-1} respectively)(271). The values of γ were substituted into Equation 3.1 for each plate and the average value of e was found to be 0.015 ± 0.005cm (i.e. for a plate of L = 0.506cm and L^1 = 0.033cm the end correction alters γ by about 2%).

3.1.7 Surface and interfacial tensions

A platinum plate of dimensions L = 0.506cm, L^1 = 0.033cm and e = 0.015cm was used in all investigations of surface and interfacial tensions. Calibration of the electrical balance enables a rapid direct-reading procedure to be adopted from which tensions ($\pm$ 0.1 mN m^{-1}) can be calculated as follows:-

$$\gamma = \Delta mg / 2 \ (L = L^1 + e) \qquad 3.2$$

$$= 885 \, \Delta m ,$$

where γ is the surface or interfacial tension (N m^{-1}) and $g = 9.81 \ m \ s^{-2}$.

3.1.8 Interfacial adsorption

Interfacial tension data were collected over a wide range of surfactant concentrations (10^{-6} to 10^{-1} mol dm^{-3}). The area (A) occupied by each surfactant molecule at the interface was calculated using the derived Gibbs surface excess equation (Equation 1.13b). At low surfactant concentrations it can be assumed that the surfactant activity can be substituted by the concentration in mol dm^{-3} (c) so that Equation 1.13b becomes

$$\Gamma = (1 / 2kT) (d\gamma / d\ln c), \qquad 3.3$$

and

$$\Lambda = 1/\Gamma \qquad 3.4$$

Interfacial tension vs. ln concentration data were fitted by computer (Application Program UA 01; University of Aston in Birmingham Computer Centre) to a polynomial of the second degree; i.e.

$$\gamma = a_0 + a_1 \ln c + a_2 \ln^2 c \qquad . 3.5$$

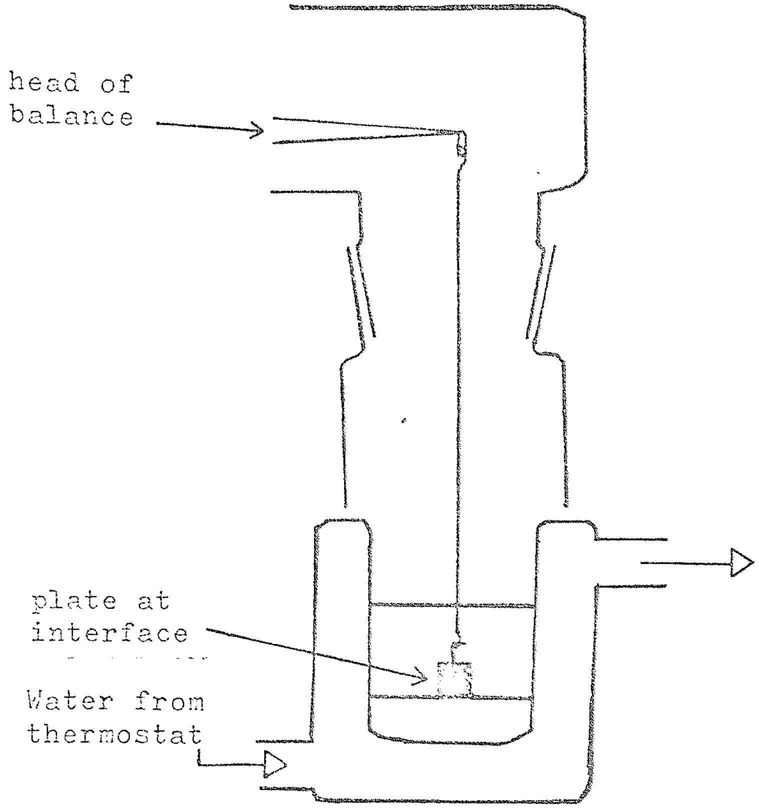
Thus:

$$d\gamma / d \ln c = a_1 + 2a_2 \ln c \qquad . 3.6$$

Further terms (ie. third and fourth degrees) were also computed but these did not improve the fit of the data.

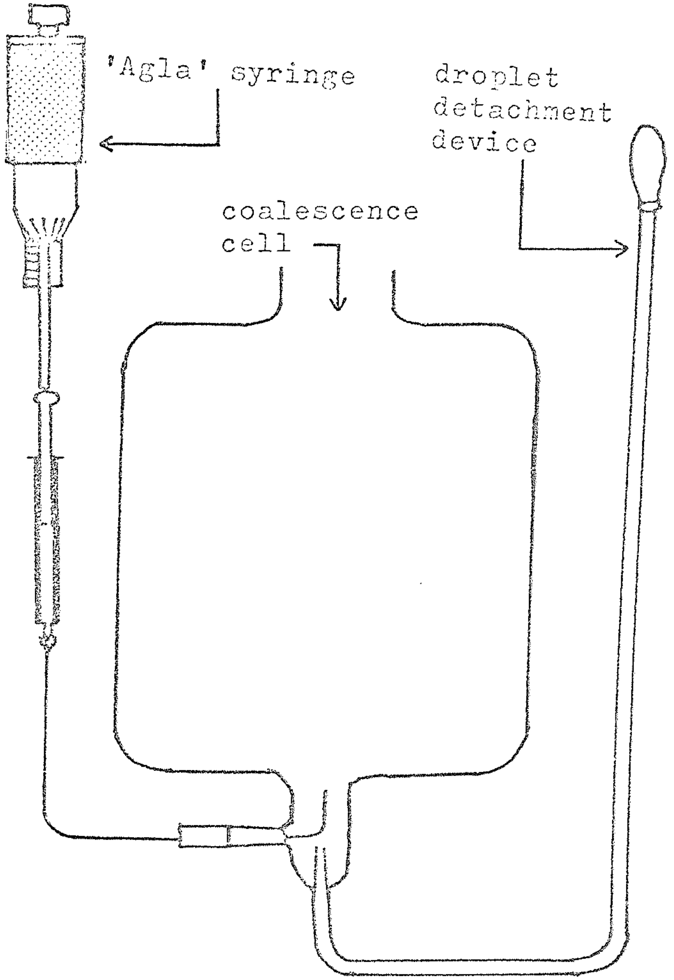
PLATE 1
Apparatus for interfacial tension measurement, showing (left to right) the chart recorder, balance control panel and balance head in operating position.

FIGURE 6



WILHELMY PLATE APPARATUS

FIGURE 7



DROPLET COALESCENCE APPARATUS

3.2 DROPLET STABILITY

3.2.1 Design of coalescence cell

Two all glass cells were constructed on the basis of the design of Nielsen *et al* (272) but with certain refinements (Figure 7). The cylindrical chamber of one cell had an internal diameter of 8cm and the other was 10cm in diameter.

Oil droplets of known volume were inflated singly at the tip of a 38cm filling canula (A.R. Horwell Ltd.) by means of an 'Agla' micrometer syringe (Luer fitting; Wellcome Reagents Ltd.). Access for the canula was provided near the base of the cell in the form of a 10/19 socket. A range of canulae of different bore were sealed with 'Araldite' (Ciba-Geigy) into plain ended glass cones of the appropriate size. In this way the droplet volumes could be controlled for oils with widely differing interfacial tensions.

Further provision was made for droplets of the selected volume to be released from the canula tip. A simple drop-release device was designed (Figure 7) through which detachment was achieved by a flow of liquid through a small nozzle situated immediately below the canula tip. This flow was caused simply by expelling air gently from a teat fitted onto a capillary continuous with the nozzle.

3.2.2 Cleaning and thermostatting

The glass cell was rinsed thoroughly with distilled water then completely filled with freshly prepared chromic acid and allowed to soak overnight. The cell was then rinsed at least twelve times with distilled water and at least twice with the appropriate surfactant solution.

The 'Agla' syringe and canula arrangement was rinsed through five times with organic phase and fitted immediately to the freshly cleaned cell.

Preliminary studies showed that reproducible results could not be obtained simply by using a water bath to thermostat the apparatus, presumably because of leakage around the dry joint accommodating the canula. Consequently the entire apparatus was clamped in position in an air bath, a large glass beaker ($5dm^3$) weighted down in the water bath (as used previously). The top of the beaker was closed off with foil and the water bath lid (viscometric type; Townson & Mercer Ltd.) fitted, with the top of the coalescence cell and the micrometer barrel of the syringe accessible through adjacent holes in the lid. The remaining holes were covered and the apparatus was viewed through the side windows of the water bath.

3.2.3 Operation

The cell and 'Agla' syringe arrangement were cleaned, assembled immediately, and clamped into position. The surfactant solution ($200cm^3$ or $500cm^3$ for the small and large cells respectively, previously brought to 25°C) was poured into the cell. After several minutes the oil phase ($15cm^3$ or $20cm^3$) was pipetted carefully onto the surface. After the necessary period of interface ageing oil droplets were inflated and aged at the canula tip, then detached. Rest-times of droplets were measured by stopwatch as the time which elapses from arrival of each droplet at the interface to its coalescence. A minimum of 50 droplets was found to give reproducible estimates of stability in agreement with previous observations (see Section 5.2.2). At least 80 droplets were measured and each experiment was repeated at least twice, giving reproducibility of better than 90%.

3.2.4 Expression of stability

In all previous studies on droplet coalescence a distribution of rest-times has been obtained (68,103). The statistical analysis of these data gives rise to a number of stability parameters. For example, Cockbain & McRoberts (104) used a simple distribution curve of N (the number of droplets remaining at time t) against t for a number of organic phases stabilized by water soluble surfactants. An initial slow decrease in N was attributed to film drainage from between the droplet and the interface. There followed a more rapid and approximately exponential part which, when plotted as logN vs. t, enabled a rate constant for coalescence to be calculated:-

$$\log N = (-k_c t / 2.303) + \text{const.} \qquad 3.7$$

The rate constant for coalescence k_c can be converted to a first order half life ($T\frac{1}{2}$) for more convenient comparison of stabilities,

$$T\tfrac{1}{2} = 0.693 / k_c \quad . \qquad 3.8$$

The general form of such a plot is shown in Figure 8. Overall stability was characterised by the time required for half the droplets observed to coalesce ($t\,\frac{1}{2}$), which may be read directly from the distribution curve. The drainage time (t_d) may also be measured graphically (106) or estimated from the difference

$$t\,\tfrac{1}{2} - T\,\tfrac{1}{2} = t_d \quad . \qquad 3.9$$

The mean rest-time (t_{mean}) is a further parameter which can be obtained readily from the measured data (108a,273,274).

In addition, a number of empirical expressions have been found to correlate droplet stability data. Elton & Picknett found that an equation of the form:

$$F_c = \propto t^n / (1 + \propto t^n) \qquad 3.10$$

correlated observed data for systems containing electrolyte. The constant $\propto$ and n were dependant on electrolyte concentration, droplet size and temperature. F_c represents the fraction of droplets which has coalesced in a given time. The related equation

$$\log (N / No) = \propto t^n \quad , \qquad 3.11$$

where No is the total number of droplets observed has also been used

(273,274).

In the absence of added surfactants the distribution of rest times obtained by Gillespie & Rideal (275) fitted the relation

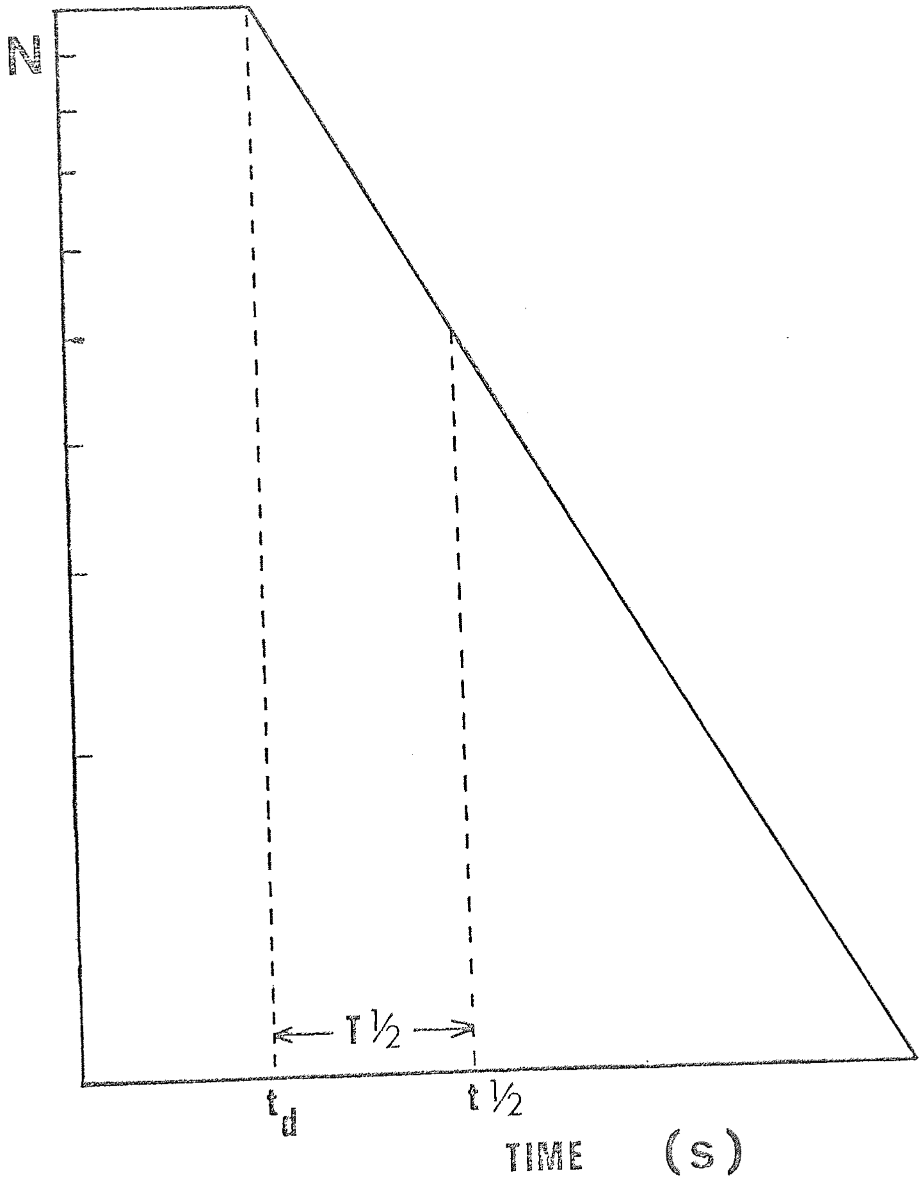
$$\log (N / No) = -\propto (t - t_o)^{3/2} , \qquad 3.12$$

(where $\propto$ is a coalescence constant and t_o is the minimum rest-time), which was derived from a consideration of the theoretical model of a deformable drop resting at a plane interface. Reservations were expressed regarding the adequacy of this relation as applied to systems containing surfactant. Nielsen et al (272) found that this equation was applicable to three component systems but better correlation was generally obtained by plotting log (N / No) vs. t. Other workers (276b,277) obtained a measure of agreement with Equation 3.12 , particularly for longer rest-times, whilst Jeffreys & Hawksley (273) found it necessary to vary the exponent. Edge & Greaves (274) further suggested that combinations of values of t_o and the exponent were possible.

An alternative approach to the analysis of coalescence data is to consider the distribution of droplet rest times about the mean. The simplest type of distribution is the normal or Gaussian distribution where the rest-time will be distributed symmetrically about t mean. Edge & Greaves (274) reported that the first-stage coalescence times for the system decanoic acid-heptane-water were approximately fitted by the normal distribution in the range 90% > N > 10%. However, in its exact form the normal distribution predicts rest-times which are as far below the mean as others are above it; negative rest-times are predicted if any droplet persists for longer than $2t_{mean}$. In these instances the data may be better fitted by a skewed type of distribution such as the log-normal in which the frequency of observation of zero rest-time is also zero. The validity of the normal or log-

FIGURE 8

PARAMETERS FOR EXPRESSION OF THE STABILITY OF SINGLE DROPLETS AT THE OIL/WATER INTERFACE



KEY

N number of droplets not coalesced

t_d film drainage time

t1/2 time at which half droplets coalesced

T1/2 first order half-life for coalescence normal distributions may be tested by plotting the percentage not coalesced on a probability scale vs. time or log-time respectively. If either distribution holds a linear result should be obtained. This is uniquely defined by two parameters, the value of t at 50% probability (M, which assumes the value $t_{\frac{1}{2}} = t_{mean}$ for normal, and $t_{\frac{1}{2}}$ for log-normal distributions) and the scatter about this point (σ, the standard deviation or geometric standard deviation for normal and log-normal distributions respectively. The selection of suitable stability parameters for this study is further discussed in Section 4.2.

3.2.5 Standardized experimental method

3.2.5.1 Introduction

Past workers have shown that a large number of factors may affect the stability of a droplet at a plane interface. These may be divided into those which are a consequence of experimental technique and those which result from the properties of the phases present. It is essential that a standard procedure must be developed to control other variables reproducibly in order to study the influence of oil phase on stability. A programme of preliminary experiments was completed in order to devise such a procedure.

3.2.5.2 Results and discussion

A. Temperature

Temperature affects the physical properties of the system (eg. interfacial tension, viscosities) and so would be expected to influence droplet stability. Gillespie & Rideal (275) attributed the distribution of droplet rest times to irregular disturbances caused by poor thermostatting. An increase in temperature has been found to decrease droplet stability markedly (272,273,276ab,278ab) unless the coalescence mechanism is altered, from a single step to a stepwise process for example (103,272).

B. Droplet size

The influence of droplet size on stability has been considered by numerous authors for both unstabilized (273,275,276b,279) and stabilized (104,272,280b) systems. An increase in droplet size has generally been found to increase rest-times, largely because of the longer drainage time required as droplets and/or interface become more distorted (275,276b,279,280ab). Hodgson & Lee (280a) have also discussed the relationship between droplet size and the pressure in the film due to buoyancy. In contrast, stability ($t_{\frac{1}{2}}$) has been found to vary little with droplet size by some workers (104,273), although Jeffreys & Hawksley (273) did find that td was slightly affected. Komasawa & Otake (281) investigated the effect of volume on the stability of quite large benzene droplets (2×10^{-5} to 2×10^{-4} dm^3) and found that rest-times increased with droplet volume. In the presence of a surfactant, however, the stability was independent of size. Nielsen et al (272) suggested that the presence of a third component could cause either an increase or a decrease of stability with increased droplet size. Lang & Wilke (102b) also report variable behaviour with increased droplet size, depending on the system under study.

The effect of droplet volume on the stability of hexadecane droplets (in 10^{-4} mol dm^{-3} SDDS solution) is summarized in Table 3-1 and Figure 9.

FIGURE 9

THE EFFECT OF DROPLET VOLUME ON STABILITY AT THE OIL/ SURFACTANT SOLUTION INTERFACE

(Oil :- hexadecane; Surfactant :- SDDS-A; see Table 3-1)

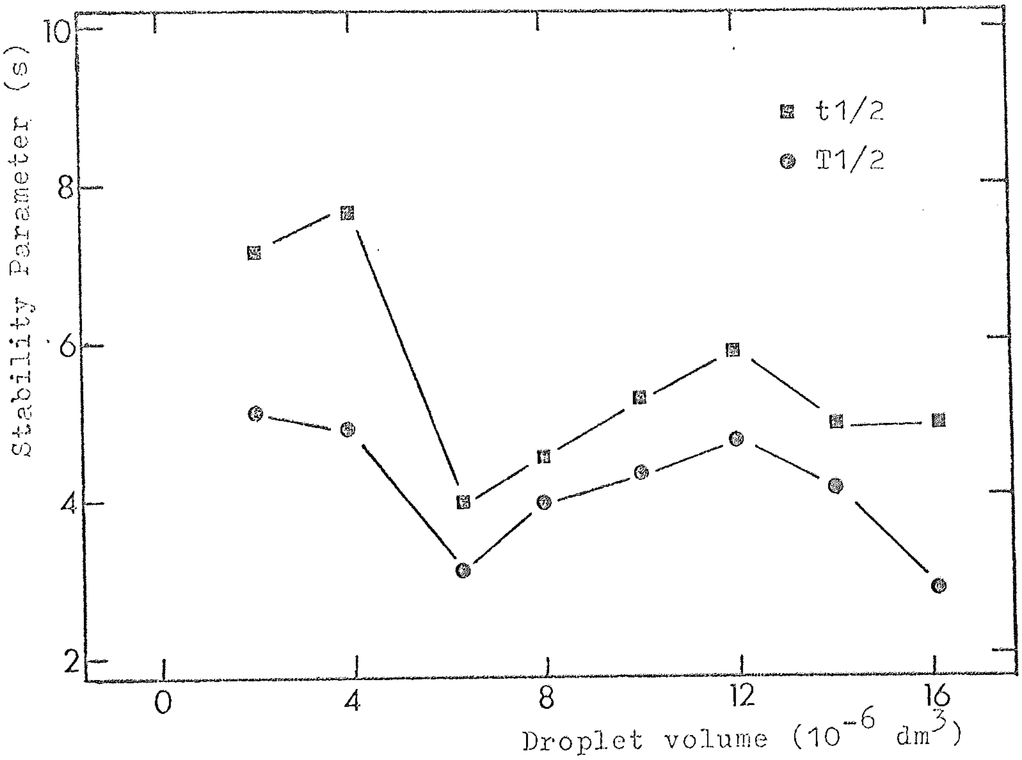


Table 3-1

The effect of droplet size on the stability of hexadecane droplets at the oil-SDDS-A solution (10^{-4} mol dm^{-3}) interface (saturation time 3 hours; droplet age 30s, cell diameter 10cm).

Drop volume (10^{-6} dm^3)	Drop diameter (cm)	tmean (s)	$T\frac{1}{2}$	$M(t\frac{1}{2})$ (s)	σg
2	0.157	12.6	5.2	7.4	2.30
4	0.197	10.3	5.0	7.8	2.06
6	0.225	6.0	3.1	4.0	1.83
8	0.248	6.3	3.9	4.5	2.31
10	0.268	7.4	4.2	5.4	2.36
12	0.284	8.7	4.9	5.9	2.38
14	0.300	6.9	4.1	5.0	2.27
16	0.313	5.9	2.8	5.0	1.93

At low droplet volume (ie. below $6x10^{-6}$ dm^3) a marked increase in stability with decreasing size was observed, but at larger droplet sizes stability increased slightly with volume. A similar pattern of behaviour was described by Cockbain & McRoberts (104) for benzene and light petroleum droplets stabilized with potassium laurate or SDDS. It was reported that $t\frac{1}{2}$ was not markedly affected by volume in the range $0.5x10^{-6}$ to $10x10^{-6}$ dm^3 but below this range stability increased rapidly with reduction in volume. The enhanced stability of very small droplets has also been reported elsewhere (272,280a). This behaviour has been attributed to electrical double layer effects arising from the presence of ionic components (103,272). Another possibility is that, since a small droplet rests upon a very small area of interface, stabilization may be due to minute islands of cohesive impurity which are too small to stabilize larger droplets.

It is also pertinent to note that theoretical analysis of droplet coalescence on the basis of a non-deformable droplet (a spherical-planar model) predicts that $t_{\frac{1}{2}}$ should be inversely related to droplet diameter (d). For deformable droplet (using a parallel disc model) it was predicted that $t_{\frac{1}{2}}$ should be related to d^5 (276a).

From a droplet volume of 6×10^{-6} dm^3 to 12×10^{-6} dm^3 a slight increase in stability was evident (Figure 9) though the estimate of td varies only slightly over this range. Above 12×10^{-6} dm^3 a slight fall in droplet stability may occur as a result of buoyancy, electrical effects or high compressibility of the interfacial film.

It seems likely that the conflicting experimental observations previously reported are due at least in part, to the different ranges of droplet diameters involved (d = 0.1 to 0.6cm (272); 0.2 to 0.9cm (273); 0.3 to 0.9 (275); 0.4 to 0.6cm (276a); 0.1 to 0.2cm (279); 0.1 to 0.5cm (280ab)). This compares with a range of 0.16 to 0.31cm investigated in this study.

C. Curvature of the interface

The effect of interface curvature on droplet stability was first examined by Nielsen et al (272) who found that droplet rest-times increased considerably when the interface was made concave towards the droplet. This was attributed to an increased resistance to drainage of the liquid film between the droplet and oil phase.

Table 3-2 summarizes the results obtained using two cells with different internal diameters to measure droplet stability for a number of phases at constant interface age, droplet age and droplet size.

Table 3-2

The effect of cell dimensions on the stability of oil droplets at the oil-SDDS-A solution (10^{-4} mol dm^{-3}) interface. (Saturation time 24 hours; droplet age 30s; droplet size 6 x $10^{-6} dm^3$)

OIL	Cell diameter 8cm tmean	$T_{\frac{1}{2}}$	$t_{\frac{1}{2}}$	Cell diameter 10cm tmean	$T_{\frac{1}{2}}$	$t_{\frac{1}{2}}$
Hexane	15.2	8.1	8.9	28.0	24.3	12.7
Octane	9.5	6.6	5.9	22.8	14.9	13.6
Decane	12.9	7.0	10.1	15.8	8.3	12.3
Dodecane	7.0	4.3	5.6	10.3	5.9	7.5
Hexadecane	5.7	3.0	5.0	6.7	3.0	6.0

Clearly, cell dimensions have a profound effect on stability parameters, particularly for the more stable systems. The interface was markedly curved in each case with the smaller cell and it appears that more rapid film drainage reduces droplet stability significantly. However, the pronounced curvature also caused a small but significant proportion of the more stable droplets to drift off the interface to the glass cell wall where they had extended rest-times. All such droplets were disregarded, thus resulting in a further contribution to the apparent lowering of stability. A similar effect has been observed by Hodgson & Woods (280b).

D. Travel distance to the interface

It has been shown previously that extending the distance of travel of a droplet to the interface may increase droplet stability (103,273). The reasons for this effect are not clear but a number of possible explanations have been suggested and discussed by Jeffreys & Davies (103). Thus, the droplet may acquire an electrostatic charge or collect surface active impurities as it passes through the aqueous phase. These alternatives are considered unlikely when the aqueous phase contains added surfactant. Indeed, under such conditions some workers have found that droplet size is independent of distance of travel (272,277). A difference in stability could result from bouncing of the droplet after it strikes the interface and the interference of ripples on film drainage. However, Hawksley (282) has shown that droplets achieve a constant terminal velocity within 15d to 20d, hence the impact of all droplets should be approximately constant, whilst rest-times continue to increase with further distances. It seems likely that the observed effect is related to the overall dimensions of the apparatus. For example, stability may be affected by the reflection of disturbances off the apparatus walls which, in turn, will depend on where the droplet first meets the interface and its subsequent motion (if any) before coalescence.

E. Vibration

Closely allied to the previous discussion is the effect of extraneous vibrations on droplet rest-times, a subject upon which there have appeared a number of conflicting reports. It has been proposed that vibrations may cause random variations in rest-times, thereby explaining the distribution of values found in all studies (102ab). However, scattered values have been reported in instances where vibrational effects were excluded (273,276b,279,280a). Nielsen et al (272) found that miscellaneous vibrations and even mild agitation had only a slight effect on droplet rest-times. However, it is generally agreed that vibrations of large amplitude can stabilize droplets by allowing the draining film to be replaced.

In this study there was no discernible difference between the results of experiments conducted in the daytime or at night. A small number of experiments were carried out using an anti-vibration mounting (Griffin & George Ltd.). The results obtained are summarized in

Table 3-3. Somewhat surprisingly a slight increase in stability (≃ 10%) was found in each case. It may be that the mounting was effective in reducing disruptive vibrations within the interface. In addition, the apparatus was slightly more susceptible to accidental disturbance during operation, which may have caused some fairly high amplitude vibrations to retard the film drainage process.

Table 3-3

The effect of vibration on the stability of oil droplets at an oil-SDDS-A solution (10^{-4} mol dm^{-3}) interface (Saturation time 24 hours; droplet age 30s; droplet size 6×10^{-6} dm^{-3}; cell diameter 10cm).

OIL PHASE	STABILITY PARAMETERS			STABILITY WITH ANTI-VIBRATION MOUNTING		
	tmean	$T_{\frac{1}{2}}$	$t_{\frac{1}{2}}$	tmean	$T_{\frac{1}{2}}$	$t_{\frac{1}{2}}$
Hexane	28.0	24.3	12.7	34.2	28.6	21.2
Hexadecane	6.7	3.0	6.0	7.0	3.3	6.6
Benzene	5.1	2.0	4.5	5.0	2.2	4.4
Toluene	12.8	8.2	8.3	18.2	13.1	15.1
m-Xylene	14.9	9.3	10.5	16.3	11.2	14.0

F. Impurities

The importance of excluding extraneous impurities from the system has been emphasized by Jeffreys & Davies (103). Surface active impurities affect stability in the same way as added surfactant (see below). The rate of coalescence may be accelerated by solid substances, especially if these are wetted by the oil phase, because rupture of the draining film is promoted (276b). The effect of contaminants in the materials used is further discussed in Section 5.2.

G. Phase equilibration

Several workers (272,276b) have demonstrated the effect of mutually saturating the aqueous and non-aqueous phases. Saturated phases always gave noticeably longer droplet rest-times than non-equilibrated phases, even when the solubilities were only slight.

The effect of pre-saturating the oil phase with water has been studied in some detail (Table 3-4). In each instance the droplet stability increased after 3 hours shaking with water or if the oil phase was shaken with water for 12 hours and then allowed to stand in contact with the water for at least 12 hours. Extending this "standing time" to up to four days produced no significant change in droplet stabilities. The aqueous phase was, in each case, saturated with the appropriate oil phase to ensure that none of the oil in the droplets dissolved during a coalescence experiment.

Table 3-4

The effect of saturation of the oil phase with water on droplet stability ($T_{\frac{1}{2}}$ s) at the oil-SDDS solution (10^{-4} mol dm^{-3}) interface (Droplet age 30s; droplet size 6×10^{-6} dm^3)

Oil phase	Cell diameter (cm)	Saturation time (hours)			
		0	3	24	144
Dodecane	8	3.5	3.9	4.3	4.0
Hexadecane	8	2.7	3.1	3.0	-
Toluene	10	7.0	6.7	8.2	8.0
Cyclopentane	10	9.4	-	10.1	10.3

II. Concentration of surfactant

The amount of added surface-active agent will have a considerable effect on droplet stability. The surfactant accumulates at both the droplet surface and interface with the result that the rate of film drainage is reduced, interfacial viscosity may be increased and the probability of film rupture is decreased (Section 1.2.3). Hodgson & Woods (280b) have related stability changes to the complex flow patterns in film drainage. Nielsen et al (272) suggested that mean droplet rest-times changed with surfactant concentration (c) according to the relation

$$t_{mean} \propto c^{n} \qquad 3.13$$

where the exponent n varied from 0.45 to 3.0.

The present study required that the enhancement of stability was significant but also that the rest-times should be short enough to permit the routine measurement for large numbers of droplets. The effect of surfactant concentration on droplet stability is shown in Table 3-5 for a number of oils. A tenfold change in concentration resulted in a 2 to 3fold change in stability.

Table 3-5

The effect of surfactant (SDDS-A) concentration on the stability of oil droplets at an interface (Saturation time 24hours; droplet age 30s; droplet size 6×10^{-6} dm^3; cell diameter 10cm).

Table 3-5

OIL	10^{-4} mol dm^{-3}			10^{-3} mol dm^{-3}			10^{-2} mol dm^{-3}		
	tmean	$T_{\frac{1}{2}}$	$t_{\frac{1}{2}}$	tmean	$T_{\frac{1}{2}}$	$t_{\frac{1}{2}}$	tmean	$T_{\frac{1}{2}}$	$t_{\frac{1}{2}}$
Hexane	28.0	24.3	12.7	50	49.5	38.4			
Dodecane	10.3	5.9	7.5	27.6	16.0	20.9			
Hexadecane	6.7	3.0	6.0	14.9	8.0	11.7	33.9	28.4	21.8
Benzene	5.1	2.0	4.5	13.5	7.5	10.0	50	24.0	37.5
Cyclohexane	9.4	5.9	6.2	30.8	18.8	23.4			
Toluene	12.8	8.2	8.3	35.7	21.0	30.0			

I. Surfactant chain length

Some preliminary studies have been conducted to determine the effect of alkyl sulphate chain length on droplet stability (Table 3-6).

Table 3-6

The effect of alkyl sulphate chain length on the stability of oil droplets at an oil-surfactant solution (10^{-4} mol dm^{-3}) interface (Saturation time 24hr; droplet age 30s; droplet size 6x10^{-6} dm^{3}; cell diameter 10cm).

OIL	SDS			SDDS		
	tmean	$T_{\frac{1}{2}}$	$t_{\frac{1}{2}}$	tmean	$T_{\frac{1}{2}}$	$t_{\frac{1}{2}}$
Hexane	27.7	18.5	20.0	28.0	24.3	12.7
Dodecane	4.2	2.1	3.3	10.3	5.9	7.5
Hexadecane	2.7	1.6	2.5	6.7	3.0	6.0
Cyclohexane	5.5	3.2	3.8	9.4	5.9	6.2
LLP	4.9	2.5	2.8	9.0	5.9	6.1

As expected, in the presence of sodium decyl sulphate (SDS) droplets were less stable than those where SDDS is used at the same molar concentration. These results are in accordance with the lower surfactance of alkyl sulphates with shorter hydrocarbon chain lengths (111c). The differences in stability reflect a twofold change in surfactance for each additional CH_2 group which is also evident from the relative cmc's measured in Section 2.2 (SDS 34 mmol dm^{-3}; SDDS 8.1 mmol dm^{-3}).

J. Ageing

The ageing of a droplet, prior to its detachment from the needle tip, can also affect the droplet rest-time (104,277). The effect of droplet age was investigated for two different oils at constant droplet size (Table 3-7). An increase in stability was evident with increased ageing time up to about 30s with 10^{-4} mol dm^{-3} of SDDS as surfactant. Hodgson & Lee (280a) found that ageing had an effect on rest-times only in experiments with surfactant and concluded that the increased stability reflected the finite time required for adsorption of surfactant molecules to the droplet surface. Recently it has also been shown that the age of the interface can exert a similar effect on stability and that the film drainage process is probably altered during interface ageing (110,280a).

Table 3-7

The effect of droplet ageing on the stability ($T_{\frac{1}{2}}$) of oil droplets at the oil-SDDS solution (10^{-4} mol dm^{-3}) interface. (Saturation time 24hours; droplet size $6x10^{-6}$ dm^3).

Table 3-7

Droplet age (s)	DODECANE		HEXADECANE	
	8cm cell	10cm cell	8cm cell	10cm cell
0	2.1	3.5	2.0	2.5
15	4.0	3.5	3.0	3.0
30	4.3	5.9	3.0	3.0
60	4.3	6.2	2.9	3.1

3.2.5.3 The standard procedure

The following were adopted as standard conditions for the experimental investigation into the effect of oil phase composition on droplet stability.

(i)	Temperature	-	thermostatted to 25 ± 0.2°C
(ii)	Droplet size	-	a droplet volume giving minimal stability was selected (ie. 6×10^{-6} dm^3)
(iii)	Curvature	-	10cm diameter coalescence cell was used in all studies.
(iv)	Travel distance	-	10cm from canula tip to interface in all experiments.
(v)	Vibration	-	no special precautions except to switch off thermostat motor during experiments.
(vi)	Impurities	-	a one-piece cell was constructed entirely of glass to facilitate cleaning; extensive cleaning procedure (Section 3.2.3) and special

precautions (above) to eliminate extraneous contamination were employed.

(vii) Phase equilibration - mutual saturation (24hours) as described.

(viii) Surfactant concentration - 10^{-4} mol dm^{-3} except where otherwise stated.

(ix) Surfactant - SDDS-A except where otherwise stated

(x) Ageing - droplet age 30s; interface age 45 minutes decided from observations on interface ageing (Section 4.1).

3.3 EMULSION STABILITY

3.3.1 Preparation and storage

Each emulsion was prepared from 160 cm^3 of surfactant solution and 40 cm^3 of oil phase which were pre-mixed by five inversions in a measuring cylinder. The system was then passed through a calibrated bench homogenizer (Ormerod) at four decreasing orifice diameters. After one further pass at the minimum orifice diameter each emulsion was transferred to two 100cm^3 bottles. The final emulsions were stored in an inverted position (Plate 4)* within an incubator maintained at 25 ± 0.5°C. All sampling was preceded by gentle re-mixing (five inversions) and the required volume was removed from the centre of the bulk by means of a wide tipped pipette.

3.3.2 Particle size analysis

In order to follow changes in a range of emulsions it was considered essential to obtain direct information on changes in droplet size distributions with time. The most reliable means of determining particle sizing data is by direct observation through the microscope. The most convenient technique for routine measurement was considered to be photomicrographic particle size analysis. Preliminary investigations using the Coulter counter (Section 1.2.2) indicated that many of the systems under study (eg. aromatic hydrocarbon emulsions) were unstable at the high dilutions required for this instrument. Even at lesser dilutions the gradual loss of droplets was apparent (Section 3.3.3). The effect is undoubtedly due largely to dissolution of the oil phase and is reduced by pre-saturating the diluent with oil, though evaporation of oil from the system may result in the disappearance of droplets. Similar observations have been recorded by other workers (70a, 72) and it has been concluded that the size distribution of emulsions can be measured by the Coulter counter only if the oil phase

*Footnote : Plate 4 is located at page 132/3.

is highly insoluble (70a).

For the present work the effect of diluting the emulsions with distilled water, SDDS solution and SDDS solution saturated with oil phase was investigated. The type and volume of diluent caused no significant difference in particle sizing data for long chain paraffins and only slight differences were observed with short chain paraffins but the cyclic hydrocarbons (cyclohexane and benzene) had lower average diameters when SDDS saturated with oil was used.

Samples of emulsion were diluted with SDDS solution of the correct concentration, previously saturated with the appropriate oil phase. The emulsion was added to approximately half of the diluent in a measuring cylinder and the remainder of the SDDS solution added slowly. One drop of the dilution was then mounted on a haemocytometer slide (Hawksley) of depth 0.02mm and allowed to cream under the cover slip for 10 minutes. Considerably coarsened emulsions were mounted on a similar slide of depth 0.1mm.

The depth of both slides was examined for small globules before photography. Photomicrographs were taken using a light microscope (Watson) fitted with an adaptor for a Watson eyepiece camera. A X10 eyepiece and a X40 objective were employed throughout. In order to achieve sufficient illumination of the sample an intense lamp (Vickers Instruments) fitted with a heat filter was used. Heating effects were minimized by operating the lamp at low voltage during the preliminary focussing. The most effective contrast was obtained using Ilford Pan F film (35mm fine grain ASA50 (DIN 18) and Kodak Bromide Hard Paper (Grade 3 white semi-matt, single weight). Initially enlargements were made to a 1000X total magnification but this was subsequently replaced by prints of 500X magnification without marked loss of resolution.

Droplet sizes were measured directly from the prints and recorded into size class intervals of 0.5 μm with reference to a photograph of the haemocytometer rulings (50 μm squares). Two photographs of the rulings were taken for each group of emulsions examined. The classification of sizes was considerably assisted by recording each set of measurements on magnetic tape for later transcription onto paper.

For all emulsions two haemocytometer slides were prepared and at least three fields were examined for each to provide sufficient (400-500) droplets for size analysis.

3.3.3 Droplet concentration

In addition to particle size analysis a number of supporting observations were conducted on the change in droplet number with time.

Emulsions were diluted as for particle size analysis except that the operation was performed in 25cm^3 volumetric flasks. The diluent preferred in these experiments was a 20% $^v/_v$ solution of glycerin in distilled water which assisted even dispersion of the droplets and reduced Brownian motion (Higher concentrations of glycerin reduced the contrast between droplets and continuous medium to an unacceptable degree).

The dilutions were allowed to cream under the cover slip in a haemocytometer slide (0.02mm), as previously. Each slide was then checked for even globule distribution with about 10-20 droplets per field. Exactly 20 fields were counted with the aid of an eyepiece graticule calibrated with a ruled micrometer. Fine globules deeper in the cell were viewed by focussing the microscope up and down. Fields were selected in five rows of four covering most of the available area of the slide. Globules were viewed at a total magnification of 400X, those being counted which lay on the left and top sides of each area but not the lower or right sides. The dilutions of alkane emulsions were found to be stable; no significant changes in globule number were detected in any of samples for up to 3 hours in the measuring cells. In each experiment the procedure was repeated twice and, provided the distribution across each slide was satisfactory, counts agreed within 5%. Some loss of droplets was detected from benzene and cyclohexane dilutions; benzene emulsion was particularly troublesome in this respect, the count falling by as much as 40 per cent within the first hour. These effects are attributable largely to the higher volatility and solubility of the oil phase (Section 3.3.2).

3.3.4 Centrifugation

Two 10cm^3 samples of a small but representative number of emulsions (benzene, cyclohexane, hexane and hexadecane stabilized by 10^{-2} mol dm^{-3} SDDS-A) were centrifuged six hours after preparation. The earliest experiments employed an I.E.C. refrigerated centrifuge (International Equipment Company; Model B-20 fitted with 873 Head) operated at 0°C. No separation of free oil was obtained after treatment for up to an hour at 6 000 g (10 000 rpm).

Further experiments were performed using an M.S.E. Automatic ultracentrifuge (Measuring & Scientific Equipment; Superspeed 50), also operated at 0°C. The emulsions were centrifuged at 85 000 g (30 000 rpm) for 10 minutes then removed from the centrifuge and examined for free oil. This procedure was repeated twice to give a total centrifugation time of 30 minutes for each emulsion. All the samples comprised of a close packed cream layer and a clear serum after the minimum centrifugation time. Samples of benzene and cyclohexane showed some separation of free oil after 20 minutes centrifugation. The remaining emulsions showed no separation and were centrifuged for a further 30 minutes. All the samples were remixed and examined for free oil at frequent intervals during storage at 25 ± 0.5°C.

3.3.5 Viscosity measurement

Viscosities were measured in a standard U-tube (Model A) viscometer (Griffin & George Ltd) which gave a flow time of 282 ± 1.0s for distilled water at the operating temperature. The instrument was mounted into a viscometer holder and maintained at 25 ± 0.05°C (Townson & Mercer Ltd.; E270 Bath with viscometer type lid). The viscometer was previously cleaned with chromic acid and rinsed thoroughly (not less than twelve times) with distilled water. After two further rinses with acetone the apparatus was dried in a stream of warm air.

Thirty minutes were allowed for thermal equilibration of the viscometer and emulsion before the instrument was filled. One flow time was measured immediately. The procedure was repeated twice, emptying and cleaning the viscometer between each run.

The relative viscosity (η_r) was determined using the formula

$$\eta_r = \eta_1 / \eta_2 = p_1 t_1 / p_2 t_2 , \qquad 3.14$$

where t_1 and t_2 are the mean flow times of two liquids with densities p_1 and p_2 respectively.

Emulsion densities were estimated from the appropriate oil densities; the density of the continuous medium was taken as 998 kg m^{-3}, the value for 10^{-2} mol dm^{-3} SDDS solution (283).

Viscosity measurements were made after an initial period of 2 hours and at frequent intervals thereafter.

3.3.6 Bulk changes

Visual observations on the extent of creaming and/or separation of free oil were also recorded. These were easily measured and gave further information regarding emulsion behaviour during storage.

3.4 ELECTROPHORESIS

3.4.1 Electrophoretic Mobility

If a dispersion of negatively charged particles (for example) is subjected to an electric field, the particles and the rigidly attached Stern layer (Section 1.2.3.2) are attracted to the positive electrode. The counter ions migrate in the opposite direction carrying solvent along with them. Electrophoresis is the movement of a charged surface relative to stationary liquid in an applied electric field. The means by which electrophoretic measurements are carried out on emulsions have been reviewed by Sherman (62a). Such measurements provide valuable information about the magnitude of electrostatic repulsive forces.

The relative movement of a particle with respect to the counter ions demands a plane of shear between the two parts of the double layer. This is likely to occur at some small distance from the Stern plane (Figure 1). The potential at this plane is known as the zeta-potential (Z) and determines the rate of particle migration from which Z may be measured experimentally. Electrophoretic measurements are usually recorded as mobilities, the electrophoretic mobility (u) is given by

$$u = v/E \quad , \qquad 3.15$$

where v is migration velocity ($\mu m\ s^{-1}$) and E is the field strength ($V\ cm^{-1}$).

The electrophoretic mobility of individual emulsion droplets was measured directly using a Rank Mark I microelectrophoresis apparatus (Plate 2) operated at $25 \pm 0.1^{\circ}C$.

3.4.2 Microelectrophoresis cell

The motion of the suspended droplets was observed in a capillary tube of cylindrical bore (Rank Bros). A portion of the tube in the centre is ground and polished flat on the viewing side in order to improve the conditions of illumination and to reduce refraction errors. Optical effects are further minimized by making the plano-convex cell wall very thin and by having both the cell and the microscope objective immersed in the thermostat bath.

At each end of the capillary access is provided for an electrode of platinum foil coated with platinum black. The electrodes are sealed into 10/19 joints surrounded by a "Teflon" sleeve (Fisons) for convenient insertion and removal from the cell. The apparatus was held firmly in place in a thermostat bath by means of a cell holder.

Initial cleaning of the cell was by soaking overnight in chromic acid and thorough rinsing in water but after assembly the cell was maintained filled with distilled water. The capillary was rinsed successively with distilled water (twice), surfactant solution (twice) and diluted emulsion (twice) before each measurement.

3.4.3 Stationary levels

Microelectrophoretic measurements are complicated by the motion of the liquid medium relative to the charged walls of the capillary tube (electro-osmosis). Within the closed system of the electrophoresis cell this necessitates a return flow of liquid with a maximum velocity at the centre of the tube the electrophoretic motion is superimposed on liquid movement and true electrophoretic velocities can only be observed at locations in the tube where electro-osmosis and return flow cancel. For a capillary of circular cross-section this so-called "stationary level" occurs at 0.707 r_e from the axis of the tube (where r_e is the tube radius). (62a,284ab,285).

3.4.4 Calibration of the cell

The exact distance between the two electrodes was obtained by measuring the conductivity of standard solutions of potassium chloride at $25^{\circ}C$. These were measured using the Wayne-Kerr conductivity bridge described previously (Section 2.2.2.2).

The conductivity K is the reciprocal of the resistance in ohms of a column of solution 1m long and $1m^2$ in cross section.

ie.
$$K = \frac{L_e}{A_e R_e} = \frac{L_e G}{r_e^2 \pi} , \qquad 3.16$$

where L_e is the length of the capillary, A_e is the cross sectional area of the capillary, R_e is the electrical resistance and G is the measured conductance ($G = 1/R_e$).

The internal radius of the capillary was measured as 0.88 mm. Therefore, from Equation 3.16

$$L_e = (2.433K/G) \times 10^{-6} \text{ metres.}$$

The conductivity for potassium chloride solutions has been well documented, the relevant values are given in Table 3-8. The capillary length was taken as 8.53×10^{-2} m.

Table 3-8

Determination of the effective length of the electrophoresis cell.

KCl concentration ($mol\ dm^{-3}$)	K ($\Omega^{-1}\ m^{-1}$)	G ($10^{-6}\ \Omega^{-1}$)	L_e (cm)
1.00	11.170	318.600	8.530
0.10	1.289	36.780	8.526

3.4.5 Operation

The apparatus was assembled as shown in Plate 2 and the water bath filled. Thirty minutes was allowed for thermal equilibration of the apparatus. The measuring microscope was focussed on the outside of the tube wall, then racked in to focus on the inside wall of the capillary. Correct positioning of the cell and the most effective illumination are achieved when the wall thickness (measured by a gauge) is at a minimum and the microscope is at right angles to the capillary. The wall thickness was found to be 66.0 μm. The microscope was then refocussed onto the outer wall; the distance (p_e) of the stationary layer from the outer wall is

$$p_e = \text{wall thickness} + (0.293\, r_e) \quad , \qquad 3.17$$

$$= 323.8$$

The microscope was racked in 323.8 μm and locked into place at the commencement of each set of measurements.

Emulsions were prepared and diluted as described previously (Section 3.3.2), the cell filled, closed by the electrodes and allowed to come to temperature (5 minutes). Care was taken to effect complete closure of the cell with the exclusion of all air. The thermostat pump was switched off whilst measurements were taken.

Particle velocities were determined by an electrical timer, individual droplets being timed over a fixed distance, usually 90 μm, on a calibrated eyepiece scale. Only those droplets in sharp focus and with no perceptible vertical motion were timed. A current of 20V was found to give reasonable transit times (ie. > 4 s) thus reducing errors due to Brownian motion and operator timing. Alternate particles were timed in opposite directions by reversing the electrode polarity. This procedure minimizes the effect of any slight drift in the sample and also prevents electrode polarization. The mean velocity and standard deviation was calculated from the timing of ten droplets in each direction.

The cell was emptied and rinsed with the aid of a suction pump.

3.4.6 Determination of zeta-potential

The zeta-potential can be obtained from the general electrophoretic equation derived by Henry (286) which, in its simplest form (for non-conducting particles) reduces to

$$u = \varepsilon Z \left(f \left[K^1 r \right] \right) / 6 \pi \eta \quad , \qquad 3.18$$

where ε is the dielectric constant for the fluid medium, η is the medium viscosity and $K^1 r$ is the ratio of radius of curvature for the particle and double layer thickness (200b,287). The function $f \left[K^1 r \right]$ depends upon the shape, size and orientation of the particle; it varies between 1.0 for small $K^1 r$ (< 1.0), where the particle can be considered as a point charge (Huckel equation), and 1.5 for large $K^1 r$ (> 200) where the particle surface can be considered flat (Smoluchowski equation).

The double layer thickness in metres, can be estimated from

$$K^1 = 0.328 \times 10^{10} \left(c \, n_z^2 \right)^{\frac{1}{2}} \qquad 3.19$$

for an aqueous solution of a symmetrical electrolyte with charge number n_z and molar concentration c at 25°C (287). The estimated values of K^1 and $K^1 r$ at a number of concentrations of electrolyte are given below (Table 3-9).

Table 3-9

Variation in reciprocal double layer thickness with concentration for a 1:1 electrolyte.

Concentration ($mol\ dm^{-3}$)	K^1 (m^{-1})	$K^1 r$ (i)	(ii)	(iii)
10^{-1}	1.0×10^9	250	500	2 500
10^{-2}	3.3×10^8	82.0	164	820
10^{-3}	1.0×10^8	25.0	50	250
10^{-4}	3.3×10^7	8.2	16.4	82
10^{-5}	1.0×10^7	2.5	5.0	25

NOTES

(i) For particles of 0.5 μm diameter.

(ii) For particles of 1.0 μm diameter.

(iii) For particles of 5.0 μm diameter.

Clearly the Hückel equation ($f\,[K^1 r] = 1.0$) is not likely to apply to the present work. For example, a particle diameter of 0.02μm would be required in an electrolyte concentration of 10^{-5} mol dm^{-3} to reduce $K^1 r$ to 0.1. In all cases considered $r \gg 1/K^1$ and it was decided to use the Smoluchowski equation. For a non-conducting particle the mobility u is independent of size and shape provided $K^1 r$ is large at all points on the surface. However, the general form of Equation 3.18 is based upon several simplifying assumptions, for example, the values of ε and η are treated as constants throughout the mobile part of the double layer. Whilst the error involved in variations of ε is probably small (288) the increase in η near the interface may be significant (Section 1.3.1), although Hunter (289) has suggested that this too has a negligible effect. An important assumption is that the applied field and double layer are simply superimposed without distortion. Consequently, corrections are often necessary for surface conductance and distortion of the double layer (relaxation effect) due to movement through an opposing current of counter ions. Both phenomena tend to reduce the measured zeta-potential. The error resulting from surface conductance can be neglected when K^1r is small. Neither does surface conductance introduce appreciable error for emulsion droplets in the presence of long chain ions, even at concentrations as high as 10^{-2} mol dm^{-3} (117 f,287). The relaxation effect becomes important between $0.5 < K^1r < 50$, particularly if zeta potential is high ($\simeq$ 100mV or greater) where discrepancies of up to 50% have been reported (117f). The error becomes proportionally less as K^1r increases and, for all practical purposes, it can be neglected if $0.1 > K^1r$ or $K^1r > 100$. For moderate values of K^1r the Henry equation (Equation 3.18) has been modified by Overbeck (285) who introduced a correction for relaxation, although the mathematical complexity of the derived expression limited its quantitative validity to zeta-potentials below 25mV. A more extensive review and treatment of the relaxation correction is that due to Wiersma <u>et al</u> (290), who have improved on previous determinations of the required correction factor (291).

At high K^1r ($f\left[K^1r\right] = 1.5$) the zeta-potential (in mV) may be estimated from Equation 3.18 which reduces to

$$Z = 12.83 \; u \qquad 3.20$$

at 25°C (117f).

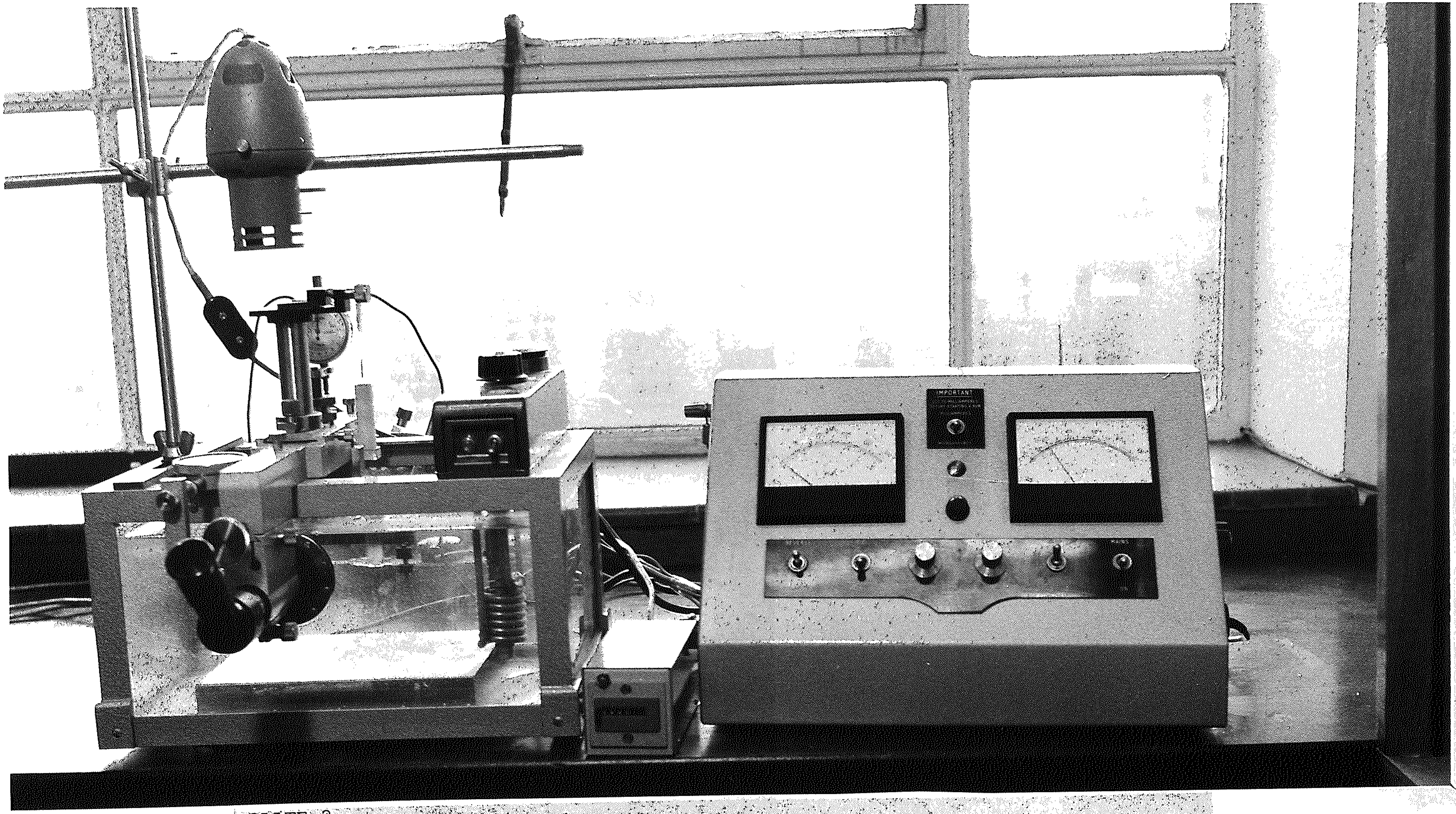


PLATE 2
Apparatus for electrophoretic mobility measurement, showing (left to right) the thermostat bath with cell, electronic timer and control panel.

4

RESULTS

4.1 INTERFACIAL TENSION AND ADSORPTION

4.1.1 Adsorption of SDDS

The interfacial tensions for a wide range of organic liquids against water or SDDS-A solution (10^{-4} mol dm^{-3}) are given in Tables 2-3 and 4-3 respectively. The measured tensions are in good agreement with values which have been previously recorded (186,237).

Interfacial tensions show a clear dependence on the nature of the oil phase in the absence or presence of surfactant. The alkanes give the highest values, increasing from 50.4 mN m^{-1} to 53.0 mN m^{-1} from hexane to hexadecane at the oil-water interface. Values for the cyclic oils are lower (eg. 46.6 mN m^{-1} for cyclohexane) and the unsaturated hydrocarbons give still lower values (eg. 41.0 and 34.6 mN m^{-1} for cyclohexene and benzene respectively). The tensions at oil-surfactant solution interfaces are naturally much lower, but they show a similar dependence on the oil phase even at surfactant concentrations approaching the cmc (see below).

A number of systems have been investigated more thoroughly, measurements of the interfacial tension (γ_{ow}) being recorded at a wide range of surfactant concentrations in order to determine the Gibbs surface excess (Section 1.3.3 and 3.1.8) of the adsorbed surfactant. Typical γ_{ow} versus log concentration curves are shown in Figure 10. The computed surface excess and area per adsorbed molecule values are listed in Table 4-1 for a number of surfactant concentrations. The coefficients of Equation 3.6 , from which surface excesses were calculated, are given for each oil in Table 4-2.

Similar surface excess and area per molecule data have been computed for SDDS-A adsorbed at the air-surfactant solution interface using the surface tension-log concentration relationship plotted in Figure 4. The adsorption data and coefficients for this interface are also included in Tables 4-1 and 4-2 respectively.

Further experiments have been conducted to obtain corresponding data for purified alkanes (hexane-P and hexadecane-P) at interfaces with SDDS- E solution. These measurements are also recorded in Tables 4-1 and 4-2.

Calculated areas per molecule at higher surfactant concentrations are more reliable than those when the concentration is low ($< 10^{-3}$ mol dm^{-3} for oil-water interfaces) since in the latter case the interfacial tension changes only slightly with quite large variations in concentration. It should also be noted that ageing of the interface, shown by a gradual change in γ_{ow} with time, was considerably more marked between about 10^{-4} and 10^{-3} mol dm^{-3} SDDS than at lower or higher concentrations, hence making the measurement of equilibrium tensions more difficult in this region. The γ_{ow} versus time curves closely resembled that illustrated by Hutchinson (234c) for the ageing of a benzene-sodium hexadecyl sulphate solution interface. The ageing phenomenon was substantially reduced in the present work by mutually saturating the two phases prior to measurement. Ageing times for the majority of systems was kept quite short ($<$10 minutes) by this means. Notable exceptions in this respect were found when unpurified hexane, cyclohexene or toluene were used as the oil phase. These oils gave rise to considerably longer periods of interfacial ageing (up to several hours in some instances), particularly at concentrations around 5x10^{-4} mol dm^{-3}. Ageing effects can arise from the migration of the surfactant molecules to the interface as this requires a finite time (117d). A gradual fall in γ_{ow} over lengthy periods probably arises from the redistribution of impurities within the system or from inefficient pre-equilibration of the two phases.

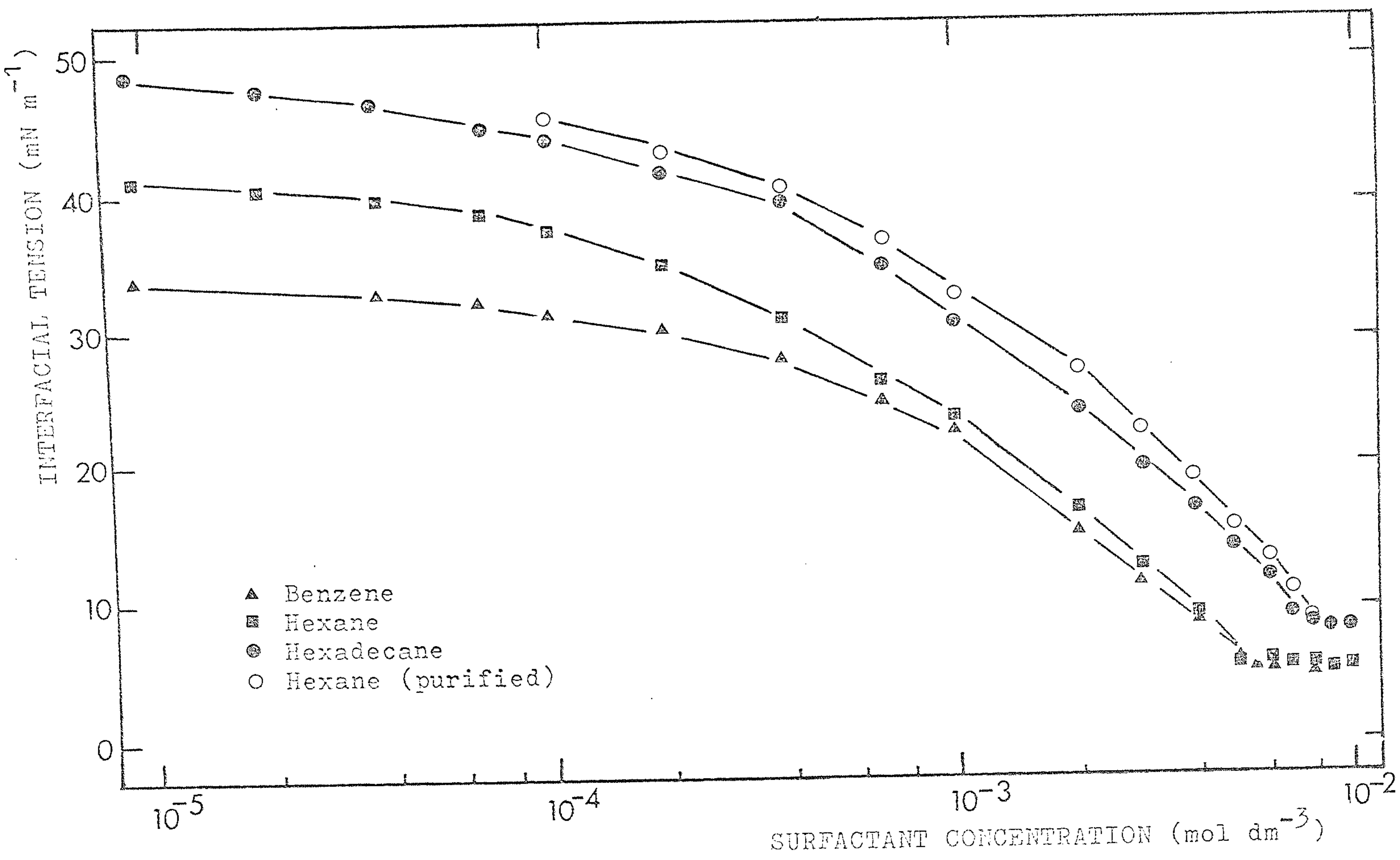


FIGURE IO

Plots of interfacial tension versus SDDS concentration for different oils.

Table 4-1

Interfacial properties of SDDS solutions at various interfaces.

NOTES:
a SDDS-A
b SDDS-E
c Hexane + Hexadecane γ_{ow} = 51.0 mN m^{-1}

Concentration mmol dm^{-3}	γ_{ow} mN m^{-1}	$\frac{d\gamma}{d\ln c}$	$\Gamma \times 10^{-18}$ molecule m^{-2}	A nm^{2}	π (A-Ao) 10^{-21} J
		AIR[a]			
7.0	33.5	-	-	-	-
6.0	33.3	-19.300	2.253	0.426	4.90
5.0	33.8	-18.496	2.249	0.445	5.57
4.0	37.8	-17.513	2.130	0.469	5.81
3.0	39.8	-16.245	1.975	0.506	6.67
2.0	45.9	-14.458	1.758	0.568	7.05
1.0	55.4	-11.403	1.387	0.721	7.07
0.7	60.5	-9.831	1.196	0.836	6.27
0.4	67.3	-7.365	0.896	1.116	4.00
0.2	69.7	-4.310	0.524	1.908	4.02
0.1	70.0	-1.255	0.153	6.550	13.75
		HEXANE[a]			
8.0	5.4	-	-	-	-
7.0	5.2	-14.021	1.705	0.587	12.97
6.0	5.6	-13.659	1.661	0.602	13.53
5.0	6.1	-13.256	1.612	0.620	14.17
4.0	8.8	-12.763	1.552	0.644	14.31
3.0	12.3	-12.097	1.471	0.680	14.47
2.0	16.8	-11.175	1.359	0.736	14.65
1.0	23.7	-9.621	1.170	0.855	14.82
0.7	27.1	-8.840	1.075	0.931	14.70
0.4	31.5	-7.574	0.921	1.085	14.84
0.2	36.6	-5.986	0.728	1.374	14.82
0.1	39.2	-4.449	0.541	1.848	17.34
		DODECANE[a]			
8.0	7.8	-13.486	1.640	0.606	13.67
7.0	9.3	-13.100	1.593	0.628	14.17
6.0	12.0	-12.689	1.543	0.648	14.09
5.0	13.7	-12.220	1.486	0.673	14.47
4.0	16.7	-11.650	1.416	0.706	14.53
3.0	19.6	-10.896	1.325	0.755	14.97
2.0	23.6	-9.860	1.199	0.834	15.43
1.0	30.8	-8.030	0.979	1.022	15.66
0.7	-	-7.155	0.870	1.149	-
0.4	36.4	-5.789	0.704	1.421	18.04
0.2	39.6	-3.906	0.425	2.104	30.96
0.1	42.1	-2.129	0.259	3.862	37.04

Concentration mmol dm^{-3}	γ_{ow} mN m^{-1}	$\frac{d\gamma}{dlnc}$	$\Gamma \times 10^{-18}$ molecule m^{-2}	A nm^2	π (A−Ao) 10^{-21} J
		HEXANE - p^b			
8.0	7.1	-14.735	1.800	0.555	11.04
7.0	9.2	-14.390	1.750	0.571	11.17
6.0	11.6	-13.990	1.701	0.588	11.17
5.0	14.4	-13.551	1.648	0.607	11.05
4.0	17.5	-13.014	1.582	0.633	10.96
3.0	20.7	-12.288	1.494	0.669	10.96
2.0	24.8	-11.334	1.378	0.726	10.91
1.0	32.5	-9.585	1.166	0.858	10.00
0.7	36.1	-8.722	1.061	0.943	9.19
0.4	39.3	-7.391	0.899	1.112	9.01
0.2	46.0	-5.618	0.683	1.464	5.12
0.1	47.8	-3.941	0.497	2.087	4.65
		HEXADECANE - p^b			
8.0	9.7	-14.788	1.798	0.556	11.08
7.0	11.6	-14.350	1.745	0.573	11.30
6.0	14.0	-13.876	1.687	0.593	11.43
5.0	15.6	-13.314	1.619	0.618	11.89
4.0	20.1	-12.626	1.535	0.651	11.55
3.0	23.8	-11.740	1.428	0.700	11.68
2.0	27.8	-10.490	1.276	0.784	12.19
1.0	34.2	-8.355	1.016	0.984	12.86
0.7	37.4	-7.256	0.882	1.134	13.01
0.4	40.3	-5.532	0.673	1.486	15.06
0.2	43.7	-3.396	0.413	2.421	19.72
0.1	46.7	-1.260	0.153	6.527	39.23

Concentration mmol dm^{-3}	γ_{ow} mN m^{-1}	$\frac{d\gamma}{dlnc}$	$\Gamma \times 10^{-18}$ molecule m^{-2}	A nm^2	π (A−Ao) 10^{-21} J
		TOLUENE^a			
7.0	5.0	-	-	-	-
6.0	5.3	-11.677	1.420	0.704	13.25
5.0	7.4	-11.268	1.370	0.730	13.20
4.0	9.7	-10.789	1.312	0.762	13.12
3.0	12.9	-10.168	1.236	0.809	12.83
2.0	16.0	-9.276	1.128	0.886	12.95
1.0	22.5	-7.780	0.946	1.057	12.38
0.7	26.0	-7.007	0.852	1.173	10.56
0.4	29.6	-5.789	0.704	1.421	9.53
0.2	33.0	-4.293	0.522	1.918	8.25
0.1	34.5	-2.780	0.338	2.959	9.57
		HEXANE + HEXADECANE $(50\%^v/v)^{ac}$			
8.0	8.3	-	-	-	
7.0	8.5	-13.060	1.588	0.630	14.03
6.0	9.0	-12.730	1.548	0.646	14.53
5.0	99.9	-12.360	1.503	0.665	15.00
4.0	11.3	-11.891	1.446	0.691	15.52
3.0	15.0	-11.299	1.374	0.728	15.41
2.0	18.3	-10.452	1.271	0.787	15.92
1.0	25.3	-9.013	1.096	0.913	15.75
0.7	29.8	-8.264	1.005	0.995	14.73
0.4	32.9	-7.104	0.864	1.158	15.53
0.2	38.5	-5.666	0.689	1.452	14.40
0.1	40.6	-4.218	0.513	1.949	17.15

Concentration mol dm^{-3}	γ_{ow} mN m^{-1}	$\frac{d\gamma}{d\ln c}$	$\Gamma \times 10^{-18}$ molecule m^{-2}	A nm^{2}	π (A−Ao) 10^{-21} J
		HEXADECANE[a]			
8.0	9.3	-13.588	1.650	0.606	13.37
7.0	9.7	-13.160	1.600	0.625	14.07
6.0	12.4	-12.694	1.544	0.648	14.13
5.0	14.4	-12.144	1.477	0.677	14.55
4.0	17.0	-11.471	1.395	0.717	15.01
3.0	20.5	-10.603	1.290	0.776	15.47
2.0	25.0	-9.380	1.141	0.877	16.16
1.0	31.3	-7.288	0.886	1.128	17.97
0.7	35.0	-6.212	0.755	1.324	18.43
0.4	39.0	-4.523	0.550	1.818	21.25
0.2	41.8	-2.431	0.296	3.383	34.52
		CYCLOHEXANE[a]			
7.0	5.6	-13.170	1.602	0.624	13.28
6.0	6.8	-12.787	1.555	0.643	13.65
5.0	8.3	-12.335	1.500	0.665	13.98
4.0	11.9	-11.784	1.433	0.698	13.81
3.0	15.6	-11.069	1.346	0.743	13.73
2.0	20.7	-10.070	1.224	0.817	13.39
1.0	26.4	-8.347	1.015	0.985	13.83
0.7	29.0	-7.467	0.908	1.101	14.09
0.4	31.6	-6.085	0.740	1.351	15.76
0.2	34.1	-4.366	0.531	1.882	19.77
0.1	40.0	-2.656	0.323	3.092	18.43

Concentration mol dm^{-3}	γ_{ow} mN m^{-1}	$\frac{d\gamma}{d\ln c}$	$\Gamma \times 10^{-18}$ molecule m^{-2}	A nm^{2}	π (A−Ao) 10^{-21} J
		CYCLOHEXENE[a]			
7.0	4.7	-	-	-	-
6.0	4.7	-13.199	1.605	0.623	11.72
5.0	7.7	-12.697	1.544	0.648	11.59
4.0	11.0	-12.088	1.470	0.680	11.40
3.0	14.0	-11.120	1.352	0.740	11.88
2.0	17.3	-10.032	1.220	0.820	12.32
1.0	24.2	-7.960	0.968	1.033	12.31
0.7	26.8	-6.907	0.840	1.190	12.64
0.4	29.6	-5.230	0.636	1.572	14.50
0.2	32.8	-3.125	0.380	2.632	19.12
0.1	34.0	-1.085	0.132	7.576	50.95
		BENZENE[a]			
6.0	5.4	-	-	-	-
5.0	6.3	-11.612	1.412	0.710	11.60
4.0	8.7	-11.061	1.345	0.744	11.50
3.0	11.6	-10.847	1.319	0.758	10.53
2.0	15.0	-9.350	1.137	0.880	11.57
1.0	23.3	-7.853	0.955	1.048	8.45
0.7	25.9	-6.768	0.823	1.215	7.96
0.4	28.4	-5.386	0.655	1.530	7.63
0.2	30.4	-3.651	0.444	2.252	8.10
0.1	32.0	-1.981	0.241	4.155	10.02

Table 4-2

Coefficients computed from Equation 3.5 for SDDS solutions at various interfaces.

SDDS-A solution interface	a_o	a_1	a_2
Air	-127.38	-41.847	-2.2036
Hexane	-92.57	-25.212	-1.1276
Dodecane	-87.10	-25.888	-1.2894
Hexadecane	-92.04	-28.133	-1.5088
Cyclohexane	-90.90	-25.451	-1.2375
Cyclohexene	-101.93	-28.686	-1.5124
Benzene	-90.18	-24.635	-1.2276
Toluene	-82.68	-22.770	-1.0847
Hexane + Hexadecane (50%^{v}/v)	-86.01	-23.381	-1.0402
SDDS-E solution interface			
Hexane-P	-92.45	-26.611	-1.2319
Hexadecane-P	-97.87	-29.639	-1.5406

The calculated areas per adsorbed molecule (Table 4-1) show some dependence upon the nature of the phase in contact with SDDS solution. The least expanded surfactant film occurs at the air-water interface (0.42 nm^2 molecule^{-1} at the cmc). Films at the oil-water interface are invariably more expanded than at the air-water interface but also show clear dependence on the type of oil; benzene and toluene give the most expanded films (0.70 nm^2 molecule^{-1}), cyclohexane and cyclohexene are significantly more condensed (0.62 nm^2 molecule^{-1}), and the alkanes show the most condensed films (0.58 to 0.61 nm^2 molecule^{-1}). The chain length of the unpurified alkanes appears to influence the area per molecule, the longer the hydrocarbon chain the more expanded the film. Purification of the C_6 and C_{16} alkanes reduced the respective areas per molecule to 0.555 and 0.560 nm^2.

Included in Table 4-1 are values of $\pi(A-A_o)$, where the interfacial pressure (π) is the lowering of interfacial tension due to the presence of surfactant, A is the area per adsorbed molecule and A_o is the area of interface occupied by each surfactant molecule. The significanse of these values is discussed in Section 5.1.2.2.

4.1.2 The effect of additives on interfacial tension

A number of measurements have been made of interfacial tensions in the presence of a small amount of additive (alkane or alkanol). In general, the presence of a small quantity (0.04 mol dm^{-3}) of alkane in the oil phase exerts little or no effect on the interfacial tension of another alkane or even benzene (Table 4-4). In contrast, the presence of the same concentration of an aliphatic alcohol results in a considerable lowering in the interfacial tension, caused by the adsorption of alcohol molecules to produce a mixed interfacial film. This effect is illustrated by the interfacial tensions of various systems which are listed in Tables 4-4 and 5-3. Data for the mixed film SDDS + dodecanol is presented and discussed in Section 5.1.2.4.

4.2 DROPLET STABILITY

4.2.1 Analysis of the data

A distribution of droplet rest-times was obtained in each experiment. The results for a number of systems have been analysed in full according to Equations 3.7 to 3.12 (Section 3.2.4).

The values of t_{mean}, $T_{\frac{1}{2}}$ and $t_{\frac{1}{2}}$ were found to be less reproducible as the spread of values increased (i.e. as the overall stability increased). The magnitude of "drainage time" t_d and the accuracy with which it can be measured appear to give insufficient scope for the comparison of more than a few systems. This is particularly true in experiments at 10^{-4} mol dm^{-3} concentrations of SDDS where, in all cases, the value of t_d was found to be very short. However, it should be mentioned that t_d was particularly sensitive to an increase in the surfactant concentration (Section 3.2.5.2).

The empirical expression, Equation 3.10 , appears to correlate much of the data obtained for simple systems. However, plots of log $(F_c/(1-F_c))$versus log t show a marked curvature as the stability increases (Figure 11). The same is true of the Gillespie & Rideal function (275) (Equation 3.12) which gives a good correlation only for droplet rest-times distributed below about 20s. In the majority of cases the data can be fitted by Equation 3.11 where n=1 (ie. Figure 12). No other value of n was found to improve the correlation; indeed, different values of n for each system, or non integer values, are of limited usefulness since the mathematical fit obtained lacks a direct physical significance. In contrast, the simple analysis of Cockbain & McRoberts (104) (Figures 8 and 12) provides simple stability parameters.

Figure 13 shows the data replotted on a probability scale (Section 3.2.5.2). Not suprisingly a series of curves result, the curvature becoming more pronounced as the overall stability increases. Similar problems have been reported from the treatment of particle sizing data by the normal distribution function (292a). On the other hand, analysis of droplet stability data by means of the log-normal distribution enables the calculation of two parameters (M and σg) which uniquely define a given set of data (Figure 14). The results of a considerable number of experiments suggest that the parameters can be obtained graphically to within the accuracy required for subsequent droplet stability analysis although scattered data may require mathematical evaluation directly from the log-normal function:-

$$y = \frac{1}{2.303 \log \sigma g \sqrt{2\pi}} \exp \frac{-(\log x - \log M)^2}{2 \log^2 \sigma g} , \quad 4.1$$

where σg is the geometric standard deviation and M is the geometric mean (293). In fitting the best straight line to the points on a probability plot it becomes essential to attach more significance to values near the 50% line and preference should be given to such points (292b). Drinker & Hatch (294) have fitted the best straight line between the 20% and 80% limits, which appears to be a useful guide for the assessment of droplet stability. The mathematical techniques of analysis have been compared with the graphical method by Aitchison & Brown (295) who concluded that an experienced user of the log-probability chart could fit data visually, with only slight loss of accuracy, provided the scatter of experimental points was not too great.

It was decided to analyse the droplet rest-times data in terms of the readily obtainable parameters t_{mean} or $t\frac{1}{2}$ to characterize the overall stability, with $T\frac{1}{2}$ as an expression of coalescence rate and σg to describe the distribution of data around $t\frac{1}{2}$ (ie. M). This latter device defines each system uniquely and enables the regeneration of original rest-time measurements. The values of M and σg were measured graphically. $T\frac{1}{2}$ was calculated using Equations 3.7 and 3.8 for the approximately linear region of Figure 12. The best line, consistent with the log droplet number vs. time plot was chosen from multiple regression analysis at progressively increasing rest times. Where the maximum rest-time (t_{max}) <100s the data between limits of 5 to 30% t_{max}, rising by increments of 5% to 5 to 100%, were analysed. Where t_{max} > 100s the initial limits were altered to 1 to 10%, rising by 1%. In this way the initial slow decrease in N, corresponding to t_d was not included in the computation of coalescence rate. The regression was achieved by a computer program which generated values of the rate constant k_c, $T\frac{1}{2}$ and the correlation coefficient and standard deviation for each set of measurements (Appendix III).

4.2.2 The effect of oil phase

The stability parameters for a wide range of organic liquids are summarized in Table 4-3. The rest-times of alkane droplets increases with a decrease in hydrocarbon chain length (Figure 12). This behaviour is reflected by changes in $T\frac{1}{2}$, $t\frac{1}{2}$ and t_{mean}. Light and heavy liquid paraffins have similar stabilities to the long chain alkanes. The introduction of a double bond into the alkane molecule results in a reduced stability. The chain length effect is apparently repeated with the cyclic oils, though these are significantly less stable than the corresponding alkanes (eg. $T\frac{1}{2}$ = 5.9s for cyclohexane; $T\frac{1}{2}$ = 24.3s for hexane). The progressive introduction of unsaturation into a cyclic compound again reduces stability as illustrated by the $T\frac{1}{2}$ values for cyclohexane, cyclohexene and benzene (5.9s, 4.9s and 2.0s respectively).

It is important to note that the purified oils (hexane-P, hexadecane-P and benzene-P) did not exhibit significantly different stabilities from the original oils.

FIGURE 11

Graphical representation of droplet stability data from an empirical approach.

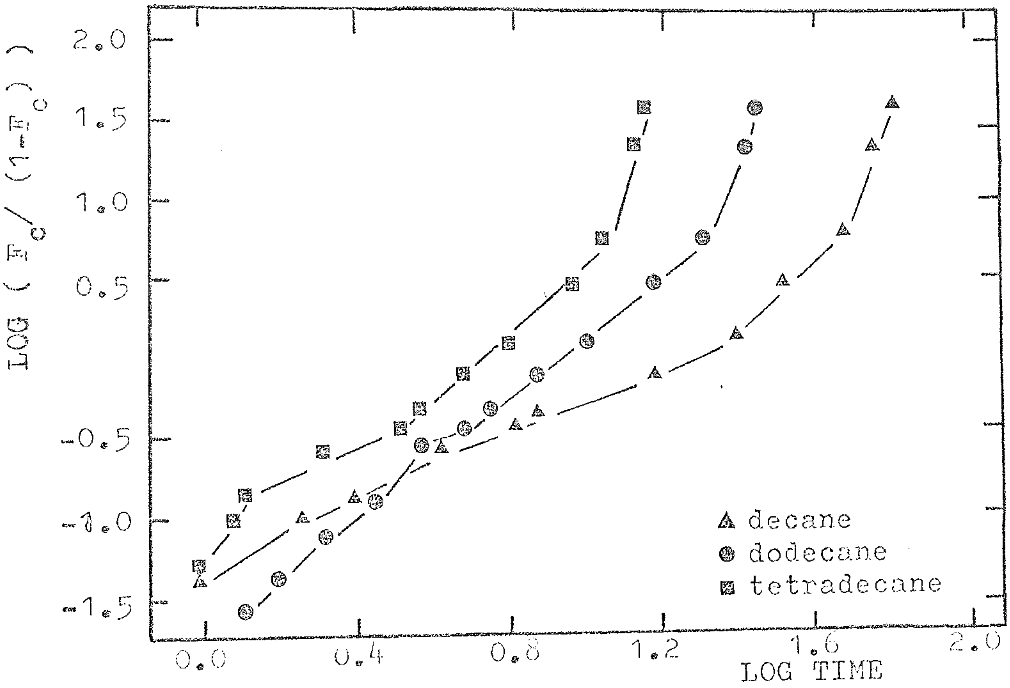


FIGURE 12

Log (number not coalesced) versus time for alkane hydrocarbons.

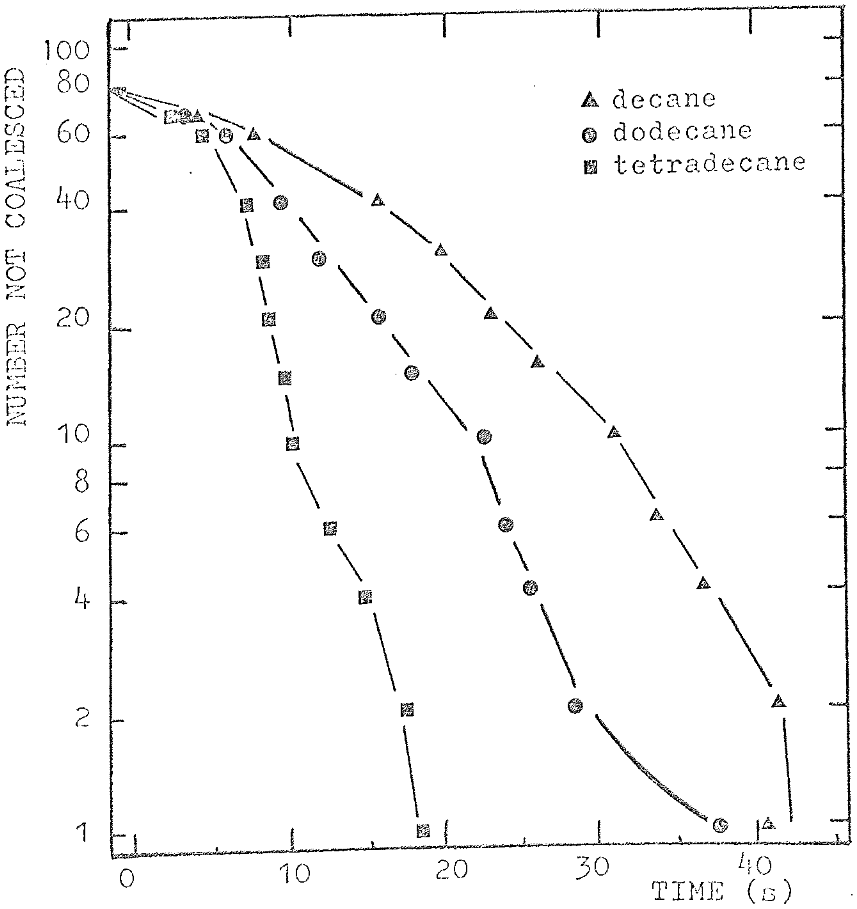


FIGURE 13

Analysis of droplet stability data on the basis of the normal distribution function.

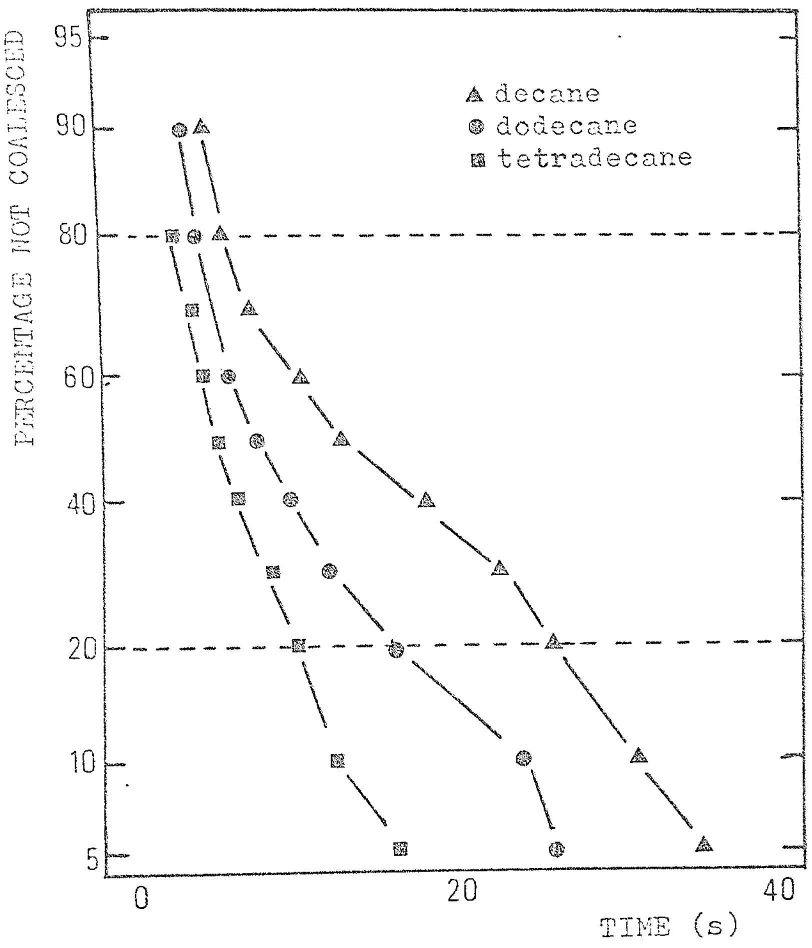


FIGURE 14

Analysis of droplet stability data by means of the log normal distribution.

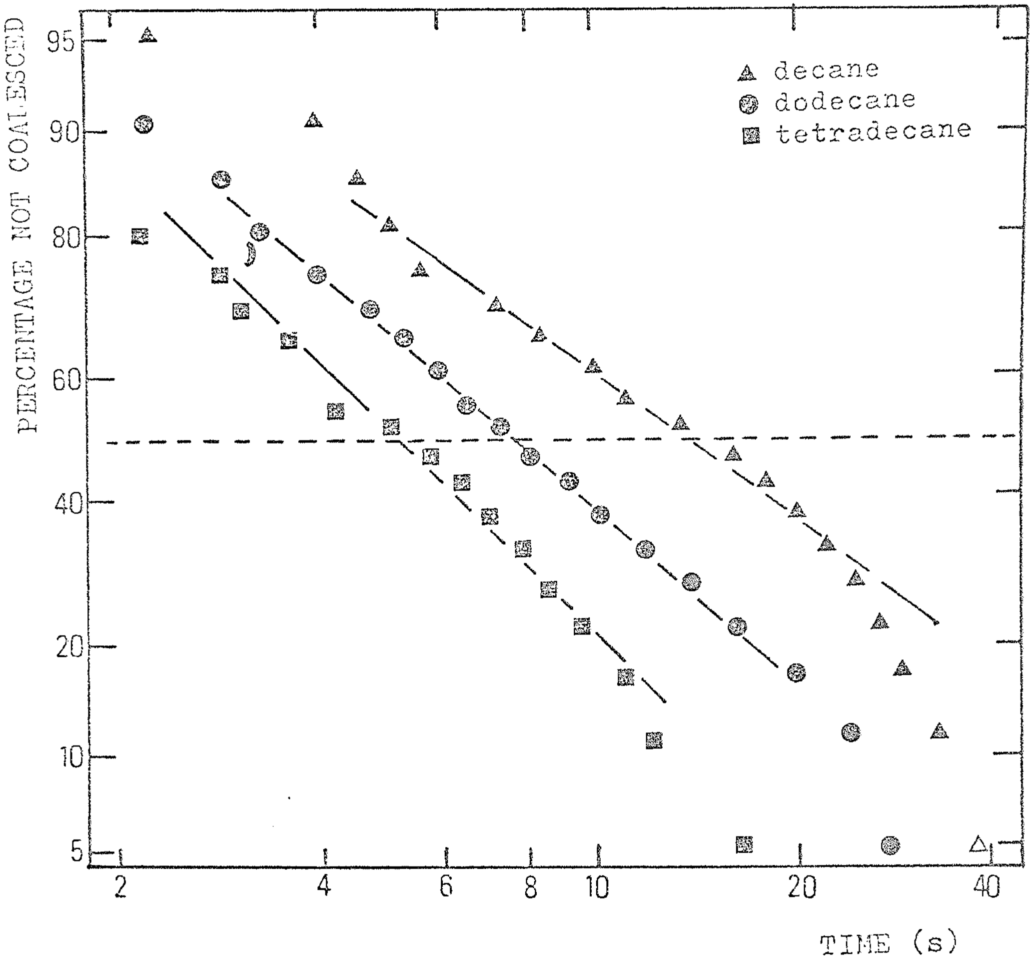


Table 4-3

Stability parameters for oil droplets stabilized by 10^{-4} mol dm^{-3} SDDS-A solution and physical properties of the oils and oil-SDDS systems (at 25°C).

OIL PHASE	t_{mean} (s)	$T_{\frac{1}{2}}$ (s)	M (s)	σ_g	γ_{ow} (mN m^{-1})	ΔP (kg m^{-3})	η (mN s m^{-2})	δ
Hexane	28.0	24.3	12.7	6.9	39.2	343	0.299	7.27
Octane	22.8	14.9	13.6	4.2	39.9	300	0.515	7.54
Decane	15.8	8.3	12.3	2.5	41.1	272	0.861	7.74
Undecane	15.9	6.7	7.6	3.1	41.4	260	–	7.81
Dodecane	10.3	5.9	7.5	2.4	42.1	253	1.378	7.92
Tridecane	9.7	4.2	6.4	1.8	42.0	244	–	–
Tetradecane	6.1	3.2	4.7	2.4	42.9	238	–	–
Hexadecane	6.7	3.0	6.0	1.8	43.7	228	–	–
Cyclopentane	17.6	10.1	12.0	2.8	35.1	258	0.416	8.10
Cyclohexane	9.4	5.9	6.2	2.4	40.0	224	0.898	8.19
Octene	18.5	11.3	13.7	2.2	36.5	237	0.447	7.60
Cyclohexene	7.9	4.9	6.0	2.6	34.0	192	0.628	8.29
Benzene	5.1	2.0	4.5	1.7	32.0	124	0.603	9.16
Toluene	12.8	8.2	8.3	2.8	34.5	136	0.552	8.93
o-Xylene	15.3	9.5	11.2	2.4	35.5	122	0.756	9.06
m-Xylene	14.9	9.3	10.5	3.1	33.5	138	0.581	8.88
p-Xylene	12.0	6.4	6.7	3.2	34.8	141	0.605	8.83
Light paraffin	9.0	5.6	6.1	2.5	42.8	148	–	–
Heavy paraffin	5.9	3.0	4.1	1.8	43.7	118	–	–
Butanol	∞	∞	∞	∞	–	192	2.410	11.60
Pentanol					–	186	3.347	11.12
Hexanol					6.0	182	4.592	10.77
Octanol					7.6	176	7.212	10.30
Decanol					7.9	172	–	10.03
Hexane-P	30.5	21.1	18.7	5.1	47.8	–	–	–
Hexadecane-P	6.0	2.9	5.5	2.0	46.7	–	–	–
Benzene-P	4.9	2.6	4.6	1.7	32.0	–	–	–

The stability parameters obtained for toluene and the xylenes were somewhat less reproducible than those of the other oil phases. This is most probably due to the interfacial "scum" which was frequently observed with these systems. The possible explanations for this phenomenon are considered to be impurities in the oil phase or spontaneous emulsification at the interface. Repeated experiments using SDDS-B or an anti-vibration mounting (Section 3.2.5.2) suffered from the same problem. Toluene is somewhat more difficult to purify than benzene (271), nevertheless there was no evidence of any marked contamination of the oil from interfacial studies (Section 4.1). Furthermore, a system of toluene against SDDS-A solution at a lower concentration (10^{-5} mol dm^{-3}) produced no clouding at the interface. The formation of the "scum" followed a pattern, increasing to a maximum within about twenty minutes (with 10^{-4} mol dm^{-3} surfactant solution) and then becoming progressively less, being completely removed within five hours or so. This observation strongly suggests that either equilibration of an impurity between the phases or spontaneous emulsification is involved. The latter may arise through diffusion between the phases (296), (unlikely in an effectively pre-equilibrated system), negative interfacial tension (at a higher surfactant concentration) or interfacial turbulence (297,298). Certainly, careful filling of the apparatus significantly reduced but did not eliminate the effect. As a consequence the results cited for toluene and the xylenes are representative of five replicate experiments. The results show that an increase in stability is brought about by methyl-substitution of benzene. The o- and m-xylene droplets are more stable than toluene although the stability using p-xylene is slightly less than that of toluene.

The aliphatic alcohols from butanol, which was slightly miscible with the aqueous phase, to decanol formed highly stable droplets. The rest-times were, with only a few exceptions, well in excess of 500s and the determination of stability parameters was impracticable.

4.2.3 The effect of additives

In a number of instances a small quantity (0.04 mol dm^{-3}) of a second oil has been added to a hydrocarbon oil and the droplet stability monitored. The results are summarized in Table 4-4. It can be seen that a small amount of long chain alkane has negligible effect on the stability of hexane or benzene droplets. Similarly, such a small amount of hexane does not affect the stability of hexadecane droplets. Indeed, a 50% by volume mixture of these two oils exhibits a predictably intermediate stability (see Table 4-3). In contrast, when the additive is an aliphatic alcohol the stability can be affected. Short chain length alkanols exert a destabilizing effect on hexadecane droplets. Alcohols of intermediate chain length (C_6 to C_{10}) appear to have little or no effect but a further increase in carbon number leads to a dramatic increase in stability. Figure 15 shows the effect of various additives on the rest-times of hexadecane droplets and also the stabilization caused by a tenfold increase in surfactant concentration. It is noticeable that those systems in which stability is enhanced by alkanol manifest a definite change in the shape of the coalescence curve by developing a "spur". The rest-time data for such systems are correlated less satisfactorily by the log-normal distribution function (Figure 16).

An additional series of experiments were arranged to determine whether alkanols were more effective in increasing droplet stability in the presence of a higher concentration of surfactant. The results are presented in Table 4-4. No definite conclusions can be drawn from these measurements although the C_4 alcohol again caused destabilization of hexane droplets. The alkanols of chain length C_5 or greater all appear to increase stability slightly. However the differences in stability are insufficient to provide any clear indication as to the relative stabilizing effects of the different alcohols.

Table 4-4

Stability parameters for oil droplets containing a small amount (0.04 mol dm^{-3}) of additive and stabilized with SDDS-A.

Oil	Additive	t_{mean} s	$T_{\frac{1}{2}}$ s	M s	σ_g	γ_{ow} (mN m^{-1})
		10^{-4} mol dm^{-3} surfactant				
Hexane	–	28.0	24.3	12.7	6.9	39.2
Hexane	Hexadecane	33.6	25.7	16.2	6.4	39.2
Hexadecane	–	6.7	3.0	6.0	1.8	43.7
Hexadecane	Hexane	5.0	2.7	4.3	1.6	43.9
Benzene	–	5.1	2.0	4.5	1.7	32.0
Benzene	Hexadecane	4.8	2.4	4.2	1.8	32.2
Hexane+ Hexadecane	50% $^v/_v$	30.9	13.0	16.7	4.4	40.6
Hexadecane	Butanol	1.2	1.0	0.7	1.8	31.0
	Pentanol	1.0	1.0	–	–	26.0
	Hexanol	8.0	3.4	4.5	2.5	25.6
	Octanol	6.0	2.9	4.3	2.1	25.9
	Decanol	6.6	3.2	4.7	2.0	24.6
	Dodecanol	12.9	5.8	8.8	2.0	24.6
	Hexadecanol	19.3	16.4	10.8	4.7	24.4
		10^{-3} mol dm^{-3} surfactant				
Hexadecane	–	14.9	8.0	11.3	2.2	31.3
	Butanol	6.8	4.3	6.0	2.1	–
	Pentanol	18.8	13.6	14.5	4.6	–
	Hexanol	31.5	16.1	21.5	4.3	–
	Dodecanol	18.1	13.2	13.5	3.3	17.8
	Hexadecanol	21.5	14.2	14.8	2.9	17.8

FIGURE 15

The effect of a small quantity (0.04 mol dm^{-3}) of alkanol or an increase in surfactant concentration on the distribution of droplet rest-times.

(● - hexadecane, △ - hexadecane + butanol, □ - hexadecane + dodecanol, all 10^{-4} mol dm^{-3} SDDS; ▲ - hexadecane, 10^{-3} mol dm^{-3} SDDS.)

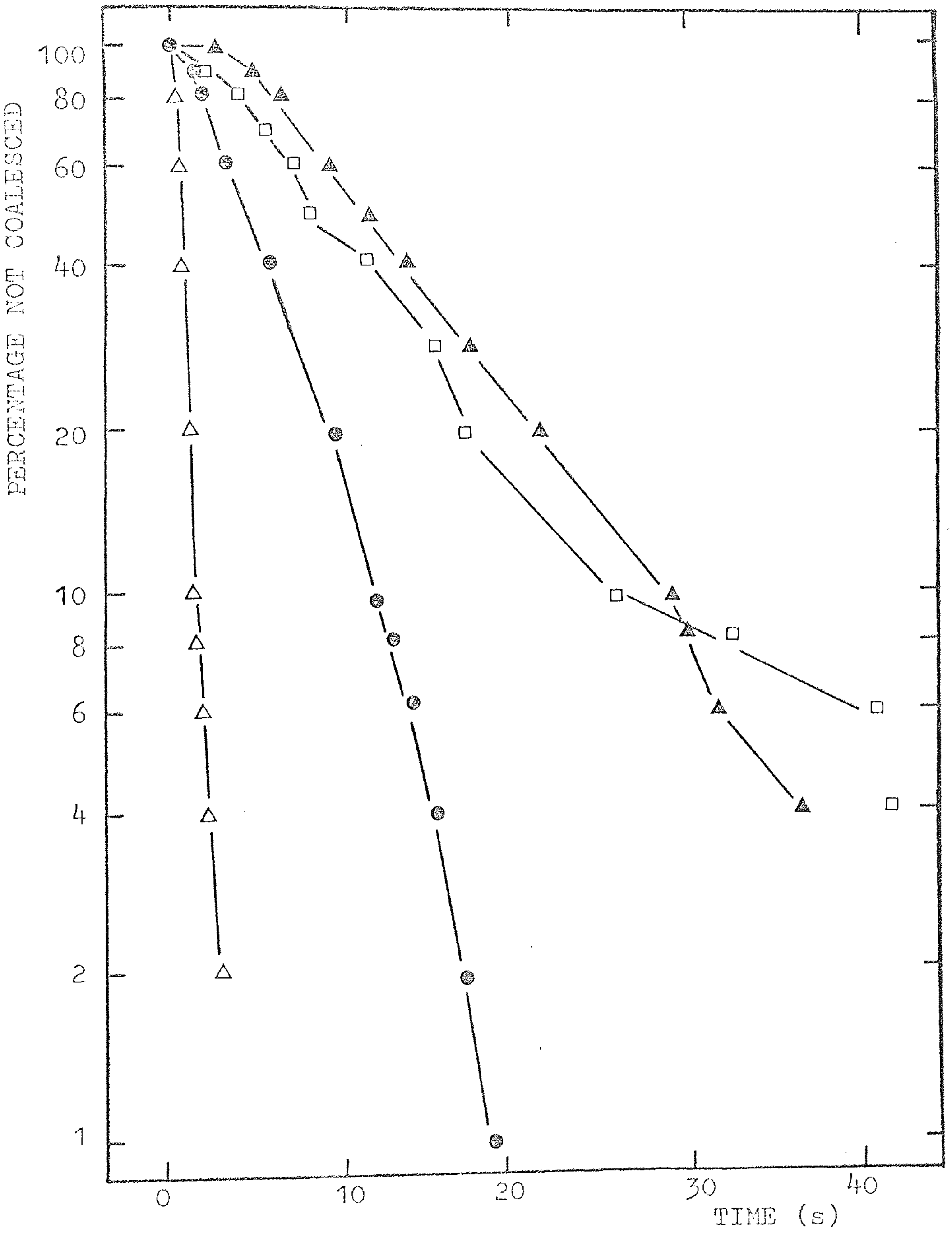
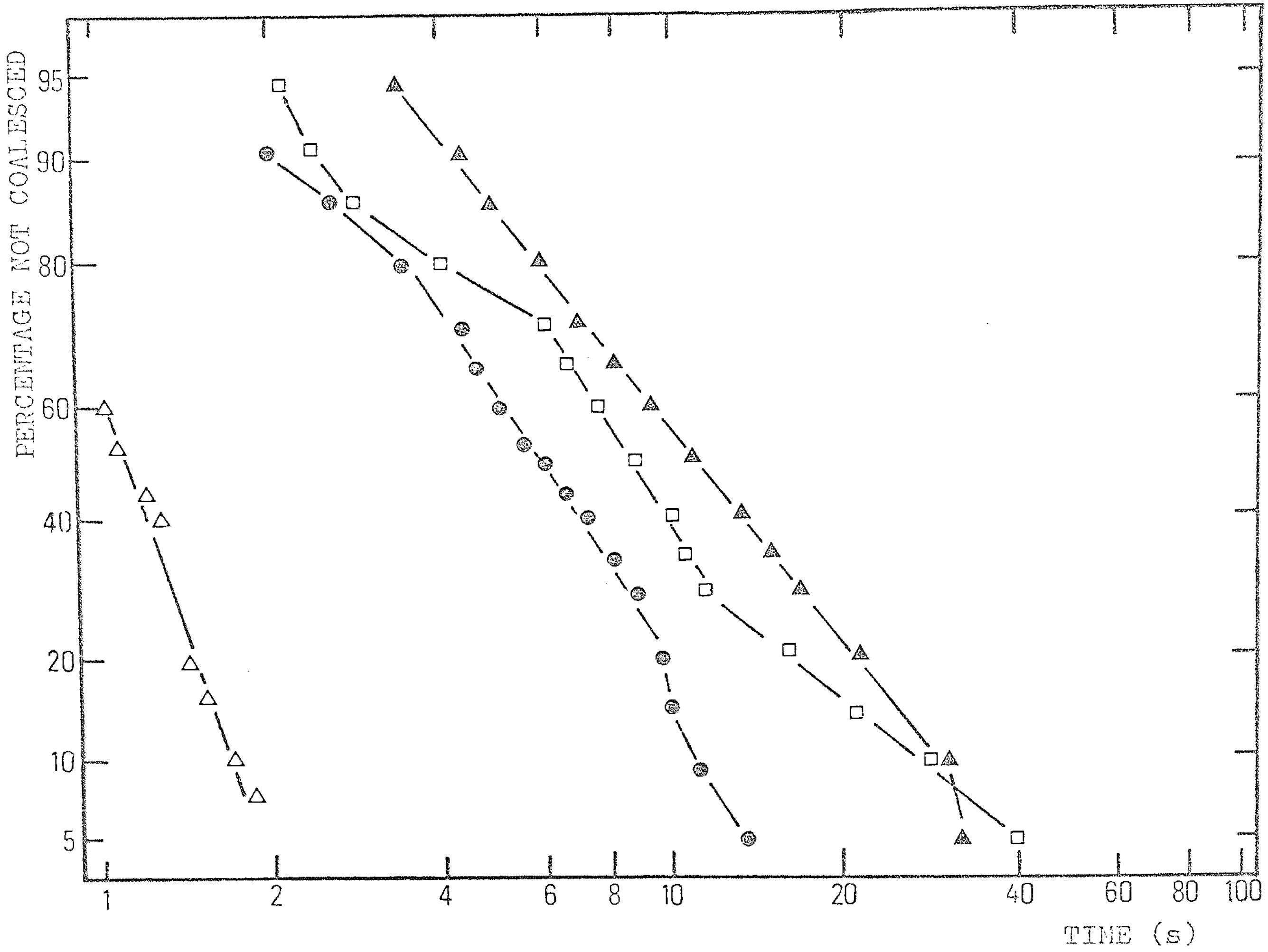


FIGURE 16

The effect of a small quantity (0.04 mol dm^{-3}) of alkanol or an increase in surfactant concentration on log - probability plots of droplet rest time data.

(● - hexadecane, △- hexadecane + butanol, □- hexadecane + dodecanol, all 10^{-4} mol dm^{-3} SDDS; ▲-hexadecane, 10^{-3} mol dm^{-3} SDDS.)



4.3 EMULSION STABILITY

4.3.1 The effect of oil phase

4.3.1.1 Droplet size measurement

The droplet size distribution plots show ageing of the emulsions by changes in the number percent versus diameter curves with time. Size distributions were measured from photomicrographs as described in Section 3.3.2. A selection of typical photomicrographic prints is presented in plates 3 and 4.

Ageing of the alkane emulsions causes a progressive broadening and flattening of the distribution curve as the modal diameter (the most frequently observed diameter) becomes larger. The results for octane, dodecane and hexadecane are shown in Figure 17 and similar curves for hexane are included in Figure 23.* Despite the fact that the results are difficult to compare in this form the figures do show that stability increases significantly with increasing carbon number for the alkanes.

Similar curves for cyclohexane (Figure 17) benzene and toluene (also Figure 17) show the lower stability for these oils as compared with the alkanes.

After considerable coarsening, the unstable systems show a significant increase in the number of small droplets. This may result from the disappearance of large droplets through coalescence into a free oil phase (Section 4.3.1.5) although it is also likely that an extremely wide distribution of sizes precludes the dilution and preparation of a truly representative sample from the bulk emulsion. The effect is clearly shown in the cyclohexane emulsion (Figure 17D) and also accounts for the fall in computed arithmetic mean diameters in benzene and toluene emulsions at longer ageing times (Table 4-5).

*Footnote : Figure 23 is located at page 133/4.

PLATE 3

SAMPLES OF PHOTOMICROGRAPHS SHOWING THE COARSENING OF HYDROCARBON EMULSIONS

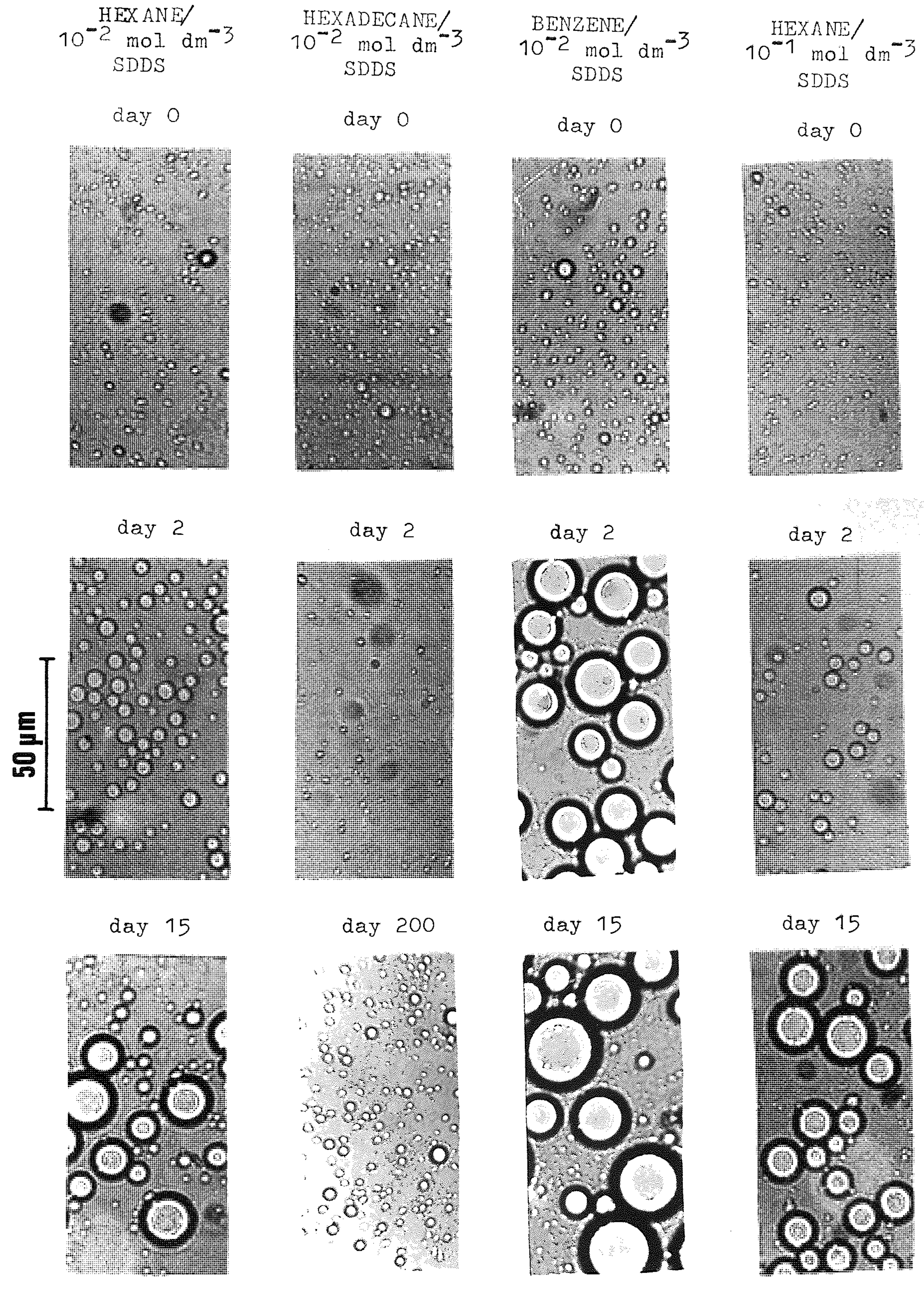


Table 4-5

Changes in mean droplet diameters (μm) during the ageing of SDDS (10^{-2} mol dm^{-3}) stabilized o/w emulsions.

Oil Phase	Size parameter	Emulsion age (days) 0	1	2	3	5	15	25	50	100	200
Hexane	d_{av}	1.38		2.29	2.80	4.10	4.52	4.97	4.64	3.90	
	d_v	1.64		2.73	3.31	5.10	6.64	7.15	7.60	6.51	-
	d_{vs}	1.95		3.19	3.86	6.26	9.00	9.74	9.68	9.60	
Octane	d_{av}	1.44		1.50		1.84	2.00	2.20	2.51	2.47	2.41
	d_v	1.69		1.80	-	2.02	2.40	2.88	3.12	2.92	2.91
	d_{vs}	1.95		2.11		2.21	2.88	3.85	3.54	3.47	3.51
Decane	d_{av}	1.42		1.40			1.60	1.70	2.32	2.80	2.84
	d_v	1.60		1.56	-	-	1.77	2.19	2.78	3.18	3.31
	d_{vs}	1.79		1.75			1.92	2.67	3.28	3.61	3.87
Dodecane	d_{av}	1.40		1.35		1.42	1.72		1.55	1.76	2.03
	d_v	1.65		1.62	-	1.73	2.03	-	2.05	2.14	2.34
	d_{vs}	1.97		1.97		2.02	2.59		2.74	2.57	2.67
Tetradecane	d_{av}	1.44		1.39		1.40			1.41	1.83	2.07
	d_v	1.68	-	1.65	-	1.68	-	-	1.71	2.09	2.27
	d_{vs}	2.12		2.10		2.08			2.04	2.38	2.53
Hexadecane	d_{av}	1.34		1.40		1.35			1.32	1.35	1.46
	d_v	1.64	-	1.66	-	1.64	-	-	1.66	1.67	1.73
	d_{vs}	1.96		2.03		2.00			2.05	2.04	2.02
LLP	d_{av}	1.54		1.48		1.55	1.67	1.67	1.85		2.07
	d_v	1.77	-	1.80	-	1.79	2.00	2.08	2.31	-	2.79
	d_{vs}	2.28		2.40		2.36	2.82	2.61	2.94		3.69
HLP	d_{av}	2.43		2.49			2.77	2.96	2.55		2.56
	d_v	3.47	-	3.37	-	-	3.56	3.85	3.69	-	3.69
	d_{vs}	4.82		4.45			4.57	4.94	5.29		5.31
Decene	d_{av}	1.35		1.48			1.62	1.90	2.20	2.55	
	d_v	1.56	-	1.79	-	-	2.03	2.42	2.73	3.31	-
	d_{vs}	1.80		2.04			2.51	2.75	3.38	4.60	

Table 4-5 - continued

Oil Phase	Size parameter	0	1	2	3	5	15	25	50	100	200
		Emulsion age (days)									
Cyclohexane	d_{av}	1.76	1.93	2.64	2.93	4.19	3.73	3.91	4.09		
	d_v	2.00	2.33	3.62	4.02	5.05	6.23	5.83	6.42	-	-
	d_{vs}	2.42	2.75	4.74	5.09	5.94	9.85	8.45	8.96		
Cyclohexene	d_{av}	1.76		2.79		4.04	4.41	4.45	6.33		
	d_v	2.10	-	3.84	-	6.10	6.45	7.29	9.58	-	-
	d_{vs}	2.63		4.94		8.50	10.30	10.96	13.20		
Benzene	d_{av}	1.36	2.75	3.17		3.28	3.69	4.87	4.12		
	d_v	1.81	4.00	5.10	-	6.97	7.53	7.96	7.60	-	-
	d_{vs}	2.36	5.57	7.54		12.95	13.24	11.58	12.70		
Toluene	d_{av}	1.56	1.85	2.56	3.98	4.62	5.10	5.00	4.81		
	d_v	1.87	2.72	4.04	5.47	6.05	6.75	7.87	7.40	-	-
	d_{vs}	2.19	3.92	6.17	7.59	8.94	8.87	12.00	9.85		
o-Xylene	d_{av}	1.50		2.51		3.37		3.19			
	d_v	1.73	-	3.28	-	4.88	-	6.31	-	-	-
	d_{vs}	1.99		3.97		7.22		8.95			
p-Xylene	d_{av}	1.54		2.54		3.46		3.59			
	d_v	1.76	-	3.85	-	6.16	-	7.21	-	-	-
	d_{vs}	2.12		5.36		8.52		9.88			
Hexanol	d_{av}	1.34		2.68			3.44		3.59		
	d_v	1.75	-	3.41	-	-	4.90	-	5.91		
	d_{vs}	2.19		4.28			7.20		9.44		
Octanol	d_{av}	1.0		1.0			1.42		1.71		
	d_v		-		-	-	1.68	-	2.23		
	d_{vs}						2.14		2.91		
Decanol	d_{av}	1.0		1.0			1.55		1.82		
	d_v		-		-	-	1.80		2.71		
	d_{vs}						2.33		3.81		

NOTES

Initial changes in emulsions

Toluene d_v = 1.98 (3 hours), 2.17 (6 hours), 2.43 (12 hours).

Benzene d_v = 1.74 (3 hours), 2.26 (6 hours), 3.40 (12 hours).

FIGURE 17 Droplet size distributions for emulsions stabilized with SDDS (10^{-2} mol dm^{-3}) after storing for 0 (●), 5 (■), 15 (▲), 50 (□) and 100 (△) days.

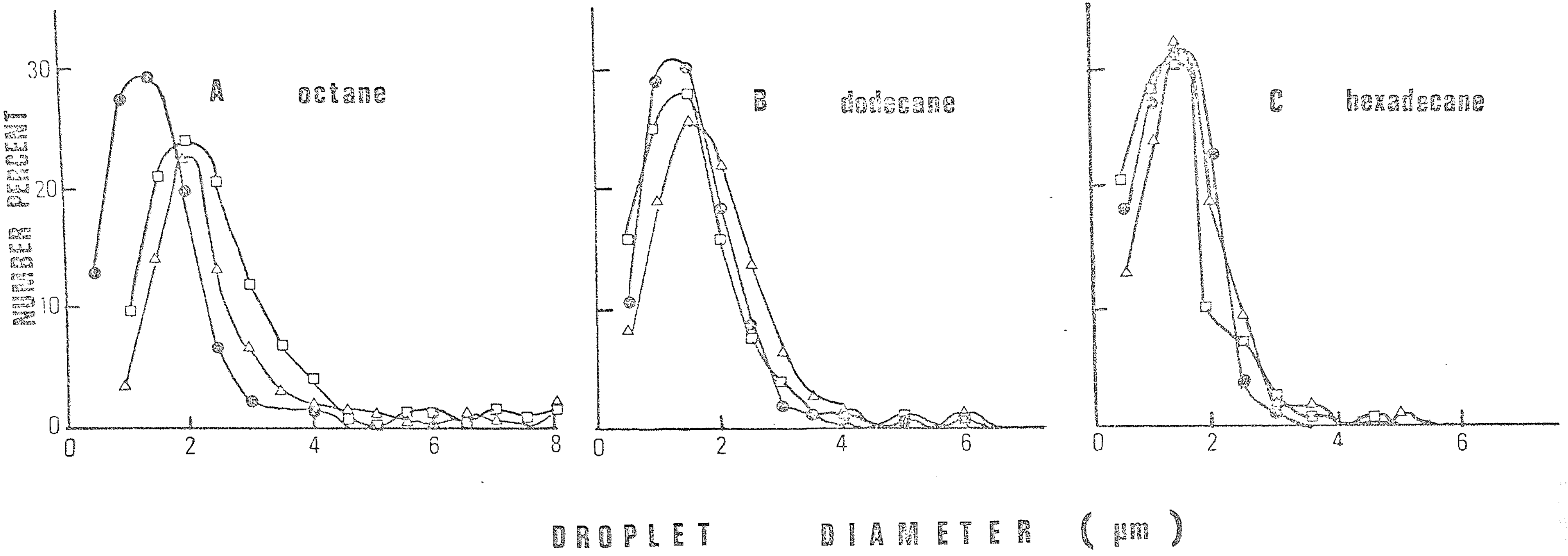


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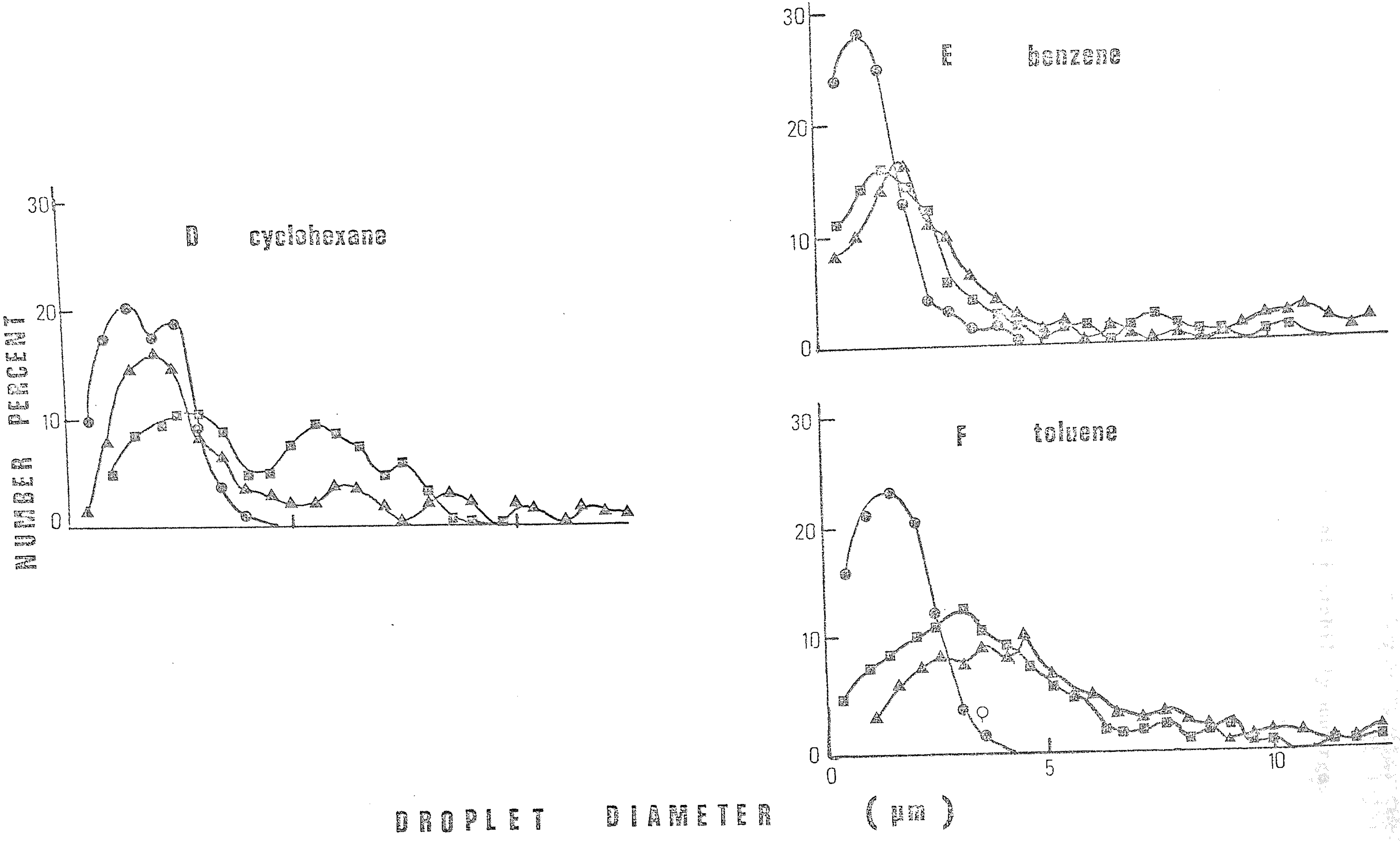
FIGURE 17 continued



Those emulsions which exhibit a high degree of instability undergo considerable changes within a few days of storage. The cyclic hydrocarbons in particular show extremely rapid changes in the shape of their size distribution curves. These changes have been followed more closely for toluene and benzene emulsions. In both cases the droplet size distribution changed measurably after only a few hours, (Table 4-5).

Attempts to correlate the droplet-size data by Gaussian or log-normal distribution functions were unsatisfactory. Many of the emulsions studied give an approximately linear plot of the cumulative percent frequency on a probability scale versus log time after some period of ageing but considerably coarsened emulsions are subject to increasing deviation and many even become bimodal (as in Figure 17).

The data from each analysis of particle size distribution has been used to compute the length (d_{av}) and volume (d_v) number mean diameters (Appendix V). In addition the volume surface mean diameter (d_{vs}) was used to calculate a specific interfacial area for each emulsion sample (Section 1.2.2.2). The computed diameters are summarized in Table 4-5.

The relative stabilities of a range of emulsions may be compared from plots against time of dt/do (the ratio of mean volume diameter to initial mean volume diameter) or the specific interfacial area. For the alkane hydrocarbons (Figures 18 and 20) an increase in stability with increase in chain length is shown with both plots. The hexane emulsion is very much less stable than those of the other alkanes, with considerable changes in dt/do and specific interface being evident during the first ten to fifteen days ageing. The rate of coarsening then appears to slow considerably. A similar pattern of behaviour is followed by the more stable alkane emulsions with the exception of tetradecane and hexadecane which show only minor changes over the ageing period. It is interesting to note the behaviour of light (LLP) and heavy

FIGURE 18 Increase in mean volume diameter with time for hexane (◉), octane (▲), decane (▩), dodecane (○), tetradecane (△), hexadecane (▽), and decene (▼) emulsions stabilized with 10^{-2}mol dm^{-3} SDDS; data are included for droplet counting (hexane ×; hexadecane +) and prevention of creaming (hexane ◑; hexadecane △).

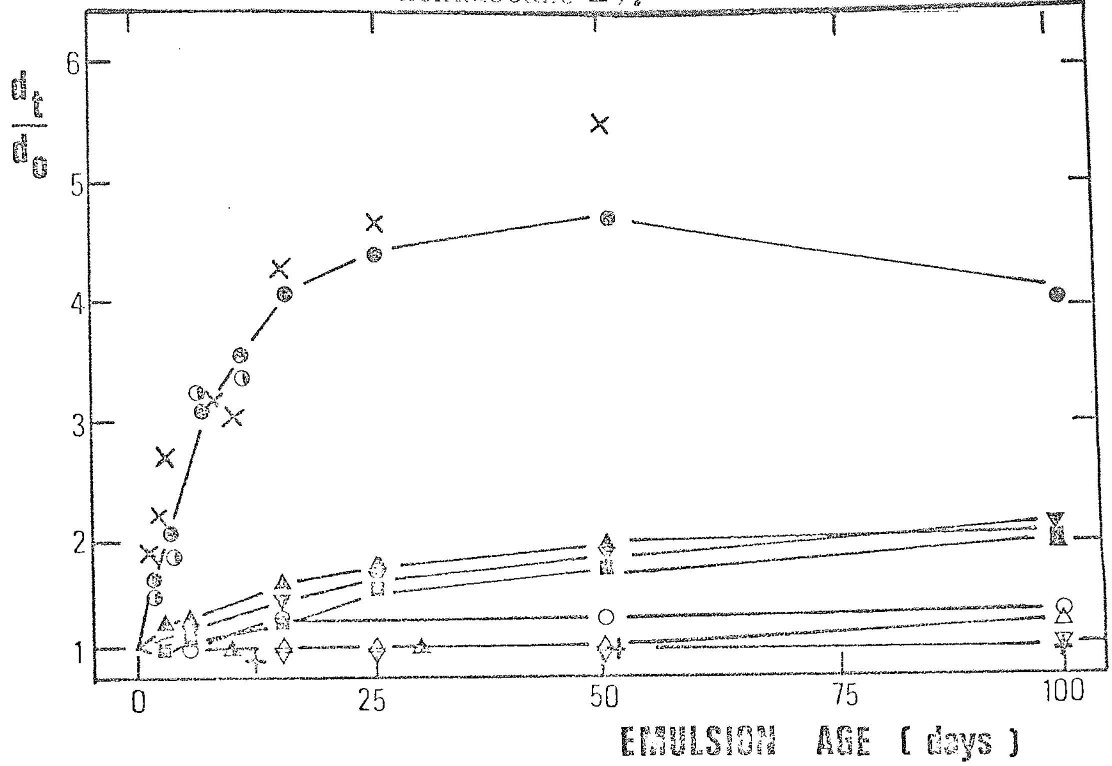


FIGURE 19

Increase in mean volume diameter with time for benzene (●), toluene (▲), o-xylene (○), p-xylene (□), cyclohexene (▩) and cyclohexane (△) emulsions stabilized with 10^{-2}mol dm^{-3} SDDS.

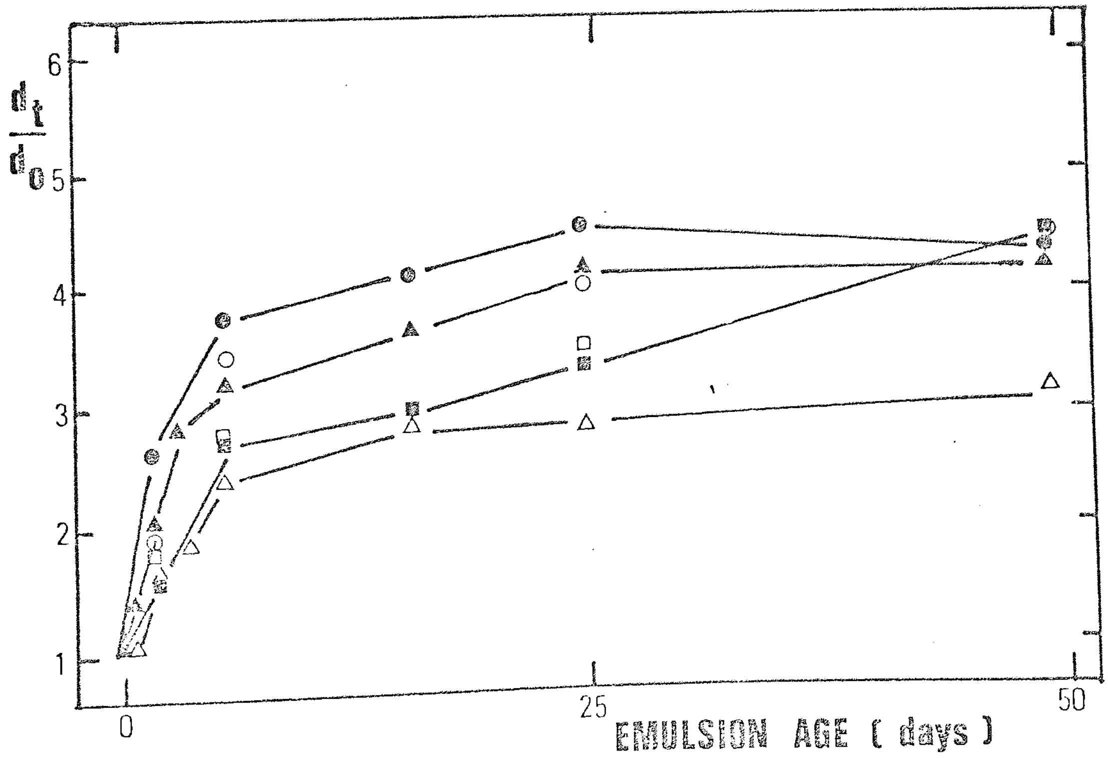


FIGURE 20

Effect of ageing on the specific interface of hexane (◉), octane (▲), decane (▣), dodecane (○), tetradecane (△), hexadecane (▽), and heavy liquid paraffin(HLP) (▼) stabilized with 10^{-2}mol dm^{-3} SDDS.

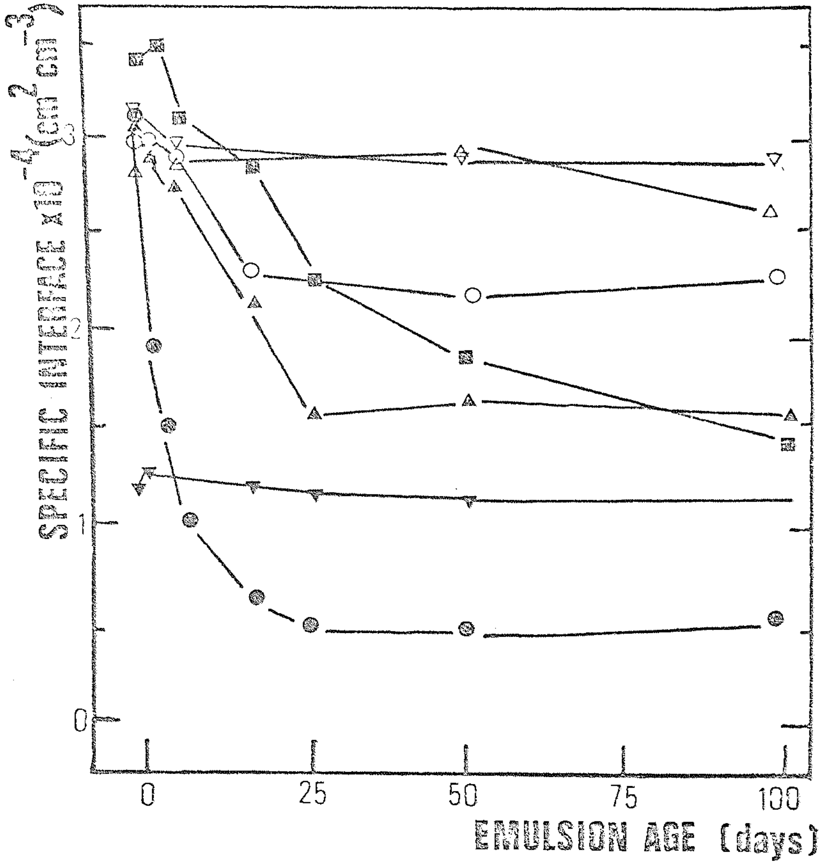
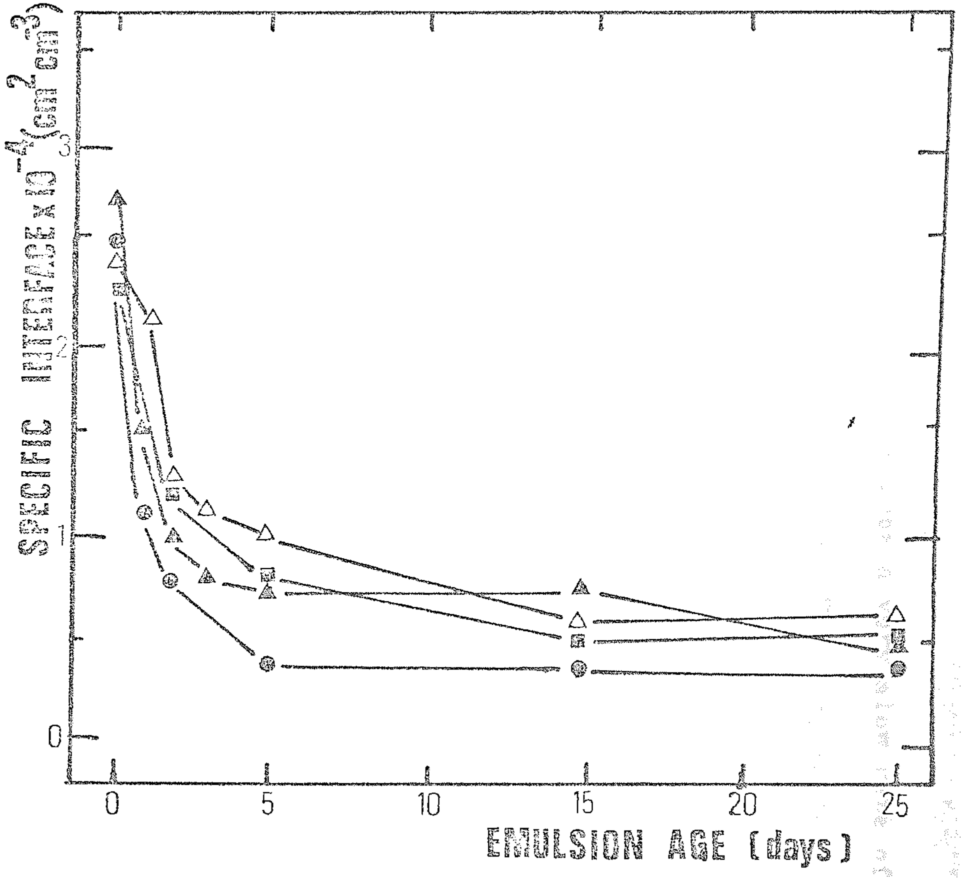


FIGURE 21

Effect of ageing on the specific interface of benzene (◉), toluene (▲), cyclohexene (▣), and cyclohexane (△) emulsions stabilized with 10^{-2} mol dm^{-3} SDDS.



(HLP) liquid paraffin emulsions, both of which show a very slow rate of breakdown similar to that of the long chain alkanes. However, whilst the LLP emulsion shows a droplet size distribution similar to that of the alkanes, the spread of sizes in HLP emulsion is very much broader. The reason for this effect is not clear although it may result from the composition of the heavy liquid paraffin which is not well definied. It is more probable that, inadvertently, the emulsion was homogenized less effectively during its preparation.

Unsaturation in the straight chain hydrocarbon reduces stability slightly, as shown by the curves for decene as compared with decane (Figure 18). The same effect is evident with the cyclic hydrocarbons cyclohexane, cyclohexene and benzene (Figures 19 and 21). Toluene and the xylenes, like the other cyclic hydrocarbons, manifest poor stability.

It is interesting to note that certain of the emulsions ,for example, decane, dodecane and tetradecane, exhibit an initial reduction in d_{av} on ageing (table 4-5) which reflects the apparent increase in the number of small droplets present (see Figure 17B for example). In addition decane and tetradecane show slight increases in the specific interface (Figure 20). Such observations imply an increase in the degree of dispersion of oil with time. The possibility that rapid combination of subvisual droplets to form those in the visible range accounts for such a phenomenon (74) is discussed elsewhere (Section 5.3). However, it should be noted that the error involved in measuring droplets in the submicron classes could also account for the observed slight decrease in mean droplet size.

4.3.1.2 Droplet number

The measurement of the number of droplets remaining in an emulsion is an attractive technique for estimating stability (Section 1.2.2.4). The counting method is particularly suited to following the initial changes in emulsions since counts may be performed at frequent time intervals.

The data obtained for hexane and hexadecane emulsions are summarized in Figure 26* where the data are plotted as log droplet number versus time. The mean volume diamter (d_v) may be estimated from droplet number provided the total volume of dispersed oil is known. Thus:-

$$d_v = \sqrt[3]{\frac{6\ \phi}{\pi\ N_v}} \qquad , \qquad 4.2$$

where ϕ is the volume fraction of dispersed oil and N_v is the droplet count (cm^{-3} of emulsion).

Examples of the measured counts and computed values of d_v are listed in Table 4-9. The mean droplet diameters agree quite well with the results of photomicrographic particle size analysis (Table 4-5) although in each case the initial mean volume diameter is somewhat lower than the corresponding value obtained by photomicrography. This discrepancy probably arises from a greater sensitivity of the counting technique to the presence of small droplets (<1 μm).

The lower stability of short chain length alkanes is again apparent using the droplet counting method. Furthermore, the log N_v versus time plots (Figure 26) suggest a change in the rate of coarsening with time, comparable with that observed in Section 4.2.1.1. The values of dt/do arising from droplet concentrations are plotted in Figure 18 to provide a direct comparison between the photomicrographic and droplet concentration methods.

It can be concluded that changes in the droplet concentration provide a convenient and reliable means of estimating the stability of alkane emulsions although no direct information is obtained regarding the actual distribution of droplet sizes.

*Footnote : Figure 26 is located at page 134/5.

Unfortunately, the same cannot be said of the results obtained for the cyclic hydrocarbon emulsions (cyclohexane and benzene). In these cases erratic droplet counts were obtained in the early stages of coarsening. Also, the initial droplet counts for benzene (1.58×10^{10} cm^{-3}) and cyclohexane (7.75×10^{10} cm^{-3}) were considerably lower than was expected, presumably owing to the dissolution of oil droplets during dilution. This conclusion was further supported by the tendency for droplet numbers to fall over a relatively short period of time within the haemocytometer counting chamber (Section 3.3.3) and by further observations on the dilution of cyclic hydrocarbon (particularly benzene) emulsions for photomicrography and electrophoresis (Sections 3.3.2. and 3.4.5).

4.3.1.3 Centrifugation

An immediate examination of the emulsions revealed that, in all cases, the dispersed oil creamed rapidly during centrifugation. It was also evident that oil had begun to separate from benzene and cyclohexane dispersions after centrifuging for 20 and 30 minutes, although it was not possible to measure the amount of free oil directly. A non-homogeneous oily surface layer separated rapidly when the benzene and cyclohexane samples were resuspended by gentle stirring. After 24 hours this layer had separated as free oil (approximately 0.5 cm^3) in the case of benzene. There was no evidence of any oil loss due to evaporation through the closure of the centrifugation vial during storage although this remains a possibility. A similar amount of oil separated from the cyclohexane dispersion after storing for two to three days.

No free oil could be detected from either the hexane or hexadecane emulsions after up to 60 minutes of centrifugation. Samples of benzene and cyclohexane emulsions were also returned to the centrifuge for this additional period without any further oil separation becoming apparent.

It seems that assessment of emulsion stability by the centrifugation technique described involves several experimental disadvantages. There is some indication that the highly unstable emulsions may be identified by this method but quantitative centrifugal stability measurements are difficult.

4.3.1.4 Viscosity

The relative viscosities of a range of emulsions were calculated from efflux time measurements in a U-tube viscometer using Equation 3.14 (Section 3.3.5). Values of the relative viscosity for each emulsion after various periods of storage are summarized in Table 4-6. The viscosity of many of the emulsions changed substantially during the ageing period. The data for each emulsion are compared in Figure 22 as a plot of the ratio of the relative viscosity at a particular time to the relative viscosity of the fresh emulsion (η_r^T / η_r^0) against time.

The viscosity ratio versus time curves for benzene, toluene, cyclohexane and hexane all show similar behaviour. In each case the relative viscosity falls very sharply during the first five days or so after which the decrease in viscosity occurs very much more slowly and almost linearly. At longer storage times creaming of the emulsion in the viscometer prevented any reliable measurement of flow times; the systems flowed normally at first but creaming in the bulb of the viscometer produced a layer of emulsion with high phase volume ratio of dispersed oil. This flowed very slowly and resulted in a dramatic increase in the overall flow time. The same effect was exhibited by a cyclohexene emulsion after only a few days storage.

Emulsions of hexadecane and HLP showed only slight changes in relative viscosity with time. The viscosity tended to increase with

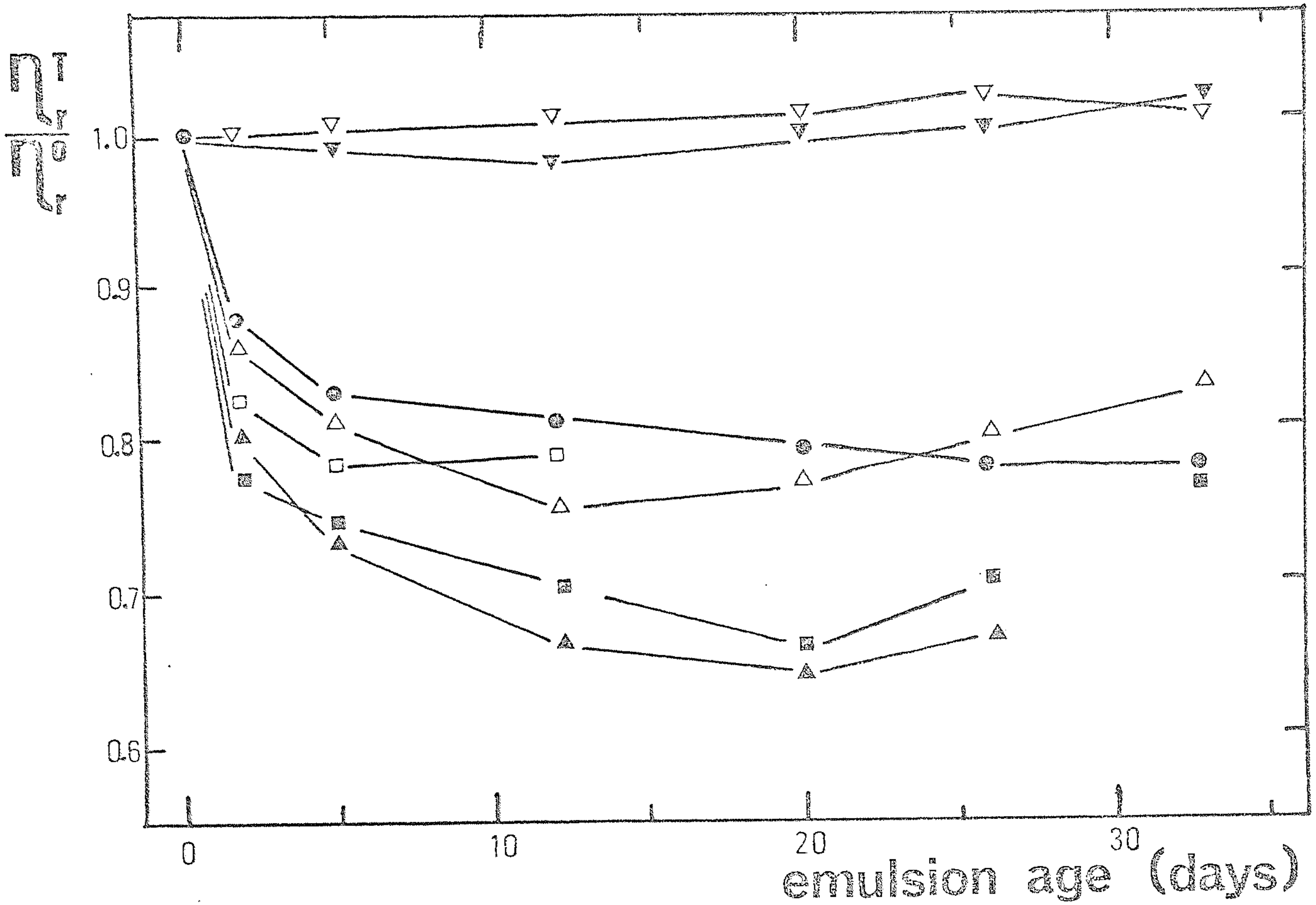
Table 4-6

Relative viscosity data for hydrocarbon oil emulsions during ageing

OIL PHASE	OIL DENSITY ($kg\ m^{-3}$)	EMULSION DENSITY ($kg\ m^{-3}$)	RELATIVE VISCOSITY							
			AGEING TIME (days)							
			0	2	5	12	20	26	33	42
Hexane	655	929	1.598	1.405	1.554	1.294	1.261	1.241	1.248	-
Hexadecane	770	932	1.668	1.668	1.671	1.678	1.688	1.705	1.691	1.705
HLP	880	974	1.592	-	1.578	1.557	1.599	1.589	1.627	-
Cyclohexane	774	955	1.568	1.556	1.270	1.185	1.206	1.257	1.500	-
Cyclohexene	806	960	1.605	1.314	1.245	1.255	-	-	-	-
Benzene	874	975	1.625	1.248	1.200	1.141	1.072	1.134	1.259	-
Toluene	862	971	1.704	1.363	1.242	1.129	1.087	1.121	-	-

FIGURE 22

Effect of ageing on the relative viscosity of hexane (●), hexadecane (▽), heavy liquid paraffin(HLP) (▼), benzene (■), toluene (▲), cyclohexene (□) and cyclohexane (△) emulsions stabilized with 10^{-2}mol dm^{-3} SDDS.



storage time, an effect which is most probably due to an increase in droplet aggregation. It would appear that aggregates are not fully dispersed during the initial mixing of stable systems after ageing.

4.3.1.5 Bulk properties

The creaming rate and separation of free oil were recorded from visual observations on the emulsions after1,2,3,5,10,15,25,50 and 100 days storage. All the emulsions showed eventual signs of creaming arising from the density difference between phases (Section 1.2.1). Cream volumes were measured as (total emulsion volume - volume of continuous serum separated) and the results are recorded as the ratio (cream volume/total emulsion volume = ϕ_c). The observations are summarized in Table 4-7 which lists the time at which creaming became apparent (t'_1), the time required for a limiting value of ϕ_c to be achieved (t'_2) and the "clearing time" for the aqueous serum (t'_3).

The cream volume for many of the emulsions became relatively constant within a few days though a further slight decrease in ϕ_c was often associated with measurable separation of free oil. The cream in emulsions of hexadecane, tetradecane and HLP became more difficult to redisperse after considerable periods of storage, indicating a build up of closely packed aggregates.

Free oil separated from the emulsions of cyclic hydrocarbon oils after only a short period of storage. After a fairly rapid initial rate of oil release the volume of free oil increased more slowly. Estimates of the volume of oil discharged from the bulk emulsion after 25,50 and 100 days are listed in Table 4-7. Similar examination of the straight chain hydrocarbon emulsions showed a lesser tendency for free oil to separate. This makes comparisons difficult since the oil volumes involved are so small.

Table 4-7

Observations on the creaming and oil separation in hydrocarbon emulsions (ϕ = 0.20) stabilized with SDDS-A solution (10^{-2} mol dm^{-3}).

OIL PHASE	CREAMING					OIL SEPARATION			
	t_1'	t_2'	t_3'	ϕ_c	ϕ_c/ϕ	t_4'	V_1	V_2	V_3
Hexane	1	5	10	0.24	1.20	15	1.0	1.5	2.0
Octane	1	10	50	0.24	1.20	15	1.0	1.0	1.0
Decane	1	15	100	0.26	1.30	100	0	0	1.0
Dodecane	2	15	100	0.26	1.30	25	1.0	1.0	1.0
Tetradecane	3	100	100	0.25	1.25	15	1.0	1.0	1.5
Hexadecane	3	100	100	-	-	25	1.0	1.0	1.5
LLP	3	100	100	-	-	100	0	0	0
HLP	2	100	100	0.28	1.40	100	0	0	0
Cyclohexane	1	10	25	0.27	1.35	2	5.0	7.0	10.0
Decene	1	15	15	0.25	1.25	25	1.0	1.0	1.0
Cyclohexene	1	3	25	0.26	1.30	1	4.5	6.0	8.5
Benzene	1	3	3	0.28	1.40	1	7.0	10.0	15.0
Toluene	1	5	25	0.27	1.35	2	5.0	6.5	10.0
o-Xylene	1	5	50	0.28	1.40	3	3.0	6.0	7.5
p-Xylene	1	10	25	0.24	1.20	3	3.0	6.5	7.5
Hexanol	1	2	15	0.27	1.35	100	0	0	0

NOTES:

t_1' = time at which creaming first observed (days)
t_2' = time required for complete creaming (days)
t_3' = time required for complete clearing of aqueous serum (days)
t_4' = time of first appearance of free oil (days)
ϕ_c = cream volume ratio at t_2'
ϕ = oil phase volume ratio
V_1 = volume of separated oil after 25 days storage (cm^3)
V_2 = volume of separated oil after 50 days storage (cm^3)
V_3 = volume of separated oil after 100 days storage (cm^3)

4.3.2 The effect of additives

The influence of small quantities of added alkane or alkanol on the stability of hexane emulsions (stabilized with 10^{-2} mol dm^{-3} SDDS-A solution) has been investigated in some detail. Some observations are also recorded on the changes in stability caused by the presence of small quantities of additive in benzene and cyclohexane emulsions.

4.3.2.1 Droplet size measurement

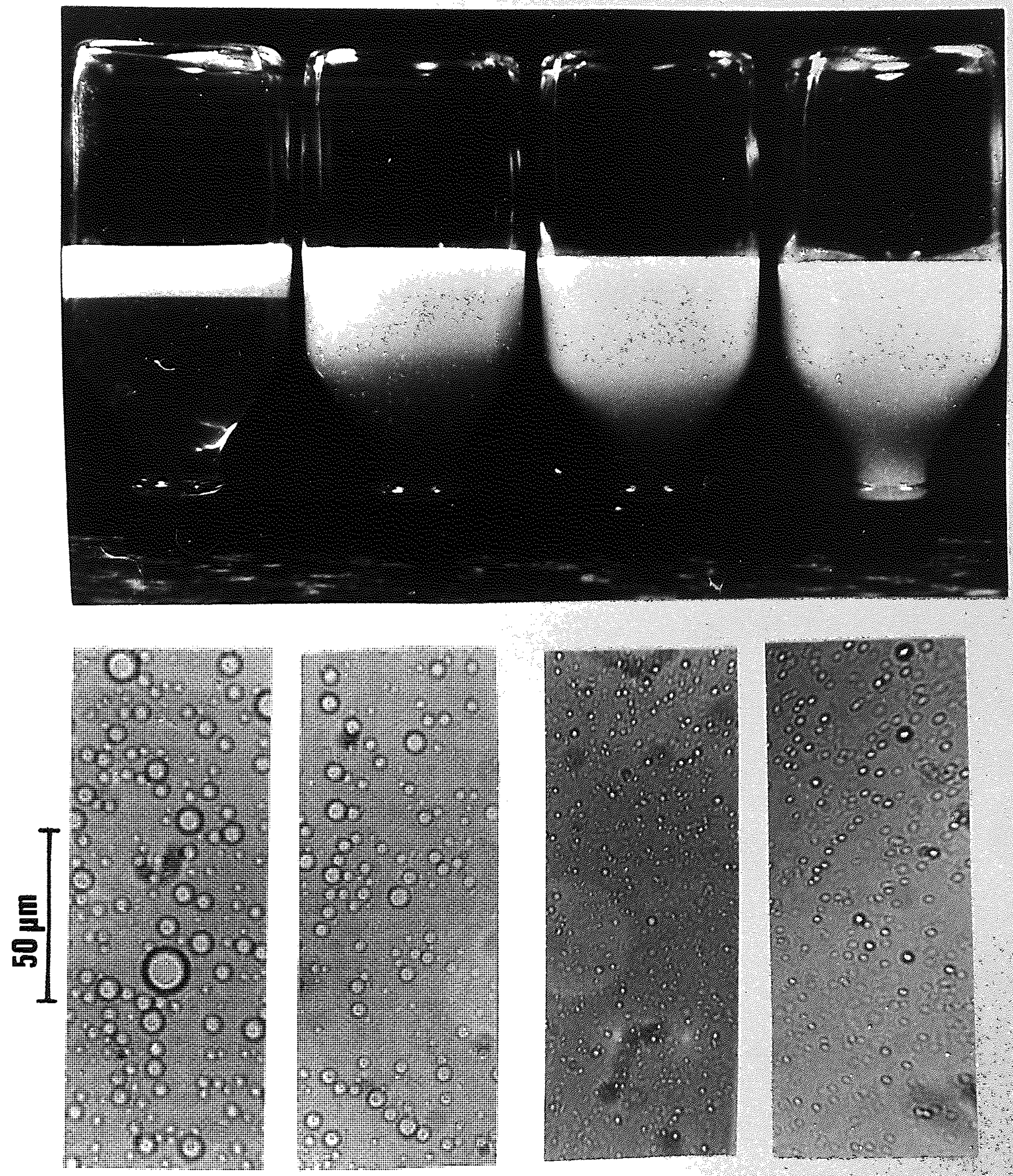
Some particle size distributions of hexane emulsions, with and without additive, are plotted in Figure 23. A hexane emulsion coarsens rapidly and the particle size distribution becomes broader whilst hexadecane emulsion (Figure 17) shows little or no change in particle size distribution. With the addition of 0.04 mol dm^{-3} of a longer chain length alkane, the hexane emulsion assumes behaviour more similar to that of hexadecane alone, this effect becoming more pronounced with increasing chain length of the additive. The inclusion of a long chain alkanol into the oil phase also results in enhanced stabilization (Figure 23) though this effect appears to be less marked than that caused by the corresponding alkane at the same molar concentration.

The relative stabilizing effect of additives is shown more clearly in Figures 24 and 25 where plots of the increase in mean volume diameter (Figure 24) or decrease in specific interfacial area (Figure 25) are presented. Both types of additive clearly improve their stabilizing potential with an increase in hydrocarbon chain length.

The droplet sizing data obtained for emulsions containing additives in the oil phase are summarized in Table 4-8. These data also emphasize the remarkably improved stability gained through the inclusion of hexadecane (0.04 mol dm^{-3}) in the oil phase of benzene or cyclohexane emulsions.

PLATE 4

THE MACROSCOPIC AND MICROSCOPIC APPEARANCE OF HEXANE EMULSIONS, WITH AND WITHOUT ADDITIVE, AFTER STORING FOR 3 DAYS AT 25°C.



HEXANE

HEXANE + HEXADECANOL

HEXANE + DODECANE

HEXANE + HEXADECANE

All emulsions stabilized with SDDS (10^{-2} mol dm^{-3}); initial size distributions all similar; 0.04 mol dm^{-3} additive in oil.

Table 4-8

Changes in mean droplet diameters during the ageing of SDDS (10^{-2} mol dm^{-3}) stabilized o/w emulsions containi various additives in the oil phase.

Oil Phase	Additive	Size parameter	Storage time (days)										
			0	1	2	3	7	10	14	25	50	100	200
Hexane	Octane	d_{av}	1.38	1.80	2.46	3.02	5.12	4.64	4.83	6.20	6.22	6.09	
		d_v	1.60	2.28	3.10	3.95	5.74	6.10	6.09	7.50	7.52	7.80	–
		d_{vs}	1.87	2.82	3.80	4.80	6.34	7.21	7.38	8.49	8.73	8.93	
	Decane	d_{av}	1.34		1.34	1.40	1.48		1.66	2.07	3.25	3.97	
		d_v	1.54	–	1.69	1.66	1.90	–	2.18	2.77	3.75	4.80	–
		d_{vs}	1.80		2.06	2.00	2.58		2.75	3.24	4.54	6.35	
	Dodecane	d_{av}	1.37		1.32	1.27	1.38		1.68	1.96	3.22	4.42	4.6
		d_v	1.62	–	1.60	1.51	1.85	–	2.10	2.41	3.66	5.33	6.4
		d_{vs}	1.87		1.83	1.78	2.44		2.58	2.82	4.12	6.42	8.4
	Hexadecane	d_{av}	1.35		1.34	1.40	1.40		1.58	1.62	1.74		2.4
		d_v	1.62	–	1.72	1.90	1.95	–	2.06	2.00	2.18	–	2.6
		d_{vs}	1.98		2.08	2.40	2.55		2.59	2.46	2.77		3.6
	Octanol	d_{av}	1.32	1.90	1.90	2.40	2.98	3.22	3.33	3.37	4.36	4.50	
		d_v	1.51	2.38	2.54	3.04	4.11	4.26	4.42	4.30	5.63	5.78	–
		d_{vs}	1.80	2.92	3.10	3.69	5.54	5.58	6.47	6.12	7.07	7.43	
	Dodecanol	d_{av}	1.28	1.47	1.79	2.23	3.10	3.43	3.43	3.61	4.35	4.54	
		d_v	1.51	1.80	2.24	2.68	3.75	4.53	4.68	4.98	5.65	6.04	–
		d_{vs}	1.76	2.17	2.75	3.19	4.42	5.94	6.20	6.30	7.15	7.74	
	Hexadecanol	d_{av}	1.32		1.48	1.38	1.87		2.81	2.77	3.29	3.50	3.67
		d_v	1.53	–	1.82	1.91	2.32	–	3.67	3.59	4.32	4.43	4.79
		d_{vs}	1.77		2.20	2.25	2.73		4.72	4.69	6.01	5.53	6.63
Cyclohexane	Hexadecane	d_{av}	1.14			1.10	1.06		1.43		1.50	1.63	1.63
		d_v	1.32	–	–	1.30	1.26	–	1.74	–	1.76	1.92	1.95
		d_{vs}	1.48			1.46	1.46		2.08		2.02	2.22	2.31
Benzene	Hexadecane	d_{av}	1.0			1.0	1.0		1.0	1.0	1.12	1.22	1.24
		d_v		–	–			–			1.33	1.56	1.56
		d_{vs}									1.49	1.81	1.79

FIGURE 23

Changes in the droplet size distribution of hexane (a), hexane + hexadecane (0.04mol dm-3) (b) and hexane+hexadecanol (0.04mol dm^{-3}) (c) emulsions after storing for 6 hours (●), 7 days (△) and 14 days (□).

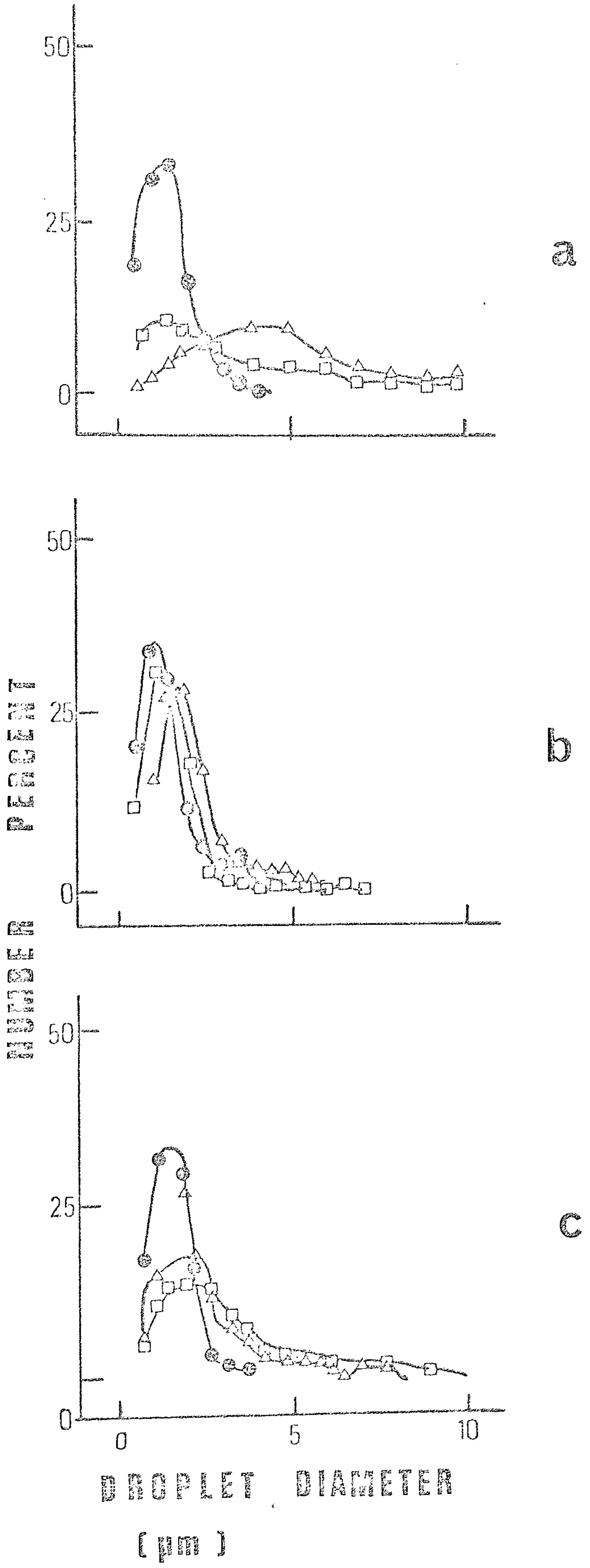


FIGURE 24

Increase in mean volume diameter with time for hexane emulsions containing various additives (0.04 mol dm-3 in the oil).

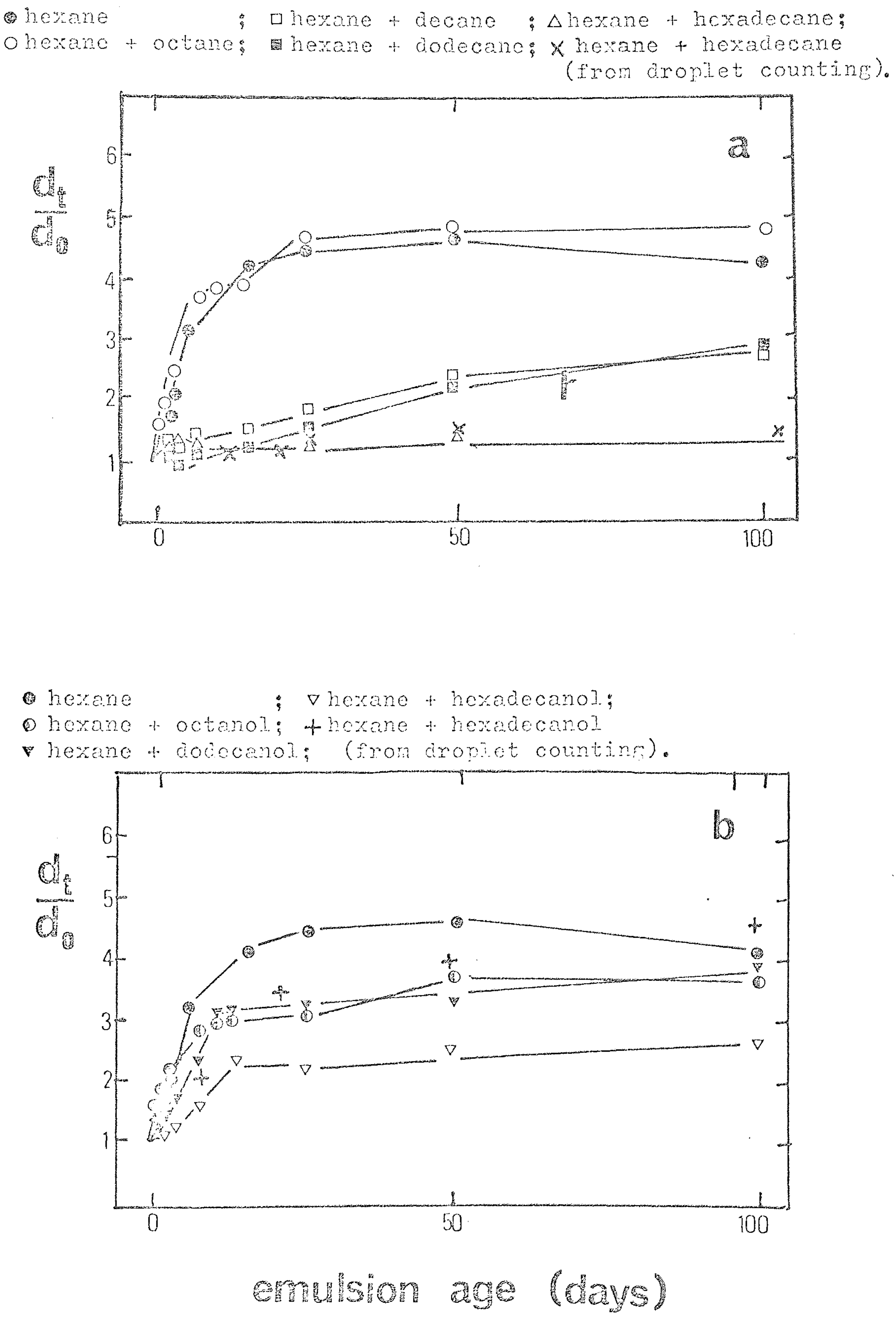


FIGURE 25

The effect of various additives*on the stability (expressed as a change of interfacial area) of hexane emulsions. (* 0.04 mol dm^{-3} in oil phase)

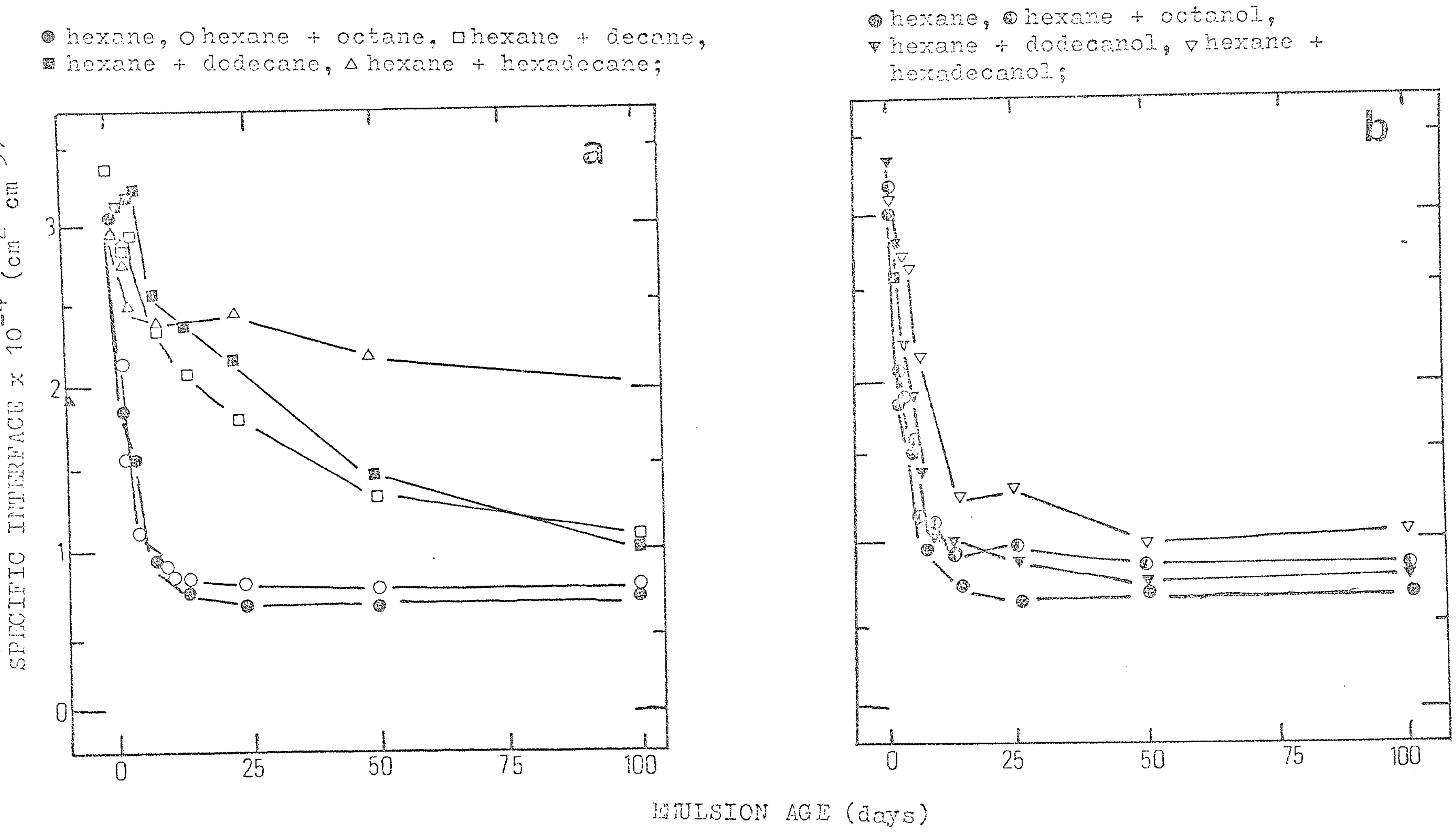


Table 4-9

Changes in droplet counts (cm^{-3} of emulsion) and computed mean droplet diameters (μm) during ageing of various emulsions.

Emulsion age (days unless stated)	Hexane		Hexadecane		Hexane + Hexadecane *		Hexane + Hexadecanol *	
	N_v	d_v	N_v	d_v	N_v	d_v	N_v	d_v
0	1.20×10^{11}	1.47	1.01×10^{11}	1.53	1.13×10^{11}	1.49	2.00×10^{11}	1.22
1 hour	1.32×10^{11}	1.43	-		-		-	
2 hour	1.65×10^{11}	1.34	-		-		-	
4 hour	5.26×10^{10}	1.94	-		1.10×10^{11}	1.51	1.96×10^{11}	1.24
24 hour	2.30×10^{10}	2.63	9.89×10^{10}	1.55	-		7.80×10^{10}	1.69
2	1.13×10^{10}	3.22	9.76×10^{10}	1.56	9.00×10^{10}	1.62	5.60×10^{10}	1.90
3	6.43×10^{9}	3.89	-		-		-	
4	4.52×10^{9}	4.38	-		-		-	
7	3.76×10^{9}	4.66	-		-		-	
8	3.99×10^{9}	4.56	-		-		2.00×10^{10}	2.67
10	2.85×10^{9}	5.10	1.06×10^{11}	1.52	6.31×10^{10}	1.82	-	
15	1.46×10^{9}	6.38	-		-		-	
20	-		-		5.00×10^{10}	1.96	5.00×10^{9}	4.23
25	1.16×10^{9}	6.84	-		4.47×10^{10}	2.04	-	
50	7.24×10^{8}	8.04	1.00×10^{11}	1.53	3.65×10^{10}	2.20	3.16×10^{9}	4.93
100	3.84×10^{8}	9.97	9.50×10^{10}	1.57	2.57×10^{10}	2.41	1.82×10^{9}	5.94

NOTE: * 0.04 mol dm^{-3} of additive in hexane

FIGURE 26

Stability of emulsions as measured by the change in droplet number.

● hexane, ○ hexadecane, ▲ hexane + hexadecane(0.04 mol dm^{-3}),
△ hexane + hexadecanol(0.04 mol dm^{-3}).

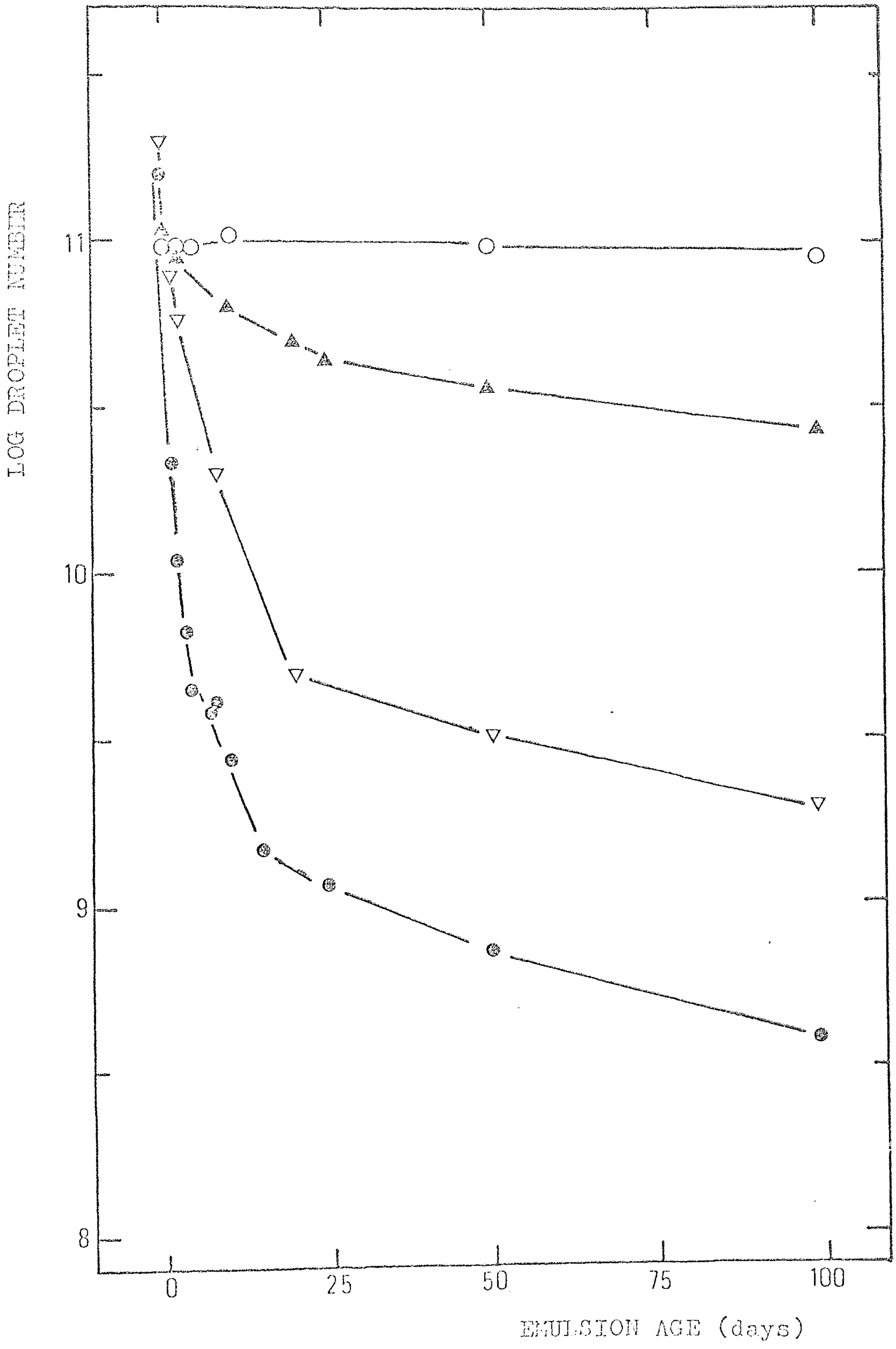


FIGURE 27

Change in relative viscosity with time for hexane emulsions containing a small quantity (0.04mol dm^{-3}) of additive.

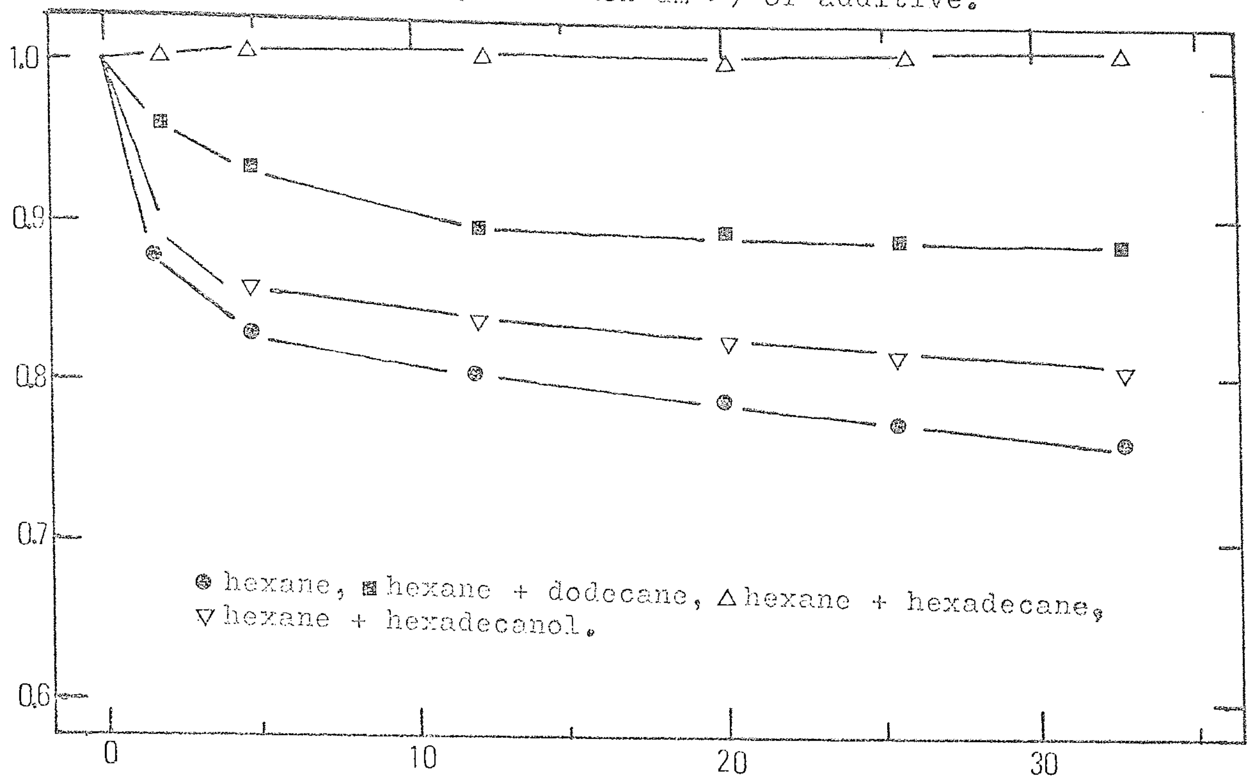
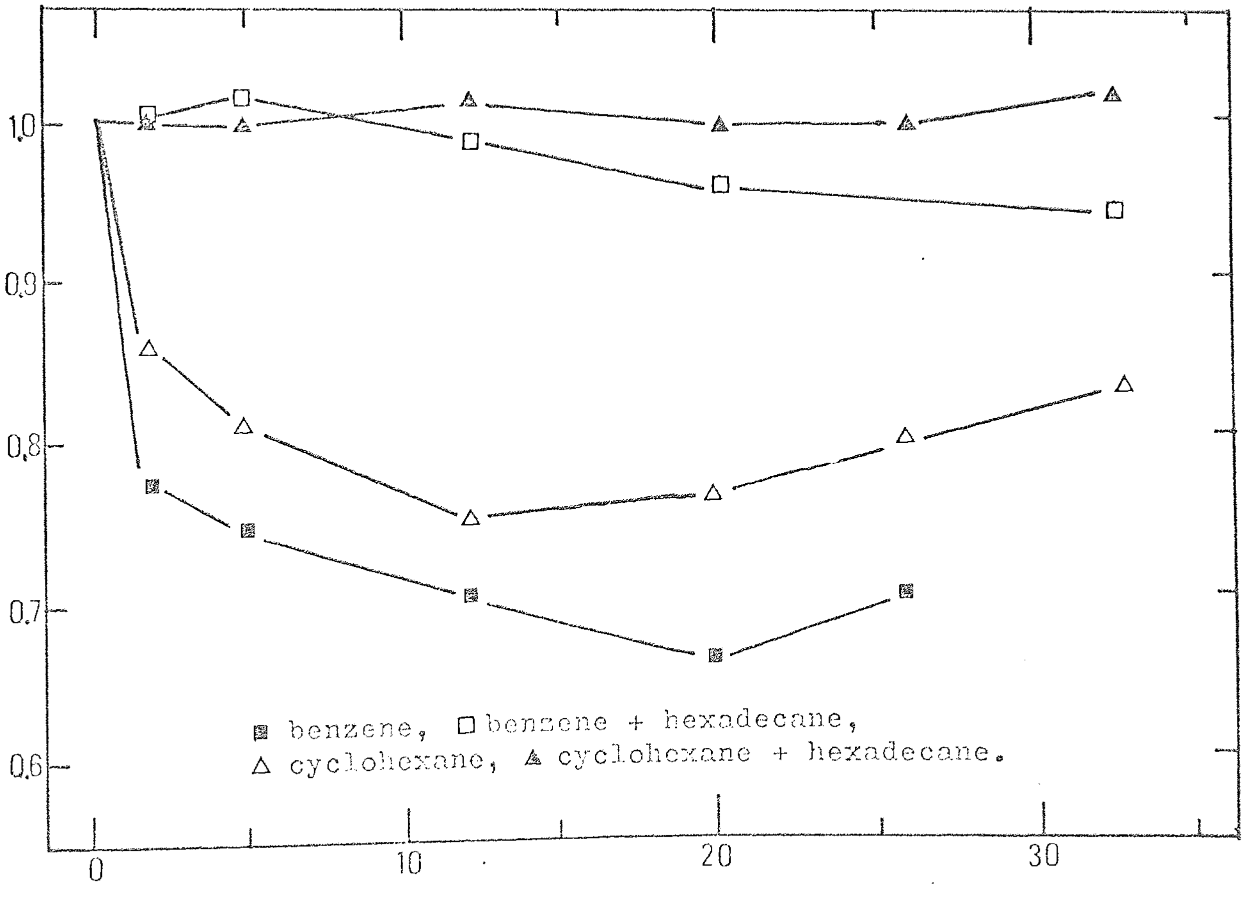


FIGURE 28

Change in relative viscosity with time for benzene and cyclohexane emulsions containing a small quantity (0.04mol dm^{-3}) of hexadecane.



Some typical photomicrographs showing the relative effects of additives are presented in Plate 4.

4.3.2.2 Droplet number

The fall in droplet concentration with time is plotted in Figure 26 for emulsions of hexane and hexadecane alone and hexane containing either hexadecane or hexadecanol as additives. A considerable increase in stability is caused by the inclusion of long chain **alcohol.** In the presence of hexadecane, however, the dispersion exhibits a high degree of stability.

The value of d_v computed from droplet counts (Section 4.3.1.2) are included in Table 4-9 and show reasonable agreement with photomicrographic measurements of size (Table 4-8).

4.3.2.3 Viscosity

In order to determine the relative viscosities of these emulsions it was assumed that the density of neither phase was significantly affected by the small amount of additive present. The relative viscosity ratio (Section 4.3.1.4) is plotted for hexane emulsions containing dodecane, hexadecane and hexadecanol (Figure 27). Similar plots demonstrate the effect of added hexadecane on the change in relative viscosity with time for benzene and cyclohexane emulsions (Figure 28).

The relevant initial viscosities are provided in Table 4-10.

The form of the curves in Figure 27 is similar to that described previously; viscosity falls in an approximately linear fashion after an initial more rapid decrease. The relative viscosity falls sharply during the first five days or so of ageing, this effect becoming more pronounced in the order hexane + dodecane < hexane + hexadecanol < hexane. In the presence of a small quantity of hexadecane the viscosity of hexane and cyclohexane emulsions increases slightly over the period in question (Figures 27 and 28) and the benzene emulsion (Figure 28) exhibits only marginal fall in relative viscosity values.

Table 4-10

Relative viscosities of freshly prepared hydrocarbon emulsions containing additives.

OIL PHASE	ADDITIVE	Relative viscosity
Hexane	Dodecane	1.565
	Hexadecane	1.571
	Hexadecanol	1.600
Cyclohexane	Hexadecane	1.659
Benzene	Hexadecane	1.601

4.3.2.4 Bulk properties

The creaming and oil separation data are given in Table 4-11. Data were collected by the procedures already described (Sections 3.3.6 and 4.3.1.3).

Emulsions of hexane and hexane + octane creamed rapidly (within three to five days) whilst the corresponding times required for a clear serum to evolve are 10 and 25 days respectively. The remaining emulsions retained a slight turbidity throughout 100 days despite which it appeared that all droplets had creamed from emulsions containing alkanols after 15 to 25 days. In spite of the slow rate of creaming where decane, dodecane and hexadecane were used as additives, a distinct cream layer became visible at the surface of all these samples after 1 to 2 days. In each case the layer reached an apparent phase volume ratio (ϕ_c) of at least 0.20 within 10 days. These observations suggest that submicron sized droplets may persist since these cream extremely slowly

Table 4-11

Observations on the creaming and oil separation in SDDS (10^{-2} mol dm^{-3}) stabilized emulsions of hydrocarbons containing various additives in the oil phase.

Oil	Additive	Creaming					Oil Separation			
	(0.04 mol dm^{-3})	t_1'	t_2'	t_3'	ϕ_c	$\frac{\phi_c}{\phi}$	t_4'	V_1	V_2	V_3
Hexane	-	1	5	10	0.24	1.20	15	1.0	1.5	5.0
	Octane	1	5	25	0.25	1.25	50	0	1.0	1.0
	Decane	1	15	100	0.25	1.25	25	1.0	1.0	1.0
	Dodecane	1	15	100	0.24	1.20	25	1.0	1.0	1.0
	Hexadecane	2	100	100	0.26	1.30	50	0	1.0	1.0
	Octanol	1	5	100	0.25	1.25	25	1.0	1.0	1.0
	Dodecanol	1	10	100	0.23	1.15	50	0	1.0	1.0
	Hexadecanol	1	10	100	0.23	1.15	50	0	1.0	1.0
Cyclohexane	-	1	10	25	0.27	1.35	2	5.0	7.0	10.0
	Hexadecane	5	50	100	0.26	1.30	5	1.0	1.5	2.5
Benzene	-	1	3	3	0.28	1.40	1	7.0	10.0	13.0
	Hexadecane	10	100	100	-	-	2	1.0	2.5	4.5

NOTE: See Table 4-7 for notation.

due to the effect of disturbances or Brownian motion.

The inclusion of hexadecane into benzene or cyclohexane emulsions retarded creaming considerably, consistent with the narrow particle size distribution measured (Table 4-8). However, the emergence of free oil from these emulsions is still significant, showing that some coalescence is occurring, presumably between the few larger droplets present, which will cream to the emulsion surface. The small volumes of free oil which separated from hexane emulsions with additives were too small in most cases to provide any useful comparisons.

4.3.3 The effect of impurities

Bearing in mind the results of Section 4.3.2 it is conceivable that considerable differences in stability can arise from the presence of small quantities of impurities in the oils used. In order to explore this possibility a number of purified oils (Section 2.3.2) were emulsified in SDDS-E solution (10^{-2} mol dm^{-3}) and the change in droplet size distributions with time were followed photomicrographically. Bulk properties were also noted during 50 days storage.

None of the emulsions displayed any observable differences in bulk properties from their counterparts with unpurified oils. The mean volume diameters calculated for hexane-P and benzene-P emulsions are given in Table 4-12. These are generally within 10% of d_v values measured previously where non-purified oils were used (Table 4-5). Consequently the dt/do relationship for purified systems is not markedly divergent from that illustrated in the appropriate curves of Figures 18 and 19 except where considerable coarsening has taken place. In that case emulsion breakdown creates a wide distribution of droplet sizes which can give rise to significant sampling errors (Section 4.3.1.1). An emulsion of hexadecane-P exhibited a high degree of stability (Table 4-12) consistent with that reported for the unrefined hydrocarbon (Table 4-5).

Table 4-12

Changes in mean volume diameter (μm) with time for emulsions of purified oils dispersed in SDDS-E solution (10^{-2} mol dm^{-3}).

Oil Phase	Emulsion age (days)				
	0	2	5	10	25
Hexane-P	1.60	3.19	6.20	6.44	5.92
Hexadecane-P	1.72	1.66	1.70	1.70	1.74
Benzene-P	1.57	4.31	5.69	8.21	6.92

The relative stabilities of hexane and hexane-P emulsions dispersed in 10^{-2} mol dm^{-3} SDDS-A and SDDS-E respectively are compared as plots of the change in specific interfacial area with time in Figure 29.

4.3.4 Surfactant concentration

The effect of different concentrations (10^{-1} to 10^{-4} mol dm^{-3}) of SDDS-A on emulsion stability has been investigated for a small number of oil phases.

Attempts to disperse organic liquids (hexane, hexadecane, cyclohexane and benzene) in a 10^{-4} mol dm^{-3} solution of the surfactant produced greyish emulsions in which small globules of oil remained on the surface after homogenization. These systems creamed rapidly and the oil phase separated completely within a few days.

Samples of the same oils were emulsified using 10^{-3} mol dm^{-3} surfactant solution. The data in Table 4-13 describe the observations made on the droplet size distributions of these emulsions. Creaming was rapid in all cases except the hexadecane emulsion. In the latter case creaming first became apparent after five days, although a considerable amount of free oil had separated by this time. Interestingly, the particle size distribution remained fairly narrow throughout ageing (Table 4-13), suggesting that there was rapid coalescence of creamed droplets at the emulsion surface, but little inter-droplet coalescence in the bulk emulsion. The hexane dispersion exhibited an initial broadening of the size distribution (and an increase in mean droplet diameter) as larger droplets formed, followed by a narrowing of the distribution with the disappearance of large droplets through coalescence. Both benzene and cyclohexane emulsions were highly unstable, over 75% of the oil having separated from each system within one day of storage.

Hexane and hexadecane were dispersed in 10^{-1} mol dm^{-3} surfactant solution. Microscopic examination revealed considerable clumping of oil droplets in both samples, the aggregation becoming more pronounced with ageing (Plate 3). As a consequence of aggregation the size of creaming particles was effectively increased (Equation 1.1) and these emulsions creamed extremely quickly (ie. within 5 to 10 minutes). The long chain alkane emulsion retains its characteristically high stability at this higher concentration of SDDS-A (Table 4-13). The droplet size measurements for hexane indicate a similar stability to an emulsion of the same oil dispersed in 10^{-2} mol dm^{-3} surfactant (Section 4.3.1.1). The specific interfacial area is plotted in Figure 29 for hexane emulsions in 10^{-3}, 10^{-2} and 10^{-1} mol dm^{-3} SDDS-A. The data for hexane-P emulsion dispersed in SDDS-E (10^{-2} mol dm^{-3}) are also included. The hexane emulsions appear to manifest maximum stability at the intermediate concentration.

Table 4-13

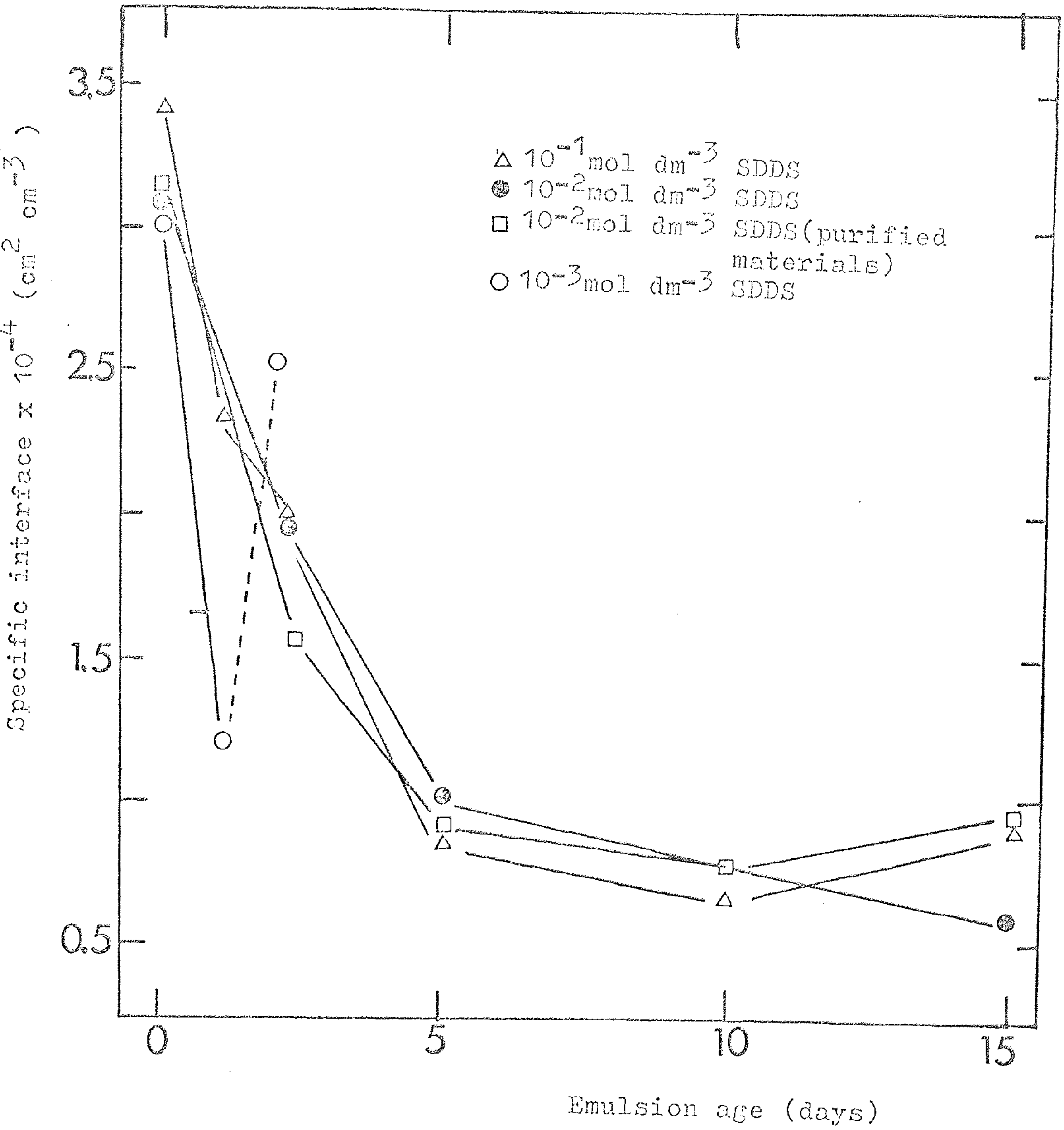
Changes in mean droplet diameters during ageing of SDDS stabilized o/w emulsions at different surfactant concentrations (see also Table 4-3).

Oil Phase		Emulsion age (days)					
		0(30min)	1	2	5	10	15
		10^{-3} mol dm^{-3}		SDDS-A			
Hexane	d_{av}	1.24	1.94	1.42			
	d_v	1.59	3.25	1.87	-	-	-
	d_{vs}	2.00	5.09	2.39			
	V	0	6.5	10.0	10.0	12.0	13.5
Hexadecane	d_{av}	1.25	1.43	1.48		1.14	1.20
	d_v	1.65	1.77	1.88	-	1.48	1.53
	d_{vs}	2.11	2.19	2.35		1.93	1.97
	V	0	2.5	5.5	7.5	12.0	12.5
Cyclohexane	d_{av}	1.74					
	d_v	2.03	-	-	-	-	-
	d_{vs}	2.31					
	V	1.0	14.0	16.0	19.5	20.0	20.0
Benzene	d_{av}	1.84	4.88				
	d_v	2.13	6.95	-			
	d_{vs}	2.65	9.70				
	V	1.0	12.0	15.0	17.5	19.5	19.5
		10^{-1} mol dm^{-3}		SDDS-A			
Hexane	d_{av}	1.29	1.79	1.98	3.51	4.41	4.83
	d_v	1.55	2.10	2.65	4.78	6.31	6.15
	d_{vs}	1.78	2.55	3.10	7.20	8.75	7.50
	V	0	0	0	0	0	0
Hexadecane	d_{av}	1.31		1.25		1.29	
	d_v	1.60	-	1.57	-	1.61	-
	d_{vs}	1.85		1.82		1.88	
	V	0	0	0	0	0	0

Notes: V = volume of oil separated (cm^3)

FIGURE 29

The effect of surfactant concentration and impurities on the change in specific interface with time for hexane emulsions



4.4 ELECTROPHORESIS

4.4.1 The effect of oil phase

The electrophoretic mobilities of emulsion droplets have been measured under carefully controlled conditions (Section 3.4) for a wide range of oil phases dispersed in 10^{-2} mol dm^{-3} SDDS-A. Emulsions were prepared and stored according to the procedures described previously (Section 3.3.1).

Table 4-14 gives a summary of the data obtained and includes the zeta potential values calculated according to Equation 3.20 . In all experiments the oil droplets migrated towards the anode indicating that a negative charge was present on the droplets.

The measured mobilities (and therefore zeta potentials) show some dependance on the nature of the oil phase. The saturated hydrocarbon droplets (alkanes, LLP, HLP, cyclo-paraffins) posess a lower charge the greater the carbon number. Unsaturation in the straight chain molecule results in a slightly lower mobility as shown by octene and decene as compared with the corresponding alkanes. Similarly, the cyclic non-substituted hydrocarbons give droplets whose mobilities increase in the order benzene < cyclohexene < cyclohexane. Droplets of toluene and the xylenes give intermediate mobility values whereas the aliphatic alcohols appear to carry a considerably lower charge.

4.4.2 The effect of additives

The emulsions containing oil soluble additives considered previously in Section 4.3.2, were also diluted and their electrophoretic mobilities measured. The results obtained are listed in Table 4-15.

Table 4-14

Electrophoretic measurements on various oil phases dispersed in SDDS-A solution (10^{-2} mol dm^{-3}). Measurements made at 25 ± 0.2°C, twentyfour hours after emulsification.

Oil	u (10^{-8} m^{2} s^{-1} V^{-1})	Z (mV)	Oil	u (10^{-8} m^{2} s^{-1} V^{-1})	Z (mV)
Hexane	10.01 ± 0.27	129.1	Benzene	8.87 ± 0.46	114.4
Hexane-P	10.00 ± 0.19	129.0	Toluene	9.56 ± 0.31	123.3
Octane	9.66 ± 0.15	124.6	o-Xylene	9.45 ± 0.24	121.6
Decane	9.45 ± 0.21	121.9	m-Xylene	9.52 ± 0.30	122.8
Dodecane	9.05 ± 0.17	116.7	p-Xylene	9.74 ± 0.28	125.6
Tetradecane	8.92 ± 0.17	113.1	Octene	9.02 ± 0.30	116.4
Hexadecane	8.94 ± 0.29	115.3	Decene	9.16 ± 0.25	118.2
LLP	9.15 ± 0.12	118.0			
HLP	8.92 ± 0.16	115.1	Butanol	7.58 ± 0.31	97.8
Cyclopentane	10.18 ± 0.34	131.3	Hexanol	7.67 ± 0.22	98.9
Cyclohexane	9.74 ± 0.49	125.6	Octanol	7.78 ± 0.25	100.4
Cyclohexene	9.00 ± 0.29	116.1	Decanol	7.87 ± 0.18	101.5

Table 4-15

Electrophoretic measurements on dispersed oils containing a small amount (0.04 mol dm^{-3}) of additive. (Measurements were made at 25 ± 0.2°C, twenty four hours after emulsification in SDDS-A solution (10^{-2} mol dm^{-3}).

OIL PHASE	ADDITIVE	u (10^{-8} m^2 s^{-1} V^{-1})	Z (mV)
Hexane	-	10.01 ± 0.27	129.1
	Octane	9.93 ± 0.20	128.1
	Decane	10.05 ± 0.21	129.6
	Dodecane	9.80 ± 0.26	126.4
	Hexadecane	9.88 ± 0.16	127.4
	Octanol	9.58 ± 0.18	123.6
	Dodecanol	9.69 ± 0.20	125.0
	Hexadecanol	9.66 ± 0.15	124.6
Benzene	-	8.87 ± 0.46	114.4
	Hexadecane	8.74 ± 0.18	112.7
Cyclohexane	-	9.74 ± 0.40	125.6
	Hexadecane	9.53 ± 0.22	122.9

The presence of a small quantity of longer chain length alkane in hexane may cause a slight reduction in the droplet mobility. However this unexpected effect is in all cases within the standard error of the mobility measurements and may be due to experimental factors. A somewhat larger discrepancy is found between the electrophoretic mobilities of hexane droplets with and without added alcohol. A decrease in mobility was repeatedly obtained when alcohol was present in the oil phase. The presence of hexadecane in benzene or cyclohexane emulsions again causes an almost imperceptible fall in the measured mobility.

4.4.3 The effect of ageing

On a number of occasions it has been suggested that changes in electrophoretic mobility may occur during ageing (42). It is possible that the interfacial film may become more condensed as coalescence proceeds (88,91,93) thus causing an increase in electrophoretic mobility. Indeed, Groves (42) and Jackson & Skauen (299) have proposed that changes in electrophoretic properties might be sufficiently distinct so as to provide an approximate index of emulsion stability.

Electrophoresis measurements were performed using emulsions which had been allowed to age for only 24 hours (Section 4.4.1). A number of observations were recorded on the change in electrophoretic mobility upon ageing (Table 4-16).

Table 4-16

The effect of ageing on the electrophoretic mobility of oil droplets dispersed in SDBS-A solution (10^{-2} mol dm^{-3}). (Measurements were made at 25 ± $0.2^{o}C$).

OIL PHASE	ELECTROPHORETIC MOBILITY				
	Emulsion age (days)				
	1	5	15	25	50
Hexane	10.01	10.08	10.14	9.89	10.12
Octane	9.66	9.57	9.67	9.71	10.00
Decane	9.45	9.30	9.40	9.58	9.37
Dodecane	9.05	9.17	8.91	9.10	8.94
Tetradecane	8.92	8.72	9.02	8.91	8.77
Hexadecane	8.94	8.80	8.97	9.13	8.87
Cyclopentane	10.18	10.24	10.06	10.33	–
Cyclohexane	9.74	9.84	9.78	9.69	–
Benzene	8.87	9.11	9.37	9.30	–
Toluene	9.56	9.66	9.74	9.69	–
Octene	9.02	9.21	9.29	9.40	9.44
Octanol	7.78	7.80	7.64	7.81	7.76

For each emulsion only those droplets which remained in focus through the entire microscope field were timed. No systematic changes in mobility are evident during the ageing period observed for emulsions of the alkanes, cycloparaffins, toluene or octanol even though considerable coarsening occurs in some of these systems (Section 4.3.1).

Slight increases in mobility do appear in the initial stages with a benzene emulsion and octene droplets exhibit a gradual increase in mobility with time. These changes may reflect instability within the system.

Overall, the results are inconclusive since many of the emulsions, including some in which the droplets show instability to a marked extent, manifest no increase in electrophoretic mobility. This suggests that no condensation of the interfacial film has arisen during storage. However, in many of the systems considerable changes in droplet sizes occur within the first 24 hours of storage. The interface may undergo sufficient rearrangement during this time to provide the maximum degree of packing. Furthermore, an initial period of high instability may cause the concentration of surfactant in the continuous phase to rise above the cmc, thus making any changes in the interfacial film difficult to detect by mobility measurement (Section 4.4.4).

4.4.4 The effect of surfactant concentration

The changes in mobility with different concentrations of surfactant are listed in Table 4-17. The data for hexane, hexadecane, cyclohexane and benzene emulsions are plotted in Figure 30.

As the SDDS concentration increases there is a sharp increase in the charge on droplets up to the region of the cmc of the surfactant. There appears to be a slight fall in droplet mobility as the concentration increases further, as shown by the u values for hexane and hexadecane dispersed in 10^{-3} mol dm^{-3} SDDS-A.

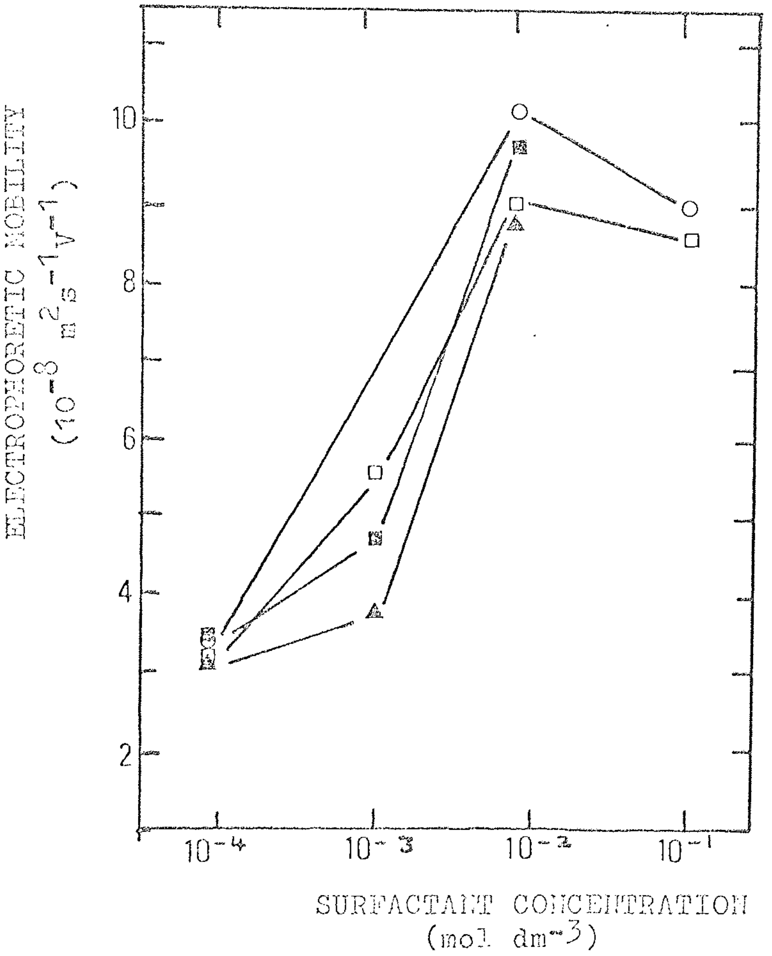
Table 4-17 The effect of surfactant concentration on electrophoretic mobility and Zeta potential

OIL	Surfactant concentration (mol dm^{-3})							
	10^{-4}		10^{-3}		10^{-2}		10^{-1}	
	u (10^{-8} $m^2s^{-1}V^{-1}$)	Z (mV)	u (10^{-8} m^2s^{-1}V-1)	Z (mV)	u (10^{-8} $m^2s^{-1}V^{-1}$)	Z (mV)	u (10^{-8} $m^2s^{-1}V^{-1}$)	Z (mV)
Hexane	3.47 ± 0.51	44.8	-	-	10.01 ± 0.27	129.1	8.94 0.52	115.3
Decane	-		5.51 ± 0.19	71.1	9.45 ± 0.21	121.9	-	-
Hexadecane	3.51 ± 0.32	42.7	5.60 ± 0.25	72.2	8.94 ± 0.29	115.3	8.81 0.19	113.6
LLP	-		5.98 ± 0.22	75.8	9.15 ± 0.12	118.0	-	-
HLP	-		5.79 ± 0.30	74.7	8.92 ± 0.16	115.1	-	-
Cyclohexane	3.51 ± 0.50	45.3	4.71 ± 0.35	60.8	9.74 ± 0.40	125.6	-	-
Benzene	3.25 ± 0.44	41.7	3.80 ± 0.56	49.0	8.87 ± 0.46	114.4	-	-
Decene	-		5.90 ± 0.25	76.1	9.16 ± 0.25	118.2	-	-
Decanol	-		4.11 ± 0.40	53.0	7.87 ± 0.18	101.5	-	-

FIGURE 30

The effect of surfactant concentration on the electrophoretic mobility of emulsion droplets.

○ hexane, □ hexadecane, ▲ benzene, ▩ cyclohexane.



5

DISCUSSION

5.1 ADSORPTION AT THE OIL-WATER INTERFACE

5.1.1 Interfacial tensions of the organic liquids against water

It is well known that the interfacial tension between two liquids depends upon the chemical nature, interaction and orientation of molecules at the interface (Section 1.3.1). The interfacial tension is also highly sensitive to the presence of small amounts of impurity or added surface active agent within either of the bulk phases. Numerous workers have attempted to interpret interfacial tension, adhesion and the phenomenon of spreading in terms of the intermolecular forces within and between two liquids. Antonow (300) was the first to suggest a simple formula for the prediction of interfacial tension (γ_{ow}) from the surface tensions (γ_o and γ_w) of two mutually saturated liquids. "Antonow's Rule" may be expressed as

$$\gamma_{ow} = \gamma_w - \gamma_o \qquad 5.1$$

The inadequacies of this simple model preclude its general use (200). Girifalco & Good (301) proposed an alternative expression for approximate interfacial tensions, viz:-

$$\gamma_{ow} = \gamma_w + \gamma_o - 2\phi_G (\gamma_o \gamma_w)^{\frac{1}{2}}, \qquad 5.2$$

where the function ϕ_G is a constant for a given system and can be obtained from molar volume data or known tension values. The value of ϕ_G was found to vary from unity in specific instances and therefore permitted the classification of liquids according to their interfacial behaviour. Thus, below $\phi_G = 0.78$ were all liquids with no capacity for forming hydrogen bonds with water, the values for cyclic hydrocarbons ranged from 0.67 to 0.73 and compounds for which $\phi_G > 0.84$ were generally capable of hydrogen bonding. Fowkes (186,302) resolved interfacial tension into two force components, the van der Waals (dispersion) forces and polar interactions (hydrogen bonding and other dipole interactions). For example,

$$\gamma_w = \gamma_w^d + \gamma_w^p \qquad 5.3$$

where γ_w^d and γ_w^p are respectively the dispersion and polar contributions to the surface tension of water. By assuming that the interaction energy across a saturated hydrocarbon-water interface was attributable solely to dispersion forces the interfacial tension was predicted by

$$\gamma_{ow} = \gamma_o + \gamma_w - 2\,(\gamma_o^d\,\gamma_w^d)^{\frac{1}{2}} \qquad 5.4$$

where γ_o^d and γ_w^d are the dispersion force contributions to γ_o and γ_w respectively. For a non-polar liquid Equation 5.3 becomes

$$\gamma_o = \gamma_o^d \qquad 5.5$$

Fowkes (186) then obtained the dispersion force contribution for water (γ_w^d) by substituting known γ_o and γ_{ow} values of the alkanes in Equation 5.4 . A constant value of 21.8 ± 0.7 mNm^{-1} (ie. the critical tension referred to in Section 1.3.1) was obtained, emphasizing the major role of polar interactions in determining the physical properties of water. The argument was extended to aromatic hydrocarbons for which experimental values of γ_{ow} were lower than predicted by Equation 5.4 . The discrepancy was presumed to arise as a result of stronger interaction with water through an additional polar component acting across the interface.

Table 5-1 lists the surface and interfacial tension data for a number of oils, as given previously (Table 2-3). The computed values of γ_{ow} according to Antonow's Rule, ϕ_G and γ_w^d are given. Also listed are the values of WA, WC and spreading coefficient (s) as defined in Section 1.3.1. The surface and interfacial tension values of alkanes increase as the hydrocarbon chain length increases whilst Antonow's rule (Equation 5.1) predicts the opposite. The values of ϕ_G show a clear dependence on hydrocarbon chain length, in contrast to the

Table 5-1 Interfacial properties at the organic liquid-water interface.

ORGANIC PHASE	γ_o	γ_{ow}	$\gamma_w - \gamma_o$	ϕ_G	γ_w^d	$\Delta\gamma_o^p$	WA	WC	s
Hexane	18.5	50.4	53.8	0.551	21.94	-	40.3	37.0	3.3
Octane	21.0	50.5	51.2	0.548	21.70	-	42.7	42.0	0.7
Decane	23.3	51.4	48.9	0.537	20.86	-	44.1	46.6	-2.5
Undecane	23.5	51.4	48.7	0.537	20.87	-	44.3	47.0	-2.7
Dodecane	24.6	52.5	47.6	0.526	19.94	-	44.3	49.2	-4.9
Tridecane	25.0	52.5	47.2	0.525	19.98	-	44.7	50.0	-5.3
Tetradecane	25.3	52.9	46.9	0.522	19.65	-	44.6	50.6	-6.0
Hexadecane	27.2	53.0	45.0	0.523	19.78	-	46.4	54.4	-8.0
Cyclopentane	21.6	45.0	50.6	0.610	27.56	+6.6	48.8	43.2	5.6
Cyclohexane	24.6	46.6	47.6	0.596	25.60	+5.2	50.2	49.2	1.0
Octene	21.0	48.8	51.2	0.570	23.46	+2.8	44.4	42.0	2.4
Cyclohexene	26.1	41.0	46.1	0.595	31.44	+11.9	57.3	52.2	5.1
Benzene	28.0	34.6	44.2	0.728	38.42	+7.6	65.6	56.0	9.6
Toluene	29.4	38.1	42.8	0.688	24.81	+14.3	63.5	58.8	4.7
o-Xylene	29.8	36.4	42.4	0.706	36.10	+16.1	65.6	59.6	6.0
Hexanol	25.2	6.7	47.0	1.065	81.61	+45.1	90.7	50.4	40.3

constant value of $\phi_G = 0.55$ reported elsewhere (253,301). Table 5-1 illustrates that the other oils used fall broadly into the categories stipulated above and are therefore in qualitative agreement with the theory of Girifalco & Good (301). The mean value of γ_w^d for the alkanes studied was found to be 20.59 ± 2.34 mN m^{-1}, a value not too far removed from that observed by Fowkes (186). Substituting the value of γ_w^d into Equation 5.4 predicts the interfacial tensions of other oils, assuming that only dispersion forces are present. The values obtained are significantly higher than measured values, the difference being a measure of the "excess polar interactions" ($\Delta\gamma_o^p$) which are also given in Table 5-1. The polar interactions of benzene toluene and the xylenes fall between 14 and 18 mN m^{-1}. The corresponding literature values (302) are 16.5 and 15.4 mN m^{-1} for benzene and toluene respectively. These forces arise from pi-bond interaction with water. The alcohols are capable of hydrogen bonding and give higher values of γ_o^p as expected. The observed interfacial tension data are not inconsistent with the simple model of interfacial forces described by Fowkes (186). However, the dispersion force interaction of the alkanes, like ϕ_G, does not appear to be a constant but shows a small but definite decrease with increase in chain length.

Recent investigations into the thermodynamic properties of purified aliphatic hydrocarbon-water interfaces (238,266) have realized similar observations. Gillap et al (266) found that both ϕ_G and γ_w^d varied in a regular manner with respect to hydrocarbon chain length. In order to explain these observations in terms of molecular structure it was necessary to invoke a more complex thermodynamic interfacial model based on that of Drost-Hansen (187). Briefly, contemporary theories of bulk water structure (Némethy & Scheraga (303) and others) were applied to the interfacial region. Clusters of water molecules have been visualized to explain certain anomalies in surface charge and tension measurements (187). From studies on hydrocarbon solubilities there is evidence of two opposing solute interactions with water (304). The hydration of solute may involve its incorporation within water clusters whilst hydrophobic bonding is favoured by attractive forces between hydrocarbon chains and the entropy gain from cluster breakdown. By analogy to the interface Gillap et al (266) have suggested that the latter process was favoured by longer chain hydrocarbons, thus disrupting water structure near the interface to an increasing extent whilst increasing γ_{ow} (and decreasing ϕ_G and γ_w^d).

More recently, Zografi & Yalkowsky (305) have related the differences in interaction at alkane-water interfaces to the number of dispersion interactions per unit area of the interface. It was found that changes in γ_w^d could be explained by the different interfacial group densities obtained with the various alkanes.

It should be stressed that the state of molecular interaction theory at an interface is still largely undeveloped (203b,305). However, these general observations appear to support the view of Rusanov (189) and others (Section 1.3.1) that the structure of an oil-water interface depends to some extent on the nature of the oil phase. Furthermore, such results illustrate the possible contribution of the oil phase in any interpretation of adsorption phenomena (238, 266) and have provided the stimulus for much of the work discussed in Section 5.1.2.

The three columns on the extreme right of Table 5-1 list the work of adhesion (WA) and cohesion (WC) and spreading coefficients (s) of the organic liquids. The work of adhesion for alkanes shows only slight variation whilst cohesion increases progressively with chain length. Spreading occurs when the coefficient S becomes positive (Section 1.3.1), that is, when the hydrocarbon chain length is below C_{10}. The critical interfacial tension for spreading is in the range 21.0 to 23.3 mN m^{-1}. Both observations are in agreement with previous investigations on purified saturated hydrocarbons (197). The slightly elevated interaction forces for the saturated cyclic compounds may be due to impurities exerting a lowering effect on γ_{ow}. Unsaturated oils and alcohols show significantly increased adhesional forces with water, leading to more positive spreading coefficients.

5.1.2 Adsorption of SDDS at the oil-water interface

5.1.2.1 Critical micelle concentration

The cmc values, taken as the concentration at the inflection point of each interfacial tension versus log concentration plot (Figure 10), show some dependence on the nature of the oil (Table 5-2).

Table 5-2

The critical micelle concentration (cmc) and corresponding limiting area per adsorbed molecule (A_{cmc}) for various hydrocarbon-SDDS solution interfaces.

OIL PHASE	cmc mmol dm^{-3}	A_{cmc} nm^2	OIL PHASE	cmc mmol dm^{-3}	A_{cmc} nm^2
Hexane	7.0	0.59	Cyclohexane	7.0	0.62
Dodecane	8.0	0.61	Cyclohexene	6.0	0.62
Hexadecane	8.0	0.61			
Hexane-P	8.0	0.56	Benzene	5.5	0.71
Hexadecane-P	8.0	0.56			
Hexane+Hexadecane (50% v/v)	7.0	0.63	Toluene	6.5	0.70

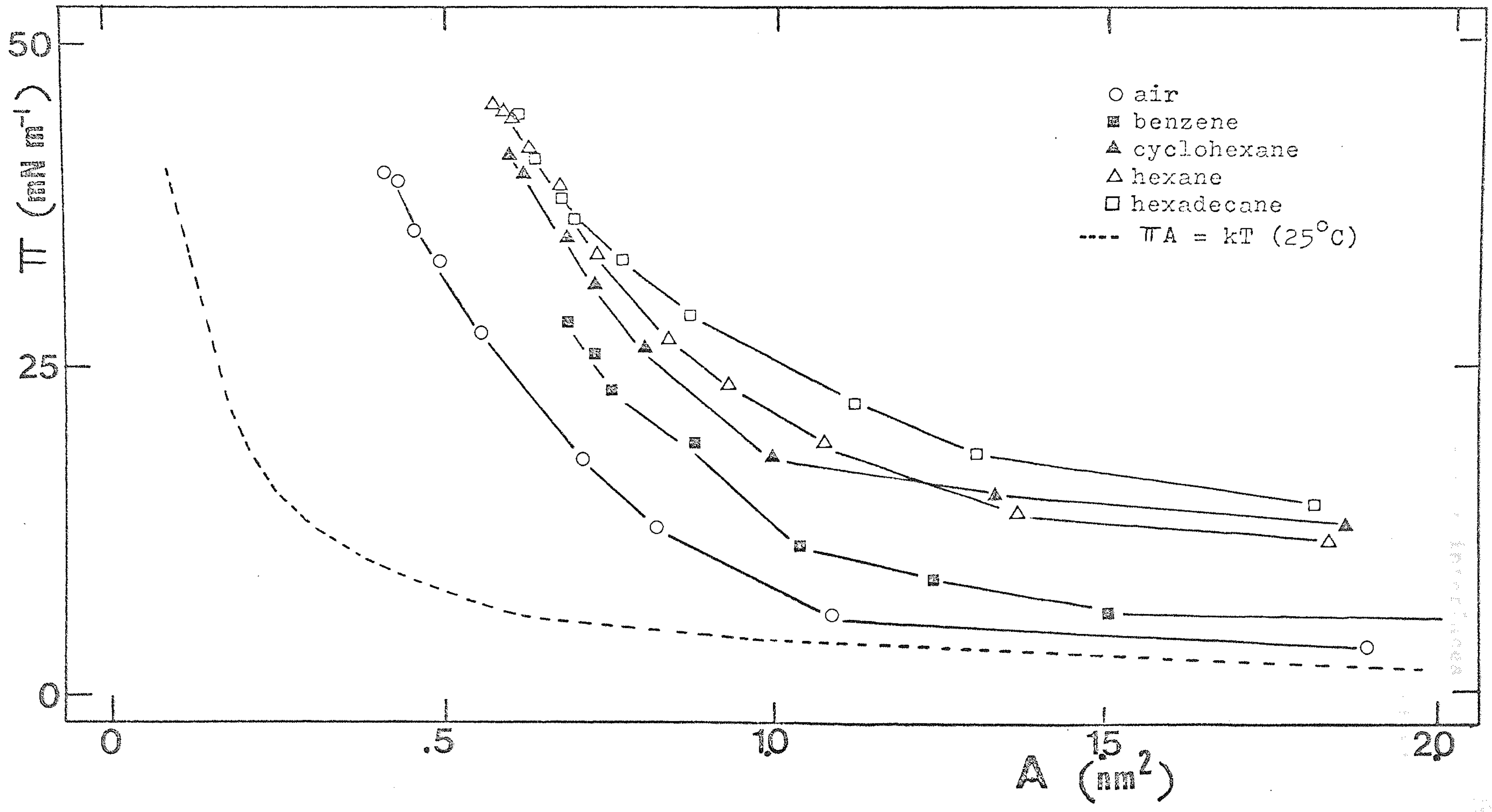
For the case of alkane interfaces, cmc values fall as the chain length is decreased. However, a purified hexane sample shows a negligible reduction of the cmc. Rehfeld (237) found that the reduction in cmc was related to the water solubility of the hydrocarbon. This certainly appears to be supported by the present results for cyclic oils where cmc depression becomes more marked from cyclohexane < toluene $\lessapprox$ cyclohexene < benzene whilst the order of water solubilities is cyclohexane < cyclohexene < toluene < benzene (296). The ability to lower cmc has been attributed to the solubilization of dissolved oil in the hydrocarbon core and at the surface of the micelle (237).

5.1.2.2 Nature of the adsorbed film

The limiting area per adsorbed SDDS molecule at the air-water interface was calculated to be 0.424 nm^2. This value is in excellent agreement with the most recent estimates of 0.450 ± 0.05 nm^2 $molecule^{-1}$ (237,233). The limiting areas at oil-water interfaces are all higher, lying in the range 0.550 to 0.710 nm^2 $molecule^{-1}$. It is generally agreed that an adsorbed SDDS film becomes more expanded at an oil-water interface because of the reduced cohesive forces between hydrocarbon chains of the surfactant (Section 1.3.3.3).

From Figure 31 it will be seen that the adsorbed films of SDDS appear to be of the "gaseous" type (Section 1.3.2.2) (234c). However, the surface pressure x area (ΠA) product exhibits considerable positive deviation from Equation 1.9b in all the systems examined. The deviation is still pronounced when correction is made for the size of the surfactant molecule (cross-section taken here as 0.30 nm^2) by using Equation 1.9c . Calculated values of $\Pi(A-A_0)$ are given in Table 4-1. The positive deviation of these values is no doubt due to the repulsion between ionic heads of the surfactant molecules (Section 1.3.2.2). This could explain why deviation from the "ideal"

FIGURE 31 Interfacial film pressure (π) versus area per adsorbed molecule (A) for SDDS adsorbed at various interfaces.



gaseous state is apparently greatest at alkane-water interfaces where cohesive forces between the hydrocarbon chains of the surfactant should be negligible (117c,203b). The deviation is slightly less for cyclic oils where slight inter-chain cohesion may occur (117d), and much lower at the air-water surface where cohesional forces are significant (Equation 1.10ab) (see Figure 31).

The present results (Table 4-1) suggest that adsorbed films of SDDS behave as non-ideal gaseous monolayers at all bulk concentrations between 10^{-4} mol dm^{-3} and the cmc. In general, the deviation from ideality decreases as the film becomes more expanded. An examination of the literature confirms that this behaviour is probable. Pethica (222) found that SDDS films adsorbed at the air-water (a-w) surface tended to be truly gaseous at high areas per molecule ($> 0.75 nm^2$). Gillap et al observed a truly ideal adsorption region at the a-w surface at extremely low SDDS concentrations ($<10^{-5}$mol dm^{-3})(219). Brady (221) has shown that the ionic repulsion introduced significant non-ideality over a concentration range of 1.6×10^{-3} to 10^{-2} mol dm^{-3}; the data conformed to Equation 1.14 (n=2). Over a similar concentration range the results of Pethica (222) approximated to Equation 1.9c when electric repulsion was attenuated by excess sodium chloride. Trace impurities may provide a neutralizing excess of electrolyte when the surfactant concentration is low (218). Observations at the oil-water interface have indicated non-ideality due to surfactant interactions above 10^{-6} mol dm^{-3} SDDS (220b).Equations 1.9b and 1.9c for ideal and neutral films respectively predict that $\Pi A \simeq 4 \times 10^{-21}$J whilst the equation of state derived by Cassie & Palmer (223) for ionized films at the o-w interface in the absence of excess electrolyte (Equation 1.14 with n=1.5) predicts a value of about 5×10^{-21}J. Several of the systems studied approach these ΠA values at low surface pressures (Table 4-1).

5.1.2.3 The effect of oil phase

The area per molecule data in Table 4-1 not only illustrate that the SDDS film at the oil-water interface is more expanded than at the air-water surface, but also that the nature of the oil phase can affect the amount of surfactant adsorbed. The data collected at or near the cmc are the most reproducible values since the rapidly changing radius of curvature of interfacial tension versus log concentration plots at lower concentrations (10^{-3} to 10^{-4} mol dm^{-3}) was found to be a source of appreciable error. Extremely precise interfacial tension measurements are required for the accurate determination of molecular areas in this region. A similar conclusion has been reached for SDDS adsorption at paraffin/water interfaces (224).

The interfacial film is evidently more expanded at aromatic oil-water interfaces (Table 4-1). This is not surprising since the adhesive forces between the surfactant hydrocarbon chain and oil molecules should be less than for alkanes. In terms of the thermodynamics of mixing, the free energy change for the transfer of each $-CH_2-$ group of the surfactant chain from water into benzene (for example) will be slightly less than for the transfer from water into alkane. Consequently the free energy of desorption will be correspondingly less for the benzene-water interface. Expressed in another way, the amount of surfactant which will "dissolve" in the "interfacial phase" is lower for benzene water interfaces than it is for alkane-water interfaces (117d). Less effective adsorption at aromatic oil-water interfaces has been reported elsewhere. Cockbain & McMullen (252) found that SDDS and alkyl alcohols were better adsorbed to the decane-water interface than if the oil was benzene. More expanded films of

SDDS have also been found at benzene-water interfaces than those of the alkanes in general (237).

The areas per molecule at the surfactant solution-alkane interfaces show a tendency towards increasingly expanded films with longer hydrocarbon chain lengths (Table 4-1) in agreement with other investigations (71,84,237). However, the calculated area is affected by the presence of impurities as is shown by the lesser expansion of surfactant solution-purified alkane interfaces. Similar area per molecule data have been presented by Rehfeld (237) although the calculated areas were lower than those obtained here, probably because of differences in the purity of the oils used. Benzene gave the most expanded films and there were clear relations between area and both the hydrocarbon chain length and degree of unsaturation.

There are several plausible explanations for the variation in the area per adsorbed molecule with alkane chain length. For example, it has been shown that the nature of the alkane may affect the interfacial structure, possibly through hydrophobic bonding which breaks interfacial "icebergs" to an increasing extent as the alkane chain is lengthened (Sections 1.3.1 & 5.3.5.2). In Section 5.2.4.1 a mechanism is advanced whereby, at low surfactant concentration, the increasing cohesion between longer alkyl chains might restrict the penetration of the dodecyl moiety into the oil phase. Alternatively, Weiner <u>et al</u> (239) have suggested that adsorbed quaternary ammonium salts can interact more favourably with short chain alkanes at low surfactant concentrations where the surfactant molecules are not aligned vertically at the interface. At higher concentrations better interaction with longer chain length alkanes was reported.

The overall shape of interfacial tension versus log concentration curves (Figure 10) is similar for each oil. At low concentrations ($<10^{-4}$ mol dm^{-3}) an approximately linear region apparently corresponds to the ideal adsorption region reported previously (219,220ab) whilst the concentration region just below the cmc could correspond to a saturated adsorption region (228ab). As a consequence of conclusions similar to those discussed in Section 5.1.1 Gillap et al (229) have investigated in some detail the effect of alkane chain length on the adsorption of sodium alkyl sulphates. The hydrocarbon chain length of the oil was found to influence adsorption by an effect on the interaction between surfactant molecules, but only with a small concentration range between the ideal and saturated concentration regions (ie. between approximately 5×10^{-5} and 10^{-3} mol dm^{-3} SDDS in this study). No effect was found for the oil phase at concentrations approaching the cmc. If this is indeed the case the differences in A_{cmc} for the alkanes would be due almost certainly to the presence of oil phase impurities*. Van Voorst Vader (228b) has studied the adsorption of SDDS in the "saturated" region. The nature of the oil was found to exert an effect on area per adsorbed molecule which depended on the presence of polar interactions of the oil with surfactant and water. Differences in polarity have been found to give significantly different areas per molecule (Tables 4-1 and 5-2).

5.1.2.4 The effect of additives

The adsorption of SDDS to interfaces with mixed alkanes shows predictably intermediate behaviour. The presence of small amounts of aliphatic alcohols, however, results in a pronounced lowering of the

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*Footnote

Recent investigations into the adsorption of SDDS at purified alkane/water interfaces suggests that this may well be the case (240). The presence of unsaturated contaminants (Section 2.3.2) would tend to increase A.

interfacial tension of alkanes against SDDS solution or water. The effect becomes slightly more marked with an increase in alcohol chain length. The combined adsorption of alcohol and SDDS gives rise to a mixed more condensed interfacial film. By using an analogue of Daltons Law of Partial Pressures a simple means is available for testing whether molecular complexing or simple mixing (Section 1.3.3.4) occurs in such a film (252). Thus, if Π_2 is the interfacial pressure due to alcohol alone, Π_1 the pressure due to SDDS alone, and Π_{12} is the experimentally observed interfacial pressure in the mixed film, it has been proposed (252,253) that

$$\Pi_{12} > \Pi_1 + \Pi_2$$

when complexation occurs. The interfacial pressure data have been analysed fully for one mixed system (SDDS + dodecanol at the hexane-water interface) and some data have been gathered for other interfaces (Table 5-3). In all cases there is considerable adsorption of the alcohol, as shown by the significant lowering of interfacial tension. In all the samples studied

$$\Pi_{12} < \Pi_1 + \Pi_2$$

indicating that no complex formation is apparent. This observation is in agreement with previous interfacial pressure measurements on SDDS films with decanol, dodecanol and hexadecanol at silicone fluid-water interfaces (253) or with octadecanol and cholesterol at benzene- or decane -water interfaces (252). Similar conclusions have been obtained from various studies on SDDS co-adsorbed with dodecanol (98) and octadecanol (91).

Columns two and five of Table 5-3 show the interfacial pressures of the surfactant alone (Π_1) and in the presence of alcohol ($\Pi_1' = \Pi_{12} - \Pi_2$). At all concentrations there appears to be appreciably less interfacial pressure arising from SDDS in the mixed film than with the anionic surfactant used alone. A similar result was found by Cockbain & McMullen (252) for SDDS adsorption with cholesterol or octadecanol at the decane-water interface. It was concluded that this was due, in part, to a reduction in the amount of SDDS adsorbed. Against benzene both components were found to adsorb to the same degree as if they were present singly (ie. Daltons Law analogue was found to hold). With decane however, the amount of alcohol adsorbed was much greater, with or without SDDS. It has since been shown that agreement between $\Pi_1 + \Pi_2$ and Π_{12} is better for less interfacially active additives and for low surfactant concentrations (253). The present results (Table 5-3) suggest that SDDS adsorption may be decreased by dodecanol as the film is nearing saturation. The loss in the interfacial pressure of SDDS in the mixed film approaches the pressure due to adsorbed alcohol. As the concentration of SDDS is reduced, the film becomes more expanded and better agreement is obtained with the partial pressure law. It is likely that interfacial pressure of SDDS in the mixed film will also be reduced to some extent by the lowering of effective repulsion between charged ionic heads (ie. Πr of Equation 1.10b becomes smaller), particularly in a closely packed film. Experimentally there appears to be little direct evidence for a reduced adsorption of SDDS in mixed films, although the direct measurement of adsorption is somewhat insensitive (Section 1.3.3.1). Nillson (214) found that dodecanol displaced tritiated SDDS only weakly at the air-water interface. It was also shown that strong adsorption of radioactively labelled dodecanol occurred even at low alcohol concentrations. Vold & Mittal (98) did not find a detectable change in the aqueous phase surfactant concentration in a Nujol emulsion stabilized with SDDS just below the cmc when dodecanol was added to the oil.

Table 5-3

Interfacial pressure data (mN m^{-1}) for mixed surfactant films.

SDDS concentration mmol dm^{-3}	Π_1	Π_{12}	$\Pi_1 + \Pi_2$	Π_1'
Hexadecane + dodecanol (0.04 mol dm^{-3})-SDDS solution[(a)]				
10.0	43.5	51.7	69.1	26.1
8.0	43.7	51.6	69.3	26.0
7.0	43.3	51.0	68.9	25.4
6.0	40.6	49.0	66.2	23.4
5.0	38.6	47.2	64.2	21.6
4.0	36.0	44.7	61.6	19.1
3.0	32.5	42.2	58.1	16.6
2.0	28.0	39.0	53.6	13.4
1.0	21.7	35.2	47.3	9.6
0.7	18.0	33.6	43.6	8.0
0.4	14.0	31.8	39.6	6.2
0.2	11.2	29.8	36.8	4.2
0.1	9.3	28.4	34.9	2.8
0.07	7.5	26.9	33.1	1.3
0.04	5.0	26.6	30.6	1.0
0.02	3.2	26.4	28.8	0.8
Hexane + Octanol (0.04 mol dm^{-3})-SDDS solution[(b)]				
1.0	26.7	33.9	50.0	10.6
0.1	11.2	25.6	34.5	2.3
Hexane + dodecanol (0.04 mol dm^{-3})-SDDS solution[(c)]				
1.0	26.7	34.4	51.7	9.4
0.1	11.2	27.2	36.2	2.2
Hexane + hexadecanol (0.04 mol dm^{-3})-SDDS solution[(d)]				
1.0	26.7	34.4	52.4	8.7
0.1	11.2	27.9	36.9	2.2

Table 5-3 continued.

NOTES:

Interfacial tension:- hexadecane - water = 53.0 mN m^{-1}
hexane - water = 50.4 mN m^{-1}

Interfacial pressures:- Π_1 = SDDS alone
Π_{12} = mixed film
Π_2 = alkanol alone

Π_2 = 25.6 (a), 23.3 (b), 25.0 (c) and 25.7 (d).

5.2 STABILITY OF OIL DROPLETS AT THE OIL-WATER INTERFACE

5.2.1 Mechanism of coalescence

Despite the many theories that have been advanced to describe the phenomenon of single droplet coalescence at a plane interface, the exact mechanism involved still remains obscure (103). The overall process can be divided into several consecutive stages as follows:-

(i) Arrival.

The droplet rises (or falls) through a fluid medium (the "continuous" phase) because of the density difference between the two phases. It can be assumed that uniformly sized droplets of a particular liquid arrive at the interface at a constant velocity (282). This velocity will vary slightly with the density of the liquid comprising the droplet.

(ii) Impact.

The droplet collides with the interface, thus causing itself to "bounce" and creating ripples across the interface. The resultant oscillation of the droplet permits a film of continuous phase to become trapped between the droplet and the plane interface.

(iii) Film drainage.

The buoyancy of the droplet is supported by the trapped film so that the overall effect of gravity is to cause a pressure distribution within the film. Continuous medium begins to drain from the film because of the radial pressure gradient. Under these circumstances either the droplet or the interface (or both) may become deformed.

(iv) Film rupture.

Eventually the film separating the droplet from its bulk phase will rupture. The thickness of the draining film will affect the probability of rupture (i.e. the thinner the film the greater the possibility of rupture).

(v) Deposition.

The contents of the droplet are transferred wholly or partially into the bulk phase.

The measured rest-time for a droplet is a composite of all processes following the arrival of the droplet at a plane interface. In practice, film drainage proceeds almost immediately after arrival provided that large amplitude vibrations are excluded from the interface. Also, transference of the contents of a droplet is completed almost instantaneously (i.e. <0.1s) (103). The measured coalescence time is determined by the time during which a droplet rests on a thinning film and the effect of any interfacial film adsorbed at the two oil-water (o-w) interfaces.

5.2.2 Spread of rest-times

In all the present experiments a distribution of the measured rest-times was obtained. The spread of values increased with an increase in overall stability. A distribution of coalescence times is a characteristic of all previous droplet stability experiments, although some reproducibility has been obtained by using interfaces immediately after an elaborate cleaning procedure (280a). The scatter of values has been attributed loosely to disturbances due to vibration (102ab), surfactant displacement (104), inhomogeneity in the adsorbed film (107,306) or thermal effects (275). Gillespie & Rideal (275) postulated that the draining film could rupture at different thicknesses. It was argued that the minimum rest-time corresponds to the maximum film thickness at which rupture can occur; therefore, droplets which persist beyond this time may coalesce whenever there happens a disturbance of sufficient magnitude to rupture the film. It is also likely that the angle of approach to the interface will vary between droplets which have travelled some distance. This may cause some variation in the initial thickness of the trapped film and hence the drainage time (100).

Despite the scatter of rest-times it has usually been possible to conduct a statistical analysis of the measurements and to derive reproducible stability parameters (Section 3.2.4). In accordance with the majority of reports (102ab, 108a, 272-275, 277, 279, 281) the present work indicated that somewhere in the region of 50 to 100 measurements are sufficient provided that the stability of individual droplets is not too great. However, some workers have recorded observations based on 40 or fewer separate measurements (104,106).

5.2.3 The effect of surfactant

The rest-times of oil droplets at the oil-water interface are extremely short. For example, the t_{mean} values for hexane and hexadecane under such conditions are about 1.0s and 0.6s respectively. These values are consistent with the rapid rate of film drainage and low resistance to rupture to be expected when no stabilizer is present (281,306). The stabilizing effect of SDDS is described in Section 3.2.5; droplet stability increases sharply as the concentration of dissolved surfactant is raised (Table 3-5). Similar observations have been reported for the stabilizing effect of SDDS and other surfactants on benzene and water droplets at the benzene-water interface (106). Indeed, many of the investigations into the coalescence of oil droplets at an interface have included a surfactant to stabilize droplets (104,106,109, 272,275,280ab,281,306-308). When surfactant is added the droplet stability may be enhanced by changes in the rate of film drainage and/or the resistance of the film to rupture.

A number of authors have proposed that the principal effect of adsorbed surfactant in stabilizing single droplets is to slow the rate of film drainage (27b,275,280ab). Hodgson and others (280ab) have shown that low concentrations of SDDS ($< 10^{-6}$ mol dm^{-3}) can act in this way. Gillespie and Rideal (275) proposed that the process of film rupture is likely to be similar both with and without the presence of surfactant. When the draining film becomes sufficiently thin it has been argued that van der Waals attraction (at film thicknesses below 100nm (306)) and random molecular motions (at thicknesses below 10nm (102a)) would rapidly thin and rupture the film.

The factors affecting film drainage are complex and interacting. It has been pointed out previously (Section 1.2.3.2) that the rheological properties of an interface are highly sensitive to adsorbed surfactant and that a viscous or viscoelastic film should retard the drainage of an aqueous lamella. A further barrier to film drainage may be provided by orientated layers of water around surfactant molecules at the interface (Sections 1.3.1 & 5.3.5.2). The presence of an adsorbed species makes possible the development of interfacial tension gradients during film drainage (Section 1.2.3.2). This may enable the film to "heal" weak spots and damp the interfacial disturbances responsible for film rupture. Hodgson and others (280ab,306,307b,308ab) demonstrated that even low concentrations of surface active agents may alter the mode of film drainage and restrict the mobility of the oil-water interface. This leads to retarded film drainage and increased stability. Immobilization of the surfactant film around the droplet inhibits internal circulation and may lead to a regime of slow drainage.

Since the droplet and interface carry a small negative charge in 10^{-4} mol dm^{-3} SDDS (Section 4.4.4), film thinning may be retarded by electrical factors. An electroviscous effect may arise when the distance of droplet-interface separation becomes less than 10^3nm (102a). Film thinning may be retarded or arrested by the electric double layer repulsion (Section 1.2.3.2). The magnitude of this repulsion is raised with an increasing potential drop across each double layer and with decreasing film thickness. The effective double layer thickness is in the region of only 50nm whilst the double layer potential, calculated using the Smoluchowski equation for a plane interface (Section 3.4.6), is about 40 to 45mV. At 10^{-3} mol dm^{-3} the respective values are 10nm and 50 to 75mV.

The decrease in interfacial tension associated with surfactant adsorption may allow greater deformation of the droplet and interface, thus increasing the area of the draining film and further inhibiting film drainage.

An alternative view is that the principal effect of surfactant when stabilizing droplets is to increase the resistance of the interfacial film to rupture. Cockbain & McRoberts (104) concluded that droplet stability was determined by the resistance of the interfacial film to wetting by the dispersed phase. A similar suggestion was made later by Nielsen et al (272). Watanabe & Kusui (106) supported the view that droplet stability at the plane interface is determined largely by the characteristics of the adsorbed film; the time required for film drainage was considered negligible. The coalescence mechanism proposed by the latter workers was that a defect formed in the film in the region of droplet-interface contact, probably through desorption of surfactant. Biswas & Haydon (107) reported that rapid drainage from aqueous lamellae occurred in the presence of viscous adsorbed films. Interestingly, stability was related simply to the ability of films to withstand the weight of a droplet. More recent studies on films of this type (108a, 277) have confirmed the dependence of stability on the resistance to film rupture.

5.2.4 The effect of oil phase on stability parameters

5.2.4.1 Single oils

A wide range of oils of differing chemical types and polarities have been investigated (Table 4-3). The nature of the oil phase has a profound effect on the stability of single droplets. Table 4-3 lists certain physical properties of the oils, namely the viscosity, the density difference between the two phases (Δp) and the interfacial tension (γ_{ow}), which have previously been considered to exert some influence on the rate of film drainage and hence the droplet rest-times (103). Also included in Table 4-3 is the solubility parameter for each of the oils, since this may affect the resistance of the adsorbed film to displacement (see below).

The role of oil phase viscosity in the film drainage and coalescence processes has been considered by a number of authors (109,276b,308b). Jeffreys & Davies (103) point out that the phase viscosity ratio will affect stability; an increase in the viscosity of the continuous phase relative to the droplet phase will retard film drainage and increase the rest-time whilst a high oil viscosity might retard film rupture. The data in Table 4-3 indicate no correlation between oil phase viscosity and droplet stability parameters.

The relationship between density difference (Δp) and stability is not a simple one. An increased Δp results in greater buoyancy leading to more rapid film drainage. However, large differences in density can also cause deformation of the droplet and/or the interface which extends the area of the draining film and leads to longer rest-times. When deformation occurs this effect tends to outweigh that of increased buoyancy. Deformation is resisted by a high interfacial tension (130), thus rest-times tend to decrease as interfacial tension increases. The stability data for the alkanes (Table 4-3) shows an increase in stability as Δp increases and as γ_{ow} decreases, in qualitative agreement with theory; however, extending the consideration to the other oil phases reveals no direct correlation with Δp or γ_{ow}.

Several authors have attempted to relate the deformation of droplets and the rate of film thinning to droplet-size, interfacial tension and density difference between the phases. Mathematical analysis has been completed for four simple theoretical models which are illustrated in Figure 32. Provided any deformation is small, and neglecting the effects due to electrical double layer repulsion, electroviscosity or the physical presence of an adsorbed film, the time (t_h) required for a film to drain evenly to a given thickness is related to interfacial tension and density difference by:

$$t_h \propto \Delta p^{-1} ,$$

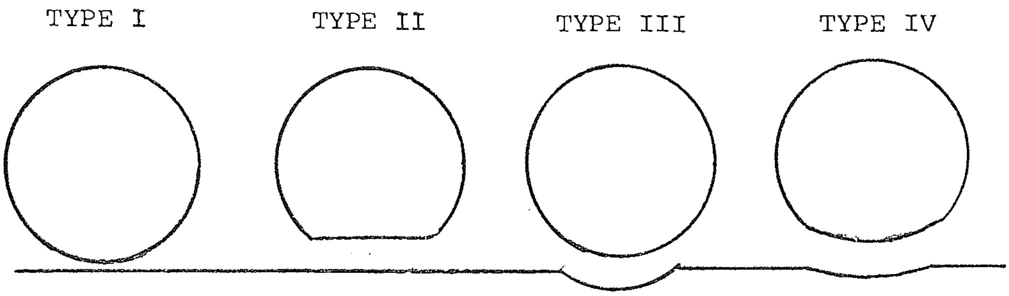
and

$$t_h \propto \Delta p / \gamma_{ow}^2$$

respectively for the spherical-planar (Type I, Figure 32) and parallel-

FIGURE 32

PROPOSED MODELS FOR THE DRAINING FILM BETWEEN A SMALL DROPLET AND A LIQUID-LIQUID INTERFACE.



TYPE I : Droplet non-deformable, Interface non-deformable
SPHERICAL - PLANAR MODEL

TYPE II : Droplet deformable, Interface non-deformable*

PARALLEL PLATE MODEL

TYPE III: Droplet non-deformable, Interface deformable*

TYPE IV : Droplet deformable, Interface deformable*

* UNIFORM FILM MODELS

plate (Type II, Figure 32) models (276b). The rates of film thinning for type III and IV models have been interpreted successfully on the same basis as the Type II model (130,275,309).

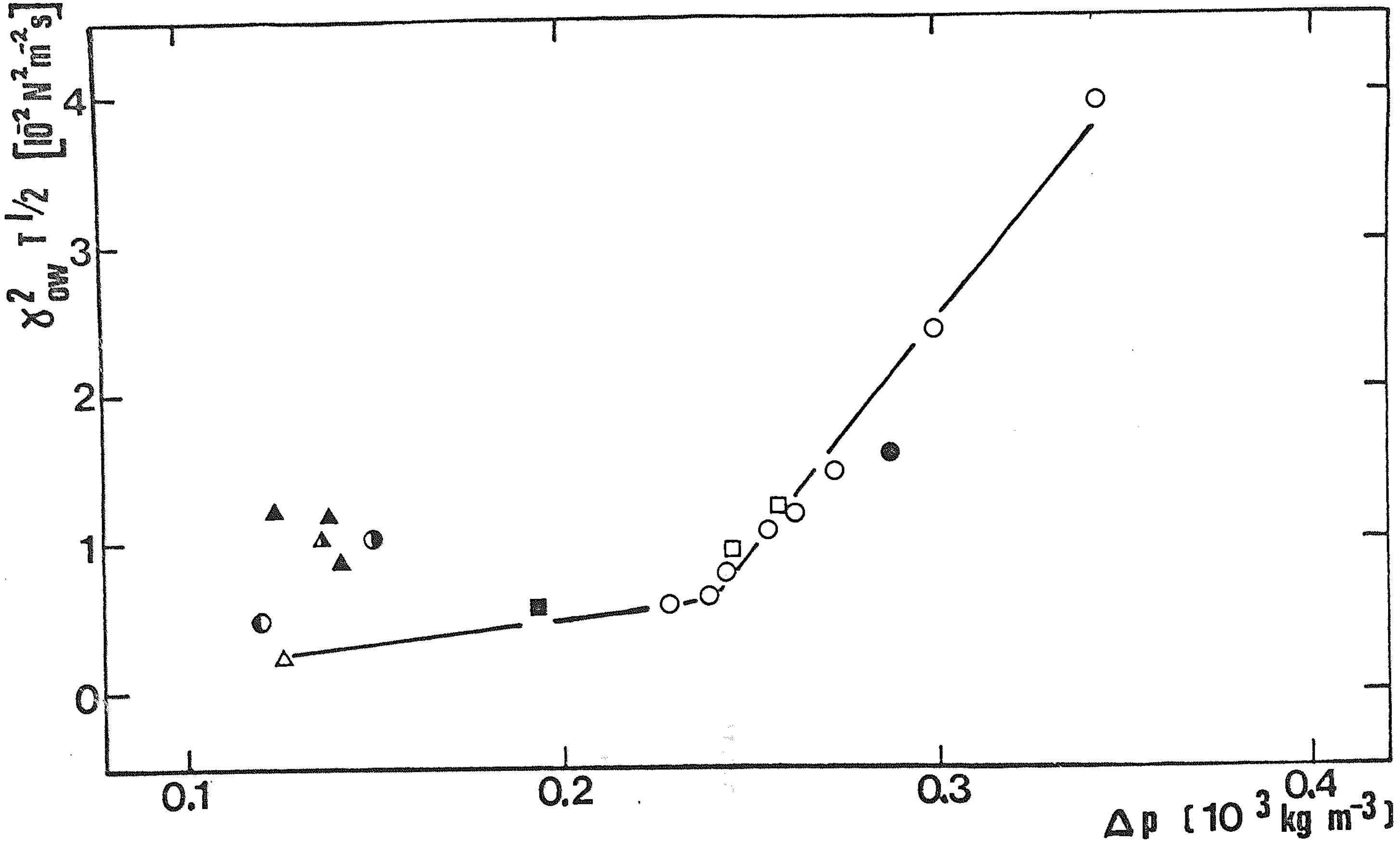
In many instances it has been found that the profile of an interfacial film is not represented by any of the theoretical models shown in Figure 32. Instead the film between a flattened drop and the interface may thin more rapidly around its perimeter, causing a thicker lens or "dimple" to form in the centre. The effect of droplet "dimpling" on film drainage has been considered (309-311ab). It is extremely difficult to compute the rate of film thinning in this geometry (102a) although calculations by Frankel & Mysels (310) indicate that the drainage rate in the thinnest region of the film is approximately the same as for the parallel-plate model (Type II, Figure 32). Hartland (311c) found that coalescence occurred most frequently at the thinnest region around the edge of a dimpled film (i.e. around the "barrier ring") unless tilting of the droplet caused irregular and rapid thinning of a particular region in the film. Similar observations have been made by Charles & Mason (276b). The analysis of Frankel & Mysels (310) also permits one to estimate the drainage rate from the centre of the droplet contact area (within the dimple). Hartland (307b) found that in some instances the bulk interface (which has normally aged for some time) can remain immobile, whilst freshly adsorbed molecules on the droplet are swept away during approach and film drainage. The net effect is that γ_{ow} may be higher at the droplet-water interface than at the bulk interface, thus changing the film profile. Mathematical expressions have been proposed for non-uniform film models, other than Type I (Figure 32), where the film may be thinnest at either its centre or periphery (311b).

The data from Table 4-3 are plotted in the form $T_{\frac{1}{2}} x \gamma_{ow}^{2}$ versus Δp in Figure 33. An approximately linear relationship is obtained for

FIGURE 33

ANALYSIS OF DROPLET COALESCENCE DATA (T1/2) BY THE UNIFORM FILM MODEL FOR FILM DRAINAGE.

○ alkanes (C_6 to C_{16}), ◑ light liquid paraffin, ◐ heavy liquid paraffin, ● octene,
□ cycloparaffins, ■ cyclohexene, △ benzene, ▲ toluene, ▲ o- m- p-xylenes.



the alkanes. It has been shown (130,275,276b,279) that the thickness (h) of the draining film at rupture can be estimated, for uniform film models (Type II and III, Figure 32), from the rest time (t) by

$$t = \frac{1}{h^2} \frac{r^5 \eta_2 \Delta pg}{4 \gamma_{ow}^2} , \qquad 5.6$$

(where r is the droplet radius, η_2 the continuous phase viscosity and g is the acceleration due to gravity). The critical rupture thickness for the alkanes can be found from the slope of the line (Figure 33) and the present results give a value of approximately 120nm (where $\eta_2 = 9.5 \times 10^{-4}$ N s m^{-2} (283)); r = 1.13mm; g = 9.81 m s^{-2}. Such a value is not unreasonable since it is somewhat higher than values reported for systems in which double layer repulsion is either absent or attenuated by electrolyte (133,279). Nevertheless, the absolute value of film thickness is difficult to establish and could be subject to significant error (276b). This is particularly true here since, as stated, no account is taken of the effect of added surfactant on the drainage mechanism. It should be noted that $T\frac{1}{2} \times \gamma_{ow}^2$ is somewhat lower (Figure 33) than predicted by the uniform film models. This discrepancy is not due to the use of $T\frac{1}{2}$ rather than the more usual but less reproducible $t\frac{1}{2}$ value since the difference t_d (Equation 3.9) is small. The substitution of $T\frac{1}{2}$ by $t\frac{1}{2}$ in Equation 5.6 alters the time-tension product by only a few percent. It is more likely that irregular thinning of the film causes more rapid drainage (see below). Unsymmetrical drainage is also promoted by tangential motion between the droplet and the interface (307ab). The experimental procedure permitted droplets to move freely across the interface.

The result for octene (Figure 33) shows a slight negative deviation from the data for alkanes. This could be due to the effect of impurities in the oil phase and experimental error although other possible causes of the discrepancy are discussed below.

Significant deviations from linearity in Figure 33 occur amongst the oils with low Δp values. The relative stabilities of these oils cannot be explained in terms of film drainage rates simply by differences in Δp and γ_{ow}. It is possible that drainage and coalescence occur by a different mechanism for the oils or that the critical film thickness for rupture is dependent on the oil phase (134). Also, deviation from linearity might be expected at lower values of Δp where double layer repulsion is not negligible in comparison with the buoyant pressure on the draining film. This would certainly account for the behaviour of benzene in relation to cyclohexene and the alkanes. The more pronounced variation of the xylenes and toluene, oils with similar Δp values to benzene can also be explained on this basis since they carry a somewhat higher charge on their droplets (Section 4.4.1)

The rest-times of alkanol droplets was immeasurably long in all experiments. On the basis of the correlation with film drainage (Figure 33) a $T_{\frac{1}{2}}$ of 100 to 150s would be required (ie. if γ_{ow}^{2} x $T_{\frac{1}{2}}=6\text{x}10^{-3}$ N^{2} m^{-2} s at Δp = 170 to 180 kg m^{-3}). In practice very few droplets coalesced within 300s and most of the droplets persisted for more than 10^{3}s. This represents a degree of stability that cannot be explained by the effect of γ_{ow} and Δp on film drainage. The zeta potentials measured for each alcohol were very similar and all were considerably lower than the corresponding values for the hydrocarbons (Table 4-14). Therefore, the degree of electrical stabilization expected would be negligible. This suggests that the nature of the interfacial film is the predominant factor in determining droplet stability for the alcohols. A similar conclusion applies to systems containing alcohol as an additive (Section 5.2.4.2). The possible role of the adsorbed film and the effect of the oil phase composition in determining stability are discussed below.

The specific effect of the adsorbed surfactant, and particularly its ease of displacement, on film drainage and rupture provides a plausible explanation of the stability data. The adsorbed film has been characterized by the area per surfactant molecule (A) (Table 4-1) and electrophoretic measurements (Tables 4-14 and 4-17). Predictably, droplet stabilities increase with a closer packing of the surfactant film (Figure 34) and with an increase in electrophoretic mobility (u), both of which should provide a more effective barrier to coalescence (Section 1.2.3). However, in neither case is the correlation particularly striking. For example, slight variations in A and u are accompanied by widely differing stabilities within the alkane series of oils. The relationship between molecular area and degree of unsaturation (Section 5.1.2.3) does correlate broadly with droplet stability measurements.

The adsorption of surfactant depends upon the chemical nature of the non-aqueous phase and is the resultant of two separate forces (220ab). At the oil-water interface oil molecules must be separated if the surfactant chain is to penetrate into the oil phase, whilst the hydrocarbon chains of the surfactant can interact with oil molecules. When SDDS is adsorbed at an alkane-water interface it is suggested that the hydrocarbon chains of surfactant molecules are aligned with those of the oil as a result of van der Waals forces (220b). At low surfactant concentrations there will be negligible self-interaction between the surfactant chains and each adsorbed molecule will be surrounded by oil molecules (117d,234c). The thermodynamics of SDDS adsorption has been investigated by Gillap *et al* (200ab) who have proposed that the surfactant will penetrate into the oil when adhesive forces between the alkyl chains of oil and surfactant exceed the cohesive forces between oil molecules.

FIGURE 34

DROPLET STABILITY (T1/2) VERSUS AREA PER ADSORBED SURFACTANT MOLECULE (at the cmc)(A_{cmc}).

○ alkanes, □ cyclohexane, ■ cyclohexene, ▲ toluene, △ benzene.

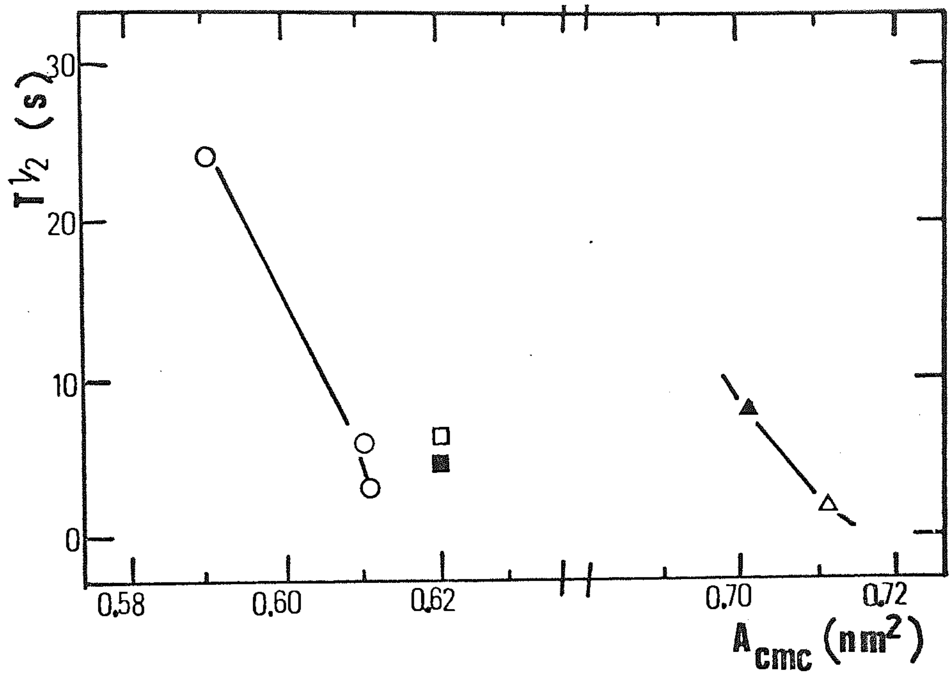
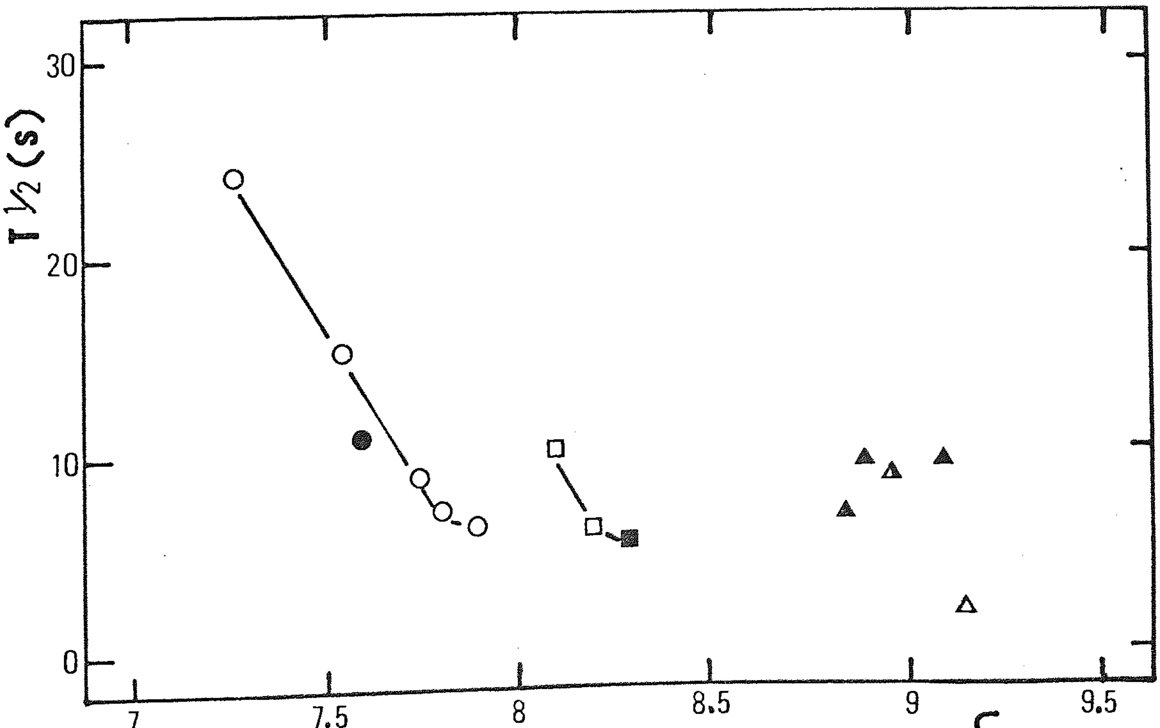


FIGURE 35

DROPLET STABILITY (T1/2) VERSUS SOLUBILITY PARAMETER (δ).

○ alkanes, ● octene, □ cycloparaffins, ■ cyclohexene, △ benzene,
▲ toluene, ▲ o- m- p- xylenes.



The cohesive nature of the oil phase may be expressed by the solubility parameter (δ) which is given by the square root of the cohesive energy density (ie. the cohesive energy per unit volume of liquid) (312). The relevant values of δ, obtained from the compilation of Hoy (313), are given in Table 4-3. The estimation of adhesive forces between oil molecules and the surfactant is more difficult (314,315). By drawing further on the analogy of the interfacial region with bulk systems to consider the thermodynamics of binary mixtures (316) some indication can be obtained as to the relative adhesive forces between SDDS and various oils. It can be supposed that the mixing of a dodecyl moiety with an alkane will be almost ideal; that is, its activity coefficient at infinite dilution will be near to unity with pure solute as the standard state (Section 5.3.6.3). For example, the activity coefficient of dodecane in hexane at 25°C is about 0.95 (Table 5-7). Qualitatively it can be assumed that forces of adhesion between adjacent methylene groups of the surfactant and alkane molecules should be constant. The total interaction between a dodecyl group and dodecane should be similar to the interaction between the same group and (for example) two hexane molecules. Thus, adhesive forces between the surfactant and alkanes are approximately constant but cohesive forces between oil molecules (solubility parameters) increase with an increase in chain length. This suggests that displacement of the surfactant may occur more easily, and hence stability will decrease, with an increase in alkane chain length.

Figure 35 shows a plot of $T_{\frac{1}{2}}$ versus solubility parameter for the hydrocarbon oils. Alkanes exhibit a decrease in stability as the solubility parameter increases. The remaining oils show the same general trend for any particular class of compounds, although quantitatively the correlation is not impressive. Unsaturation in the straight chain hydrocarbon increases the cohesiveness (solubility parameter) slightly and would also be expected to decrease adhesion between oil and surfactant molecules. The resultant greater ease of surfactant displacement would account for the slightly lower stability obtained with octene as compared with octane.

The van der Waals and dipole-induced dipole forces between hydrocarbon chains and unsaturated or aromatic solvents cannot readily be assessed (317). However there should be further deviation from the ideal type of behaviour at the interface, giving a lower degree of oil-surfactant interaction. The equivalent binary mixtures are certainly not ideal; the activity coefficients of hexane at infinite dilution in cyclohexane, toluene and benzene are 1.20,1.65 and 2.15 respectively (318). These oils have a strongly cohesive nature (Table 4-3) and a lower adhesive nature, conditions which may be favourable for the displacement of surfactant leading to low stability. The greater expansion of films at aromatic oil-water interfaces compared with alkane-water interfaces should also contribute significantly to a lower droplet stability.

Interfacial interaction forces are further complicated by the properties of charged surfactant head groups. These certainly do influence each other except at extremely low surfactant concentrations (Sections 1.3.2.2 and 5.1.2.2). The repulsion and spacing of the ionic heads may be susceptible to the nature of the oil phase (Section 1.3.3.3), particularly if the latter is significantly polar (228ab). Moreover, when the oil can undergo head group interactions very stable droplets may result. The C_4 to C_{10} alcohols, for example, are strongly cohesive (Table 4-3) due to hydrogen bonding. Their binary mixtures with alkanes are far from ideal with activity coefficients in the region of 4 (318). Nevertheless, these droplets are highly stable owing to the formation of a more condensed mixed surfactant film in which sulphate head group repulsion is reduced and there may be significant interaction between sulphate and hydroxyl groups (Section 1.3.3.4).

5.2.4.2 The effect of additives

Small quantities of one hydrocarbon added to the oil droplets and bulk interface of another hydrocarbon exert no influence on droplet stability (Table 4-4). Such an additive exerts no measurable effect on the interfacial tension, nor is it expected that the viscosity or density of the oil droplet will be significantly altered. Consequently no effect on the rate of film drainage is anticipated. The interfacial tension (Section 4.1.2) and electrophoretic measurements (Section 4.4.2) reveal no detectable change in the properties of the adsorbed surfactant film or the resultant electric double layer. A $50\%^{v}/v$ mixture of short and long chain alkanes has predictably intermediate surface properties and stability.

On the other hand the same molar concentration of added aliphatic alcohol can have destabilizing or stabilizing effects that depend upon the alcohol chain length. The short chain alkanols (carbon number $< C_5$) exert a destabilizing effect on droplets of hexadecane (Table 4-4). Presumably this effect is analogous to that of not using mutually saturated phases (Section 3.2.5.2). The water solubility of the alkanols increase with decreasing hydrocarbon chain length (Section 5.3.6.3); consequently the short chain length alcohols diffuse fairly rapidly out of the droplet and the bulk oil phase. Jeffreys & Hawksley (273) and MacKay & Mason (319ab) observed that stability could be reduced or increased by diffusion out of, or into a droplet respectively. The outward diffusing component has been shown to decrease stability by promoting the rate of symmetrical film drainage without affecting the film thickness at rupture (319ab). Such a component can cause internal circulation within the droplet, thus promoting film thinning (320). Other workers have proposed that molecular scale disturbances caused by the chemical potential gradient across the interface may increase the probability of film rupture and hence droplet stability (102a,272,306).

Alcohols with hydrocarbon chain lengths greater than C_{10} have a pronounced stabilizing influence on hexadecane droplets. Whilst the effect on interfacial tension is a significant one (Table 4-4) it can hardly be sufficient to cause changes in the rate of film drainage to account for the dramatic increase in stability. The most probable mechanism of increased stabilization is through the formation of a mixed surfactant film in which alcohol and surfactant molecules may interact (Section 1.3.3.4). This would increase the resistance of the adsorbed film to displacement, thus reducing the probability of film rupture. The characteristic shape of logN versus time curves when alcohol is present (Figure 15) indicates that some droplets coalesce at a faster rate. This may be due to the low concentration of both SDDS and alcohol, leading to inhomogeneity within the film, as in a liquid expanded film (Section 1.3.2.2) for example.

5.2.4.3 Conclusions

Two mechanism have been proposed in order to explain the relative stabilities of oil droplets at an oil-surfactant solution interface. There is some indication that the stability of alkane droplets can be related to the rate of film drainage from a uniform or dimpled film as predicted by modified hydrodynamic theory. However, stability increases progressively with alkane chain length, and therefore good correlation can be obtained with most physical data since these change monotonically as a function of chain length. Significant deviations which occur at low density differences may be due to the emergent effect of electrical double layer repulsion or other film effects under conditions of low compression on the draining film.

An alternative argument is based on the assumption that the initial rate of film drainage is high and that stability is determined by the nature of the adsorbed film. There is a qualitative agreement between the predicted resistance of the film to displacement and droplet stability for saturated and unsaturated hydrocarbons. This mechanism appears to explain the high stability of droplets around which a more condensed mixed surfactant film can form.

The process of film drainage and coalescence of a droplet at a plane interface is exceedingly complex, particularly where surfactants are present since these complicate the properties of the interface (276ab). Several authors have concluded that the prediction of rest-times in the presence of surfactants may remain virtually impossible (275,276b,306,307b). The relative magnitudes of drainage and displacement effects may possibly be elucidated by extending the range of organic phases studied. Also, the significance of adhesive and cohesive interactions should be manifested in the interfacial viscosity. Ishida _et al_ (109) have suggested the importance of this parameter in droplet stability studies but the relevant data have been reported only for macromolecular films (107,108a,277) in which the nature of the film is known to determine stability; corresponding data for gaseous or expanded adsorbed films are difficult to obtain (Sections 1.2.3.2 and 5.3.5.2).

It might seem that the adsorbed films produced in the present systems (ie. with 10^{-4} mol dm^{-3} SDDS) are too highly expanded to offer significant resistance to displacement from the area of droplet-interface contact. The principal factor involved in determining the stability is probably the rate of film drainage. However, it has been shown (280ab,306,307b,308ab) that very low concentrations of SDDS can appreciably influence the nature of the interface through an effect on film mobility. It may well be that the amount of surfactant adsorbed, film drainage, surfactant displacement and possibly electrical effects (electro-viscosity and repulsion) all play a part in determining the overall stability of droplets.

5.3 EMULSION STABILITY

5.3.1 Theory of coalescence

It has been pointed out in Section 1.2.3 that the presence of an adsorbed surfactant can permit emulsion droplets to lie in close proximity without coalescing. Also, in well stabilized emulsions an extremely small proportion of droplet collisions results in coalescence. Under such conditions it has been argued that the rate-determining process in the coarsening of emulsions is the rupture of the film between adjacent droplets (133). According to Schulman & Cockbain (175a) the most effective conditions for the stabilization of oil-in-water (o/w) emulsions are:-

(i) the interfacial surfactant film should be stable and as closely packed as possible.

(ii) the interfacial film must be electrically charged.

The mechanism of coalescence has been described as a rearrangement of the surfactant film, during droplet contact, to permit closer approach of the droplets and coalescence (113). Such a "rearrangement" of adsorbed molecules can occur in a variety of ways. For instance, Cockbain & McRoberts (104) proposed that displacement of the interfacial film was necessary before coalescence could occur. It was suggested that wetting of the adsorbed species by dispersed phase determined the probability of droplet coalescence. A similar process was envisaged by Sumner (321) although the oil was thought to penetrate through the adsorbed film to unite adjacent droplets. The ease of desorption of a surfactant film into either the oil or continuous phase has also been related with resistance to coalescence (138). The presence of a charged monolayer on the droplets gives rise to the further possibility that lateral displacement of the film can result from the interionic repulsion between adsorbed molecules (153). Although this effect is opposed by interfacial tension gradients it was thought to account for the greater stabilizing ability of more condensed and therefore less compressible films (117c).

Van den Tempel (133) has demonstrated that droplets "in contact" are still separated by a water film at lease 10nm thick. This factor has frequently been neglected in earlier studies where the adsorbed film has been considered in isolation. It has since been postulated that the principal effect of emulsion stabilizers is to decrease the probability of rupture of the aqueous film or lamella (37b). Certainly, more emphasis has been given recently to the stability and properties of thin films in relation to the stability of emulsions; there is a need, however, for the mechanism of thinning for aqueous films in oil to be elucidated (37b,322). The occurrence and properties of aqueous lamellae are further discussed in Sections 1.2.3.2 and 5.2.2.

In the present study all the dispersions investigated consisted of charged droplets. A high degree of electrical repulsion may prevent droplets from approaching, and hence postpone coalescence although the required magnitude of this repulsion is difficult to estimate (Section 1.2.3.2). When two droplets approach, as in a collision or in the creamed layer, there is an increasing degree of electrical repulsion which may maintain an aqueous lamella between droplets. Coalescence may then occur through any of the"rearrangement" processes and rupture of the aqueous film as described above. If the repulsive barrier is overcome the droplets will approach through the increasing van der Waals forces and coalescence will only be resisted by the adsorbed film molecules. If the film is of the expanded type penetration or lateral displacement should occur quite readily; condensed or macromolecular films may provide a significant mechanical barrier to coalescence.

5.3.2 The significance of creaming

5.3.2.1 Cream volume

In a monodisperse suspension of rigid spheres the closest possible packing results in the spheres occupying a volume fraction (ϕ) of a little over $\phi = 0.74$ within the whole volume (323). That is, the cream layer will contain a maximum of around 74% by volume of dispersed phase droplets. In practice however the polydispersity of emulsion droplets can permit a closer degree of packing. Other factors can also influence the closeness of the packing. Flattening of droplets against each other will reduce the cream volume whilst the presence of lamellae between adjacent droplets will produce the opposite effect. Furthermore, under normal conditions the cream may not achieve the densest possible arrangement of droplets, but a more open loose network within which a further amount of continuous medium is trapped. The exact contribution of these effects remains in some doubt. For example Lissant (323) has suggested that flattening of droplets becomes important in polydisperse systems at $\phi > 0.90$ and dispersed phase volume fractions of $\phi = 0.94$ or greater were visualized. Van den Tempel (88) allowed continuous phase to evaporate gradually from a liquid paraffin/water emulsion. A sharp increase in the rate of coalescence did not occur until the oil concentration reached about 93%. Moreover, emulsions containing dispersed phase concentrations as high as $\phi = 0.99$ have been reported in the literature (324). However, a very high degree of polydispersity would be necessary if the oil concentration was to rise above 90% or so (323, 324). Sherman (32) found that fresh emulsions of $\phi > 0.85$ could be prepared quite readily; but examination revealed that such systems assumed a complex multiple phase structure.

For every system examined in this study the limiting value of cream volume ratio (ϕ_c) was somewhat greater than the volume ratio of oil ($\phi = 0.20$) used to prepare the emulsion (Tables 4-7 and 4-11). The volume fraction of the cream layer, with $\phi = 0.20$, would be $\phi_c = 0.270$ and $\phi_c = 0.212$ respectively if 74% and 95% of the cream volume was occupied by dispersed droplets. The observed values of ϕ all fall between 0.23 and 0.28 but show little dependence on the nature of the oil phase. There is possibly a slight tendency for ϕ_c to increase as the stability increases with aliphatic hydrocarbon and hexane + longer chain alkane emulsions. For example, the ϕ_c values of hexane, dodecane, hexane + hexadecane and HLP are 0.24, 0.26, 0.26 and 0.28 respectively. This could be attributed to the effect on packing geometry of a narrower size distribution in the more stable emulsions. However this postulate is not substantiated by results for the aromatic oils which have ϕ_c values of 0.26 to 0.28 (except p-Xylene) and broad size distributions (Section 4.3.1.1). It is possible that the lower density difference ($\triangle p$) for these oils permits a lesser degree of packing. Emulsions of the alcohols cream extremely rapidly owing to the lower electrostatic repulsion and rapid droplet aggregation (Section 4.3.1.5) but each shows a similar cream volume to the other oils ($\phi_c = 0.25$ to 0.27). In the presence of alcohols the creaming of hexane emulsions is largely unaffected (ie. $\phi_c = 0.23$ to 0.25).

The cream volumes comprise between 71.4 to 87.0 per cent of dispersed oil which indicates that the effect of distribution of sizes is to decrease the cream volume slightly, though this is offset in many instances by a loose degree of droplet packing.

5.3.2.2 Effect of creaming on stability

The stability of droplets in a creamed layer may be lower than those in a non-creamed emulsion owing to the long periods of close contact between droplets. Such conditions might be expected to offer the most favourable situation for coalescence to occur. In addition, the larger emulsion droplets tend to accumulate near the emulsion surface. Here the upward pressure exerted by the droplets in the cream is at its highest and the lamellae between droplets will be thinnest. Therefore the probability of coalescence should be increased (88) (Section 5.3.5). Nevertheless, creamed emulsions may be highly stable since the interfacial film will still resist droplet coalescence.

The results in Figure 18 illustrate the effect of agitating emulsions of hexane and hexadecane on their stabilities during the initial storage period. The initial changes in d_v for both samples were not significantly altered from those of the free standing systems, suggesting that coalescence is little affected by droplet creaming.

A more precise study of creaming effects by Hallworth & Carless (71) supports this view. Both creaming and increased aggregation (through the addition of sodium chloride) were reported as having a negligible effect on the stability of liquid paraffin droplets emulsified in SDDS; hexane and light petroleum emulsions were similarly unaffected until considerable coarsening had occurred, then the largest droplets coalesced more rapidly in the creamed and aggregated systems.

From the stability results (Section 4.3) it seems more likely that the onset of creaming is a result rather than a cause of emulsion coarsening for many of the hydrocarbon systems. Small droplets (diameter $< 1\mu m$) show extremely slow rates of creaming (Equation 1.1). If aggregation is known to be negligible, emulsion creaming may be an indication of the disappearance of small droplets. For instance, the presence of hexadecane as an additive in each of the emulsions hexane, cyclohexane and benzene, exerts little or no effect on interfacial tension (Table 4-4)and droplet charge (Table 4-15). The initial size distributions with and without additive are similar (Section 4.3) and aggregation effects should not be significantly altered. Neither should such a small amount of hexadecane (0.04 mol dm^{-3}) significantly affect the oil phase density. However, in each case emulsion creaming is relatively rapid in the absence of additive (Table 4-7) where the emulsions are unstable, whilst in the presence of hexadecane both creaming (Table 4-11) and coarsening occur extremely slowly.

It is interesting to compare the creaming rates of a range of hexane emulsions containing different additives. Assuming that the additive does not significantly alter the density of the dispersed phase or viscosity of the medium, the creaming rate will depend upon the droplet size or aggregation effects (Equation 1.1). Plate 4 provides an excellent illustration of this point. As can be seen from Table 4-11 the rate of creaming parallels the results on droplet size increase reported in Section 4.3.2.1, and therefore, may reflect the rapid rate of disappearance of small droplets. However, a comparison with the properties of alkanol emulsions (Table 4-7) or alkane emulsions at higher surfactant concentrations (Section 4.3.4), both of which exhibit very rapid creaming owing to aggregation, illustrates the potential hazard of using creaming rate per se as a parameter of emulsion stability. Nevertheless such measurements have been reported as an index of stability (49,325).

5.3.3 Viscometry and stability

The measurement of rheological properties during the ageing of an emulsion appears to offer a sensitive means of detecting changes within the system with the added attraction that dilution, which may itself affect stability measurements, is avoided. Certainly it has been shown on a number of occasions that rheological properties can be dependent upon the particle size or distribution of sizes in dispersed systems (38,62b,326-328). However, the rheological behaviour of emulsions is also influenced not only by other properties of the dispersed phase (eg. phase volume ratio ϕ or viscosity) but by the nature of both the continuous medium and the surfactant. The whole range of factors affecting emulsion rheology have been catalogued and reviewed by Sherman (19b,40,62b). The effect of emulsion ageing on rheological properties has also been investigated in considerable detail (32,39) with a view to relating such changes to emulsion stability.

For emulsions in which an increase in mean droplet diameter was accompanied by only slight changes in the limits of the size distribution, the rate of decrease in relative viscosity (η_r) has been related to the rate of increase in mean volume diameter (d_v) (32,39). By measuring η_r at a high shear rate the effect of droplet aggregation (which would tend to increase η_r as the emulsion aged) was eliminated. By plotting the resulting viscosity data against the mean separation distance (q) of droplets, obtained from

$$q = d_v \left[(\phi\text{max}/\phi)^{\frac{1}{3}} - 1 \right] \qquad 5.7$$

(where ϕmax is the maximum volume fraction of dispersed phase which can be incorporated into the emulsion), it was found that the effect of a change in q on η_r was the same for freshly prepared or aged w/o emulsions and therefore that an increase in d_v was the only ageing process having a measurable effect on η_r (39). The same was also true of o/w emulsions though the possibility of internal circulation within the droplet and droplet distortion (which tend to reduce and increase η_r respectively) was greater (35).

The viscometric observations reported in Sections 4.3.1.4 and 4.3.2.3 were originally intended as a convenient and rapid test designed to detect initial changes in each undiluted system. As such they were performed in a simple U-tube viscometer, that is at relatively low shear rate. The emulsions tested were of low phase volume ratio ($\phi = 0.20$) and initial viscosity (η_r^o). Under similar conditions Leviton & Leighton (329) found that the droplet size exerted no effect on η_r in dilute ($\phi < 0.30$) o/w emulsions. In spite of this significant changes in η_r are evident (Figures 22 and 27) which show sufficient similarity to changes in d_v (Figures 18,19 and 24) to warrant further comparison.

Figures 36A and 36B show plots of η_r against the values of d_v and estimates of q from equation 5.7 (assuming that aggregation effects are negligible and $\phi max = 0.74$ (Section 5.3.2.1)). From Figure 36A it appears that the principal factor determining the change in η_r for a range of emulsified oils is an increase in d_v. There is some scatter of points at both low and high q which could arise from errors in measuring d_v. For example, the aromatic oils appear to give higher initial η_r values than the alkanes, which could be due to greater number of very small droplets or droplet deformation arising because of the lower interfacial tension in aromatic oil emulsions. Some scatter is to be expected in considerably coarsened samples (high q) for which the photomicrographic size analysis becomes somewhat insensitive to slight differences in the numbers of small droplets, and where pronounced changes in droplet size distribution have occurred (39). As mentioned, the nature of the oil phase and the adsorbed film may also give rise to some differences in η_r (62b,161,162ab). Internal circulation and droplet deformation can also affect viscosity (see above) though these factors are probably negligible at low ϕ in the presence of surfactant provided the droplet size is not too large. The slight increase in η_r during the ageing of emulsions containing hexadecane as the bulk oil phase (Figure 22) or as an additive (Figure 27) is probably due to the aggregation of droplets which will immobilize some of the continuous medium and result in an apparent increase in ϕ. This effect is reduced by a high zeta potential and, for the other emulsions, it seems to be negligible compared with the large viscosity changes caused by an increase of q (Figure 36AB). However, aggregation may become more significant as the distribution of sizes broadens.

Not surprisingly, the scatter is much less for the emulsions containing additives (Figure 36B) which, excepting one, consist largely of hexane dispersed in SDDS solution. The oil phase properties are essentially constant and the size distribution remains fairly narrow throughout. The viscosities agree well with the values for a hexane emulsion at similar d_v although the fall in η_r is more gradual than for hexane alone. The absence of any apparent effect due to the mixed adsorbed film (SDDS + hexadecanol) is noteworthy.

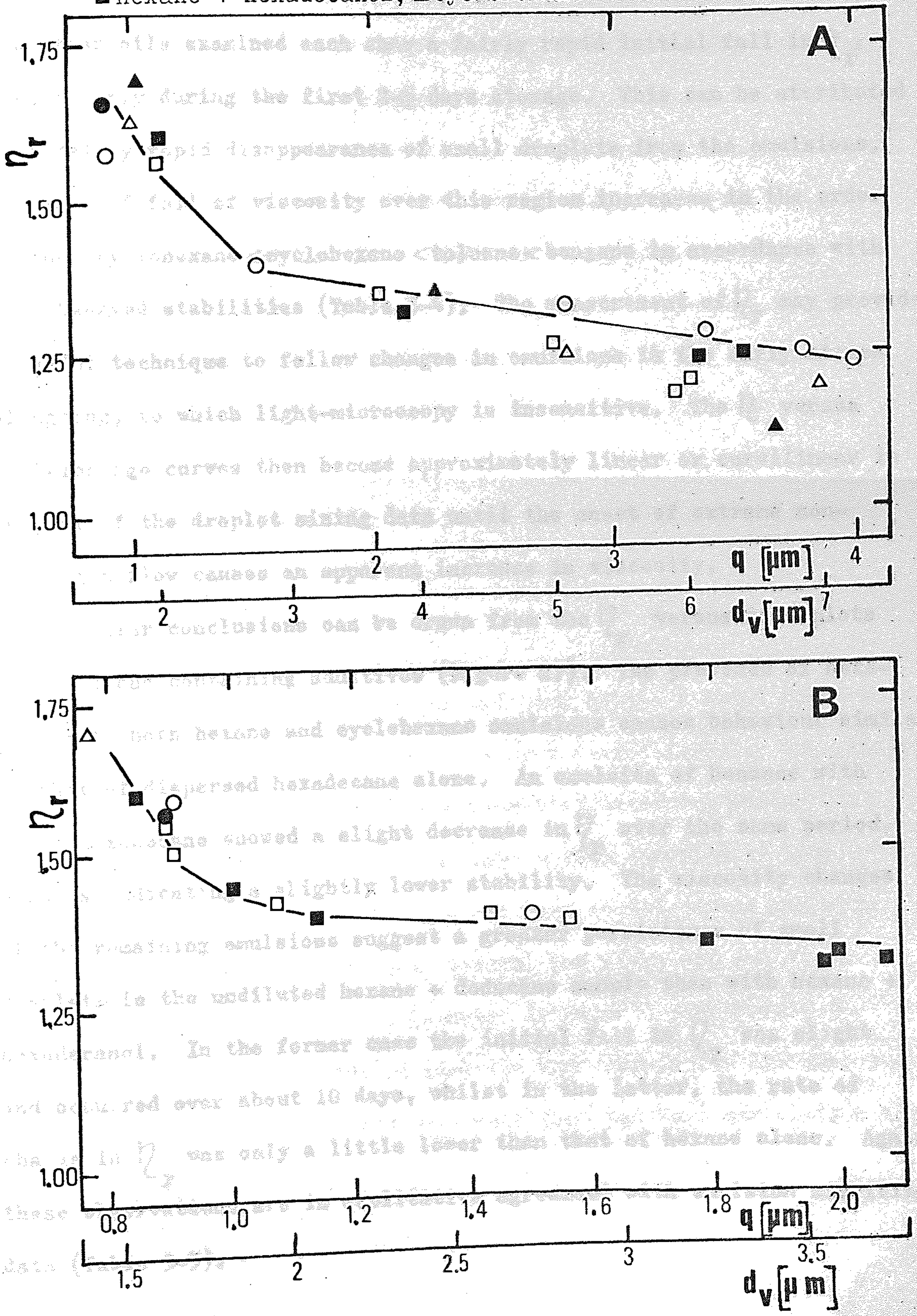
In both Figures 36A and 36B the value of η_r falls a little more sharply where $q < 1\mu m$ although the actual values of q in this region are probably overestimated. It was shown by Sherman (38) that emulsion viscosity began to increase sharply when the separation distance q fell below a critical value. Conversely, the value of η_r should be highly sensitive to changes in q and d_v within this region. These effects were less pronounced in o/w emulsions than in w/o systems, presumably because of the lower viscosity of the adsorbed film. Where q is significantly greater than 1µm the sizing and viscosity data show an approximately linear relationship (Figure 36AB).

FIGURE 36

THE INFLUENCE OF MEAN VOLUME DIAMETER (d_v) AND MEAN DISTANCE OF SEPARATION (q) OF DROPLETS ON η_r DURING EMULSION AGEING.

A For a range of oil phases:
○hexane, ●hexadecane, □cyclohexane, ■cyclohexene,
△benzene, ▲toluene.

B For emulsions containing additive (0.04 mol dm^{-3}):
○hexane, ●hexane + hexadecane, □ hexane + dodecane,
■hexane + hexadecanol, △cyclohexane + hexadecane.



Qualitatively at least, the measurements recorded for η_r for each of the unstable emulsions can be related to changes in d_v during ageing. The viscosity data plotted in Figure 22 reflects no marked coarsening of hexadecane during the total ageing period, though there appears to be some effect due to aggregation as emulsion age increases. The other oils examined each show a fairly rapid initial fall in η_r, particularly during the first 2-5 days storage. This can be attributed to a fairly rapid disappearance of small droplets from the emulsions. The rate of fall of viscosity over this region increases in the order hexane < cyclohexane < cyclohexene < toluene < benzene in accordance with the observed stabilities (Table 5-4). The measurement of η_r may provide a useful technique to follow changes in emulsions in the early stages of ageing, to which light-microscopy is insensitive. The η_r versus emulsion age curves then become approximately linear or curvilinear in support of the droplet sizing data until the onset of extreme non-Newtonian flow causes an apparent increase in viscosity.

Similar conclusions can be drawn from the η_r versus time plots of emulsions containing additives (Figure 27). The presence of hexadecane in both hexane and cyclohexane emulsions causes behaviour similar to that of dispersed hexadecane alone. An emulsion of benzene with added hexadecane showed a slight decrease in η_r over the same period, perhaps indicating a slightly lower stability. The viscosity changes of the remaining emulsions suggest a greater persistence of small droplets in the undiluted hexane + dodecane sample than with hexane + hexadecanol. In the former case the initial fall in η_r was slight and occurred over about 10 days, whilst in the latter, the rate of change in η_r was only a little lower than that of hexane alone. Again, these observations are in qualitative agreement with emulsion stability data (Table 5-5).

5.3.4 Kinetics of emulsion breakdown

The problems involved in deciding upon an appropriate index of stability have been introduced in Section 1.2.2. As emulsions coarsen the average droplet size, the breadth and shape of the distribution, and possibly its skewness all change. These quantities characterize the emulsion though it is usually necessary to suppose that the size distribution takes a simple mathematical form (Section 1.2.2.2). More usually emulsions are characterized by average quantities such as the droplet size, droplet volume or interfacial area. In order to collate experimental observations several rate laws have been derived.

The first exhaustive study of the coalescence kinetics of soap stabilized emulsions was made by King & Mukherjee (75). The best representation of the coalescence rate was found to be a relation between the specific interface (S) and emulsion age. A stability factor (f) was defined as the reciprocal of the decrease in specific area per unit time per unit interfacial area:-

$$\frac{-dS}{dt} = \frac{S_o}{f} \qquad 5.8$$

where So is the initial specific interfacial area. A short rapid rate of change in S was found, followed by a much slower rate for the remaining period of emulsion storage. Subsequently Lotzkar & Maclay (81) assumed that the change in S was an exponential function of time. Approximately linear plots of S (logarithmic scale) versus emulsion age were obtained for cottonseed, mineral and olive oil emulsions stabilized with macromolecules (acacia, tragacanth and pectin). Jellinek & Anson (77) evaluated numerous expressions for the measurement of stability kinetics but concluded that the best correlation was between S and emulsion age.

These relatively simple treatments of the kinetics of emulsion breakdown were formulated on the basis that emulsions were unstable owing to a large interfacial area of the dispersed phase, so that a reasonable representation of coalescence should be a measure of the decrease in the specific interface with time. The results obtained were in reasonable agreement with this theory.

In the present study this is not the case. The most unstable systems (benzene, toluene, xylenes, cyclohexene, hexane and hexanol) show a very rapid change in specific interfacial area during the first 5 days ageing, (Figures 20 and 21) which results in the presence of numerous large droplets and a broad droplet size distribution (Figure 17). This initial period of coarsening can be adequately represented by Equation 5.8 . Emulsions of intermediate stability (octane, decane, dodecane and decene) show similar behaviour during 15 to 25 days ageing, then plots of S versus emulsion age exhibit marked curvature as the rate of change in interfacial area becomes progressively slower. Hexane emulsions in the presence of various additives also show a sharp initial decrease in specific interface before the plots against time (Figure 25) assume a pronounced curvature. The highly stable emulsions show only a slight fall in S during long periods of storage and their stabilities can be described by Equation 5.8 .

The unstable systems and emulsions containing additives give a linear relation in log S versus time plots only over an initial ageing period comparable to that described above. For moderately stable emulsions the agreement is somewhat improved although deviations from linearity still appear after 25 days or more.

As a further attempt to linearize the results the relationship between specific interface and log (emulsion age) was tried but apart from an approximate correlation with the limited data for hexanol emulsions the fit was generally poor.

The stability of dispersions is frequently represented by the measurement of a rate constant for the fall in concentration of particles. The flocculation of hydrophobic sols has been treated in a kinetic study by Smoluchowski (330). His classical theory assumes that particles diffuse into contact and unite at the first collision. The proportion of collisions which result in the coalescence of stabilized emulsion droplets can be extremely small. Lawrence & Mills (79) have modified the Smoluchowski theory for emulsions by means of an efficiency factor for ineffective collisions. In this way an energy barrier to coalescence was estimated for stabilized systems. According to this modified theory the only functions to vary linearly with time are the mean droplet volume and the reciprocal of the number of droplets per unit volume of emulsion (N_v). This behaviour was confirmed for ditolyl and liquid paraffin emulsions ($\phi = 0.01$) stabilized with sodium oleate. Interestingly, other authors have reported a linear increase in N_v^{-1} with time for more concentrated emulsions, in formal agreement with this theory (77).

Using the data from Tables 4-5 and 4-8 the relationship between d_v^3 and emulsion age has been tested. All the plots showed some curvature as the age increased although the unstable emulsions again gave an approximately linear relation during the initial period of coarsening. The more stable alkane systems (ie. with 10 or more carbon atoms) gave the least deviations from linearity. The data from Figure 26 were also replotted as N_v^{-1} versus emulsion age; emulsions of hexane, hexane + hexadecanol and hexane + hexadecane gave approximately linear plots only within the range 0 to 25 days, followed by a slower rate of increase in N_v^{-1}.

According to Hill & Knight (80), the diffusion rate of droplets will determine colloidal stability only when the coagulation process is very rapid; when many encounters are required to unite the particles other factors such as the rate of coagulation itself, the collision frequency and the duration of collisions are of greater importance. A separate kinetic theory, not applicable to rapid coagulation, was developed for emulsion stability. It was assumed that droplets move as gas molecules and collide with a frequency predicted by kinetic theory rather than according to the diffusional model. Consequently, electrical effects were assumed to be negligible whilst collisions were considered of short duration and to involve only small droplet deformation. The theory derived by Hill & Knight predicts that the reciprocal of total droplet area should increase linearly with time. Such a relation has been found to hold for anisole and chlorobenzene emulsions well stabilized with cetomacrogol (65a) though it is less likely to apply to dispersions in ionic surfactants.

It is evident from Figures 20, 21 and 25 that reciprocal of the droplet area does not vary in a linear manner with respect to time over the entire range of emulsion ages examined.

Van den Tempel (87bc,88) has investigated the kinetics of emulsion breakdown in considerable detail. The processes of flocculation and coalescence were considered separately. It was postulated that flocculation proceeds according to Smoluchowski theory by the diffusion of oil droplets as affected by their mutual interactions. Coalescence was assumed to occur between aggregated droplets immediately upon rupture of the intervening aqueous film. It was argued, therefore, that flocculation could determine the rate of coagulation (flocculation and coalescence) in dilute systems of low or moderate stability whilst the coalescence rate controlled coagulation in more concentrated systems.

The rate of formation of aggregates was estimated from Smoluchowski theory (87b,88):-

$$N_v^t = N_v^o / (1 + a' N_v^o t) \quad , \qquad 5.9$$

where a' is the frequency of droplet collisions resulting in aggregation, N_v^o is the initial droplet number and N_v^t is the droplet number after time t.

On the assumption that the number of contact points between droplets does not alter (ie. aggregates consist of a large number of droplets and the distribution of droplet sizes does not alter considerably) and the stability of other contact points remains unaffected by coalescence, the following relation was derived (87bc,88):-

$$N_v^t = N_v^o \exp (-b't) \quad , \qquad 5.10$$

where b' is the rate of coalescence determined by the average life-time of the film separating droplets. The rate constant b' was derived from the gradient of the linear relation between $\log N_v$ and time. From equation 5.9 it is seen that the time necessary for combining half of the droplets into aggregates is $(a'N_v^o)^{-1}$ whilst about half of the flocculated droplets coalesce after a time b'^{-1}. The relative rates were predicted from the ratio $a'N_v^o / b'$ (87bc,88). Thus, if the ratio exceeds 1.0 flocculation is very rapid with respect to coalescence but if $a'N_v^o / b' < 1.0$ coalescence is rapid and flocculation determines the overall stability.

By varying the inital droplet concentration van den Tempel (88) confirmed that the coagulation of liquid paraffin emulsions ($N_v^o > 10^6$ cm^{-3}) stabilized with SDDS or Aerosol OT was determined by a first order rate of breakdown in which other droplet contact points were not affected by coalescence. A short initial period of more rapid decrease in droplet concentration was attributed to non-equilibrium of the adsorbed surfactant film.

The data plotted in Figure 26 indicate non-linear relations between N_v (logarithmic scale) and emulsion age. A gradual decrease in coalescence rate occurs with the unstable and moderately stable systems, which may indicate a reduction in the number, or increased resistance, of droplet contact points during emulsion breakdown (87b,88).

The initial coalescence rates for emulsions of hexane, hexane + hexadecanol and hexane + hexadecane stabilized with 10^{-2} mol dm^{-3} SDDS (Figure 26) are respectively 2.39×10^{-5}, 1.06×10^{-5} and 2.31×10^{-6} s^{-1}. A rate for "rapid coagulation" was estimated by van den Tempel (87b,88) to be $a' = 10^{-11}$ cm^3 s^{-1}. The corresponding value for liquid paraffin emulsion stabilized with 10^{-2} mol dm^{-3} SDDS was calculated to be about 10^{-10} to 10^{-11} cm^3 s^{-1} (88). Assuming such a rate in the present study for a hexane emulsion (ie. a relatively unstable system), then $a'N_v^o/b' = 4 \times 10^4$ to 4×10^5, where $N_v^o = 10^{11}$ cm^3. Consequently, the stability of the emulsions studied in the present work should be determined by coalescence with the flocculation rate having a negligible effect over the range of droplet concentrations involved (ie. about 10^8 to 10^{11} cm^{-3}).

In examining the kinetics of emulsion breakdown it is important to note that several workers have observed a changing rate of coarsening during emulsion ageing. In the presence of sufficient surfactant to provide a closely packed monomolecular film, an initial fast fall in droplet concentration lasting up to 24 hours and followed by a slower linear change, has been reported for liquid paraffin emulsions stabilized with SDDS (88) or sorbitan monolaurate (90). King & Mukherjee (75) have reported a similar two-phase fall in interfacial area for soap stabilized emulsions of kerosene and olive oil. Van den Tempel (88) has attributed such behaviour to an initial non- equilibrium condition at the interface, or to a change in droplet packing and the number of contact points between droplets. Sherman (90) suggests that the adsorbed film around small droplets is initially loosely packed because these droplets compete less successfully than droplets with a larger radius of curvature, for surfactant molecules. Therefore, the smaller droplets coalesce at a faster rate than larger droplets.

Other workers have produced arguments for the more rapid disappearance of small droplets. Higuchi and others (153,331) have shown that an initial period of rapid coalescence may occur where stabilization is due primarily to electrical repulsion. For moderately stable systems, from DLVO theory (Section 1.2.3.2) it was predicted that small droplets may aggregate or coalesce with themselves or larger droplets at rates up to 50 times that of particles ten times larger (331). Higuchi *et al* (153) subscribe to the view that a low degree of condensation of the adsorbed film in fresh emulsions accounts for a period of rapid coalescence. It was argued that initially the surfactant molecules are displaced more easily and that stability is predicted by VR (Section 1.2.3.2) calculated for a constant surface potential. As the interfacial area falls, so the film becomes more closely packed and the increased VR (and therefore stability) was predicted by a model for constant surface charge.

The theory of molecular diffusion also predicts that small emulsion droplets will disappear more rapidly from the emulsion through dissolution (even for oils with fairly low solubilities) and diffusion to larger droplets (49,331,332)(Section 5.3.6).

The present observations, with emulsions of low or moderate stability, show a rapid rate of coarsening during the first few days of ageing. In general, however, the stability measurements indicate a gradual decrease in the rate of emulsion breakdown rather than a simple two phase process. Viscosity measurements show a rapid initial fall followed by an approximately linear decrease for moderately stable systems (Figures 22 and 27) but droplet counting (Figure 26), which is the most sensitive measure of changes in relatively coarse emulsions, again shows a progressive decrease in the rate of breakdown. Similarly, curved plots of logN versus emulsion age have been reported recently for paraffin emulsions stabilized with SDDS (71,91,92), and CTAB or sodium dodecyl benzene sulphonate alone or in mixed films with polyvinyl alcohol (93). In each case this behaviour has been interpreted, through the theory of van den Tempel (87bc,88), as a gradual reduction in the number of droplet contact points and/or an increase in the resistance of each contact point to rupture as coalescence proceeds. It may be that the simple first-order approach is inadequate to describe the kinetics of emulsion breakdown. Van den Tempel (88) restricted droplet counts to $N_v^t > 0.4N_v^o$ and stipulated that the droplet size distribution should not broaden considerably during measurement, in order to avoid significant changes in the number of contact points. This factor must exert an effect after considerable coarsening has taken place. However, several of the emulsions studied in the present work show a slowing in the rate of breakdown when the size distribution remains narrow and N_v^t is considerably greater than $0.4N_o$ (see Figure 26 for example).

There is some indication that the resistance of droplet contact points to rupture increases. This will occur if the packing of surfactant molecules at the interface becomes more complete. Initially, as small droplets disappear, the interfacial film may become considerably more condensed (153). If it is assumed that the limiting area per adsorbed molecule (A) is about 0.60 nm^2 for the alkanes and 0.70 nm^2 for aromatic oils, the concentration of surfactant in the aqueous phase should reach the cmc at specific interfacial areas (S) of below 2.9×10^4 and 3.37×10^4 cm^2 cm^{-3} respectively (Table 5-6). In none of the emulsions studied (excepting possibly the mixed systems containing SDDS and an alkanol) should the surfactant concentration be significantly depleted. Therefore, a short period of ageing should be sufficient to provide a saturated adsorbed film around the oil droplets (88,90). (See also Section 5.3.5.1). In many of the systems studied d_v undergoes a two to five fold increase during the "initial" period of coarsening, which cannot be accounted for on the basis of a non-equilibrated film around the droplets. The investigations on the effect of ageing on electrophoretic mobility (Section 4.4.3) support the view that an optimum degree of interfacial packing arises in a relatively short time.

A more condensed interfacial film can arise from the hydrolysis of SDDS to dodecanol during emulsion ageing. The non-ionic character of dodecanol enables it to co-adsorb strongly with SDDS. The presence of only a small amount of the alcohol can exert a profound effect on the properties of an adsorbed SDDS film and emulsion stability (Sections 1.2.5 and 1.3.3.4) and could account for the apparent increase in resistance of the film to rupture. There is some doubt as to the rate at which SDDS hydrolysis occurs. Harrold (261) found that the surface tension of a 7.9×10^{-3} mol dm^{-3} solution of SDDS fell by almost 2 mN m^{-1} during the first 24 hours of storage. The same author detected a minimum in the surface tension versus log concentration plot (Section 2.2.2.2) after this period. Motsavage & Kostenbauder (333) found that the rate of hydrolysis in acidic medium was accelerated by interfacial adsorption or by the presence of micelles and that hydrolysis was autocatalysed by the dodecanol formed. However, studies carried out on neutral or alkaline solutions of SDDS have shown that the hydrolysis occurs slowly and the rate is little affected by interfacial adsorption or by raising the surfactant concentration above the cmc (334,335). Nogami et al (335) first detected SDDS hydrolysis after 5 to 10 days in solutions above the cmc and stored at 70°C.

It seems probable that the hydrolysis of SDDS to dodecanol can contribute to a fall in the rate of droplet coalescence during ageing. The effect should be negligible until several days (at least) have elapsed, particularly if the original surfactant sample is of high purity and the aqueous phase solutions are freshly prepared. Wide differences in emulsion stability have been observed during an initial ageing period throughout which there is an approximately linear change in the various stability parameters such as specific interfacial area, mean volume diameter and droplet concentration. Simple stability parameters such as the rate of change in S or d_v appear to provide a reasonable means of quantifying the quite large differences in stability for the present range of systems. The stability factor (Equation 5.8) is given in Table 5-4 for emulsions of various oils, and in Table 5-5 for emulsions containing additives. The significance of various properties of the oils and additives given in Tables 5-4 and 5-5 are discussed below.

5.3.5 The influence of dispersed phase composition on droplet coalescence

The results (Section 4.3.1) indicate that stability has a definite dependence upon the nature of the oil phase in emulsions stabilized with SDDS. The stability factor (f) obtained from Equation 5.8 is given in Table 5-4 for a range of oils. In general, an increase in the polarity of the oil phase causes a decrease in stability. This conclusion is consistent with previous observations on various emulsion systems (Section 1.2.5). The order of increasing stability for cyclic oil emulsions is benzene < toluene < p-xylene < o-xylene < cyclohexene < cyclohexane. Changes occur extremely rapidly in the initial ageing period of these emulsions and oil separates freely within a few days (Table 4-7). The alkanes produce emulsions of greater stability and there is also a definite relationship between stability and the hydrocarbon chain length of the oil, alkanes with longer chain lengths giving more stable emulsions. The introduction of unsaturation into the alkyl chain of the oil causes a slight fall in stability.

Emulsion stability is enhanced by the inclusion of a long chain aliphatic alcohol into the oil phase, the longer the chain length of the additive the greater its stabilizing effect (Table 5-5). Similar observations have been made by numerous workers (Section 1.2.5). Not surprisingly, the alcohols produce highly stable emulsions when dispersed alone in SDDS solution (Table 4-5). A marked increase in the stability of hydrocarbon emulsions (eg. hexane, benzene, cyclohexane) is caused by the inclusion of long chain alkane (eg. hexadecane) into the oil phase (Table 4-8). Indeed, such an emulsion exhibits a degree of stability almost as high as that of a dispersion comprising the long chain hydrocarbon alone in SDDS solution.

Generally, the stability factor f gives an adequate description of the relative stabilities of the systems studied during the first few days of ageing. Problems arise with a number of systems (particularly where C_{12} and C_{16} alkanes are included as additives in hexane emulsions) where a slight increase in the measured droplet size (or a fall of interfacial area) is followed by a high degree of stability. In these cases the f value tends to give a misleading impression of the overall stability, although a qualitative indication of relative stabilities is still obtained.

The influence of dispersed phase composition on emulsion stability has been examined in terms of the properties of the oil phase and their probable effects on the mechanism of coalescence.

Table 5-4 Emulsion stability for various oil phases; properties which may affect stability in the oil-SDDS solution (10^{-2} mol dm^{-3}) system.

OIL PHASE	Stability factor (f)	Interfacial tension $mN\ m^{-1}$	Spreading Coefficient $mN\ m^{-1}$	required HLB	Z mV	Oil-in-water solubility $mol\ dm^{-3}$
Hexane	7.3	5.4	9.6	11.0	129.1	1.10×10^{-4} a
Octane	50	6.9	5.6	10.0	124.6	5.79×10^{-6} a
Decane	68	7.1	3.1	-	121.9	3.87×10^{-7} a
Dodecane	75	8.0	0.9	9.5	116.7	4.71×10^{-8} a
Tetradecane	865	9.5	-1.3	8.5	115.1	3.54×10^{-8} a
Hexadecane	1550	9.5	-3.2	-	115.3	2.65×10^{-8} a
LLP	658	9.0	-3.7	-	118.0	-
HLP	1000	10.4	-6.3	-	115.1	-
Cyclohexane	6.0	5.5	3.4	12.0	125.6	6.50×10^{-4} b
Decene	53	6.5	4.1	-	118.2	-
Cyclohexene	4.2	4.5	2.9	-	116.1	2.60×10^{-3} b
Benzene	1.8	5.2	0.3	12.0	114.4	2.28×10^{-2} b
Toluene	2.5	5.0	-0.9	12.0	123.3	5.59×10^{-3} b
o-Xylene	4.0	5.0	-1.3	12.0	121.6	1.65×10^{-3} b
p-Xylene	3.3	-	-	12.0	125.6	1.79×10^{-3} b
Hexanol	4.2	(1.0)	(7.3)	-	98.9	6.95×10^{-2} b

NOTES a Reference (361ab) b Reference (271)

Table 5-5

The stability of hexane emulsions in the presence of various additives; hexane-water partition coefficient ($K_d(y)$) and partition coefficient ratio ($F_d(y) = K_d(y)/K_d$ (hexane)) for each additive; properties which may affect stability in the oil-SDDS solution (10^{-2} mol dm^{-3}) system.

ADDITIVE 0.04mol dm^{-3}	Stability factor (f)	Interfacial tension mN m^{-1}	Spreading coefficient mN m^{-1}	$k_d(y)^a$	F_d^a
None	7.3	5.4	9.6	5.0×10^5	1
Octane	5.5	-	-	7.7×10^6	15
Decane	25	-	-	1.3×10^8	260
Dodecane	28	-	-	1.1×10^9	2200
Hexadecane	35	5.5	9.4	1.9×10^9	3800
Octanol	10	-	-	3.5×10^2	7×10^{-4}
Dodecanol	14	-	-	1.1×10^5	2×10^{-1}
Hexadecanol	22	(1.0)	19.5	4.0×10^7	80

NOTES a see Section 5.3.6.3

5.3.5.1 The interfacial tension

The various oils manifest widely differing interfacial tensions when in contact with water (Table 2-3) or surfactant solution (Tables 4-1, 4-3 and 5-4). It has been argued that a low interfacial tension should favour a high emulsion stability (Section 1.2.3.2). This postulate is not supported by the present results, indeed, in some instances the converse appears to apply. For instance, the cyclic hydrocarbons exhibit the lowest tensions against aqueous surfactant solution (eg. benzene 5.2 mN m^{-1}, toluene 5.0 mN m^{-1}, cyclohexane 5.5 mN m^{-1}; against 10^{-2} mol dm^{-3} SDDS) and also manifest the lowest emulsion stabilities. The alkanes give somewhat higher interfacial tensions (eg. hexane 5.4 mN m^{-1}, hexane-P 7.1 mN m^{-1}, hexadecane 9.5 mN m^{-1}; against 10^{-2} mol dm^{-3} SDDS) which cannot explain their widely differing stabilities although the oils with lower interfacial tensions again produce the least stable systems.

Lawrence (118) suggested that a low interfacial tension could, in fact, favour the coalescence process by facilitating the initial dilation of the interface during droplet contact. The dispersal of one liquid within another is greatly facilitated by a low interfacial tension (58,336). Therefore, it might be expected that a standard procedure of emulsification would produce a more effective dispersal of oils (ie. greater interfacial area) exhibiting low tensions. Indeed, a direct relationship has been reported between the interfacial tensions of alkane hydrocarbons and their respective interfacial areas when dispersed in non-ionic surfactant (Tween 20 or Tween 81) solutions (336). This gives rise to an alternative explanation of any relationship between low emulsion stability and low interfacial tension. A large area of interface in an emulsion might succeed in depleting the surfactant concentration in the continous phase sufficiently to prevent the adsorption of a closely packed interfacial film around each droplet. Under such conditions an initial rapid rate of coalescence should be evident (Section 5.3.4). In order to examine this possibility the total interfacial area of dispersed oil has been estimated for a number of conditions using Equation 1.2 . The areas per adsorbed molecule (at the cmc) given in Section 4.1.1 have been used to calculate the total amount of SDDS adsorbed, and hence the concentration of surfactant remaining in the aqueous medium. The values obtained are listed in Table 5-6.

Table 5-6

Estimation of the concentration of unadsorbed SDDS for emulsions containing 20% by volume of oil in 10^{-2} mol dm^{-3} SDDS solution.

OIL PHASE	d_{vs} (μm)	Specific interface (10^4 cm^2 cm^{-3})	Area per molecule (nm^2)	Adsorbed molecules ($x10^{-19}$)	Aqueous phase concentration (10^{-3} mol dm^{-3})
Hexane	1.95	3.08	0.59	10.44	7.83
Decane	1.79	3.35	0.60	11.17	7.69
Cyclohexane	2.42	2.47	0.62	7.97	8.34
Cyclohexene	2.63	2.28	0.62	7.35	8.47
Benzene	2.36	2.54	0.71	7.15	8.51
Toluene	2.19	2.73	0.70	7.80	8.38
Specific interface required to lower SDDS concentration to a given level.	1.03	5.78	0.60	19.27	6.00
	0.82	7.23	0.60	24.09	5.00
	0.69	8.67	0.60	28.91	4.00
	0.59	10.14	0.60	33.73	3.00

If the aqueous phase concentrations in Table 5-6 are compared with the adsorption data in Table 4-1 it can be seen that sufficient surfactant remains to provide a "saturated" adsorbed film in all the systems considered. Although these calculations should only be regarded as approximate it is anticipated that a short period of coarsening would raise the surfactant concentration to the region of the cmc in all the emulsions studied. Calculation of the approximate interfacial area which will reduce the SDDS concentration from 10^{-2} mol dm^{-3} to a particular value (between 6×10^{-3} and 3×10^{-3} mol dm^{-3}) supports this statement (Table 5-6). For example, the alkanes cause the greatest lowering in SDDS concentration by adsorption. In order to affect the packing of the interfacial film significantly a surfactant concentration of 3×10^{-3} to 4×10^{-3} mol dm^{-3} or less would be required (Table 4-1). This can arise only if the specific interface is greater than about 8×10^{4} cm^{2} cm^{-3}, which corresponds to d_{vs} = 0.75µm. It is concluded that the large changes in droplet size distribution cannot be explained on the basis of surfactant depletion, and consequently, that the qualitative relationship between low interfacial tension and low stability does not arise through this mechanism.

Further evidence for this view comes from the measurements on systems containing equimolecular proportions of various additives in the oil. The stabilizing effect of added alkanol is accompanied by a marked decrease in interfacial tension (Table 5-3) and a measurable increase in initial interfacial area (eg. hexane = 6.14×10^{5} cm^{2}; hexane + dodecanol = 6.82×10^{5} cm^{2}) (Table 4-8). Similarly, emulsions of aliphatic alcohol dispersed in 10^{-2} mol dm^{-3} SDDS exhibit a high interfacial area and stability with a low interfacial tension. The presence of a small amount of hexadecane in hexane (for example) results in an extremely high degree of stabilization without significantly affecting the interfacial tension (Table 5-5).

In conclusion, there appears to be no direct relationship between the interfacial tension between an oil and surfactant (SDDS) solution and emulsion stability provided that sufficient surfactant is present to maintain a saturated monomolecular adsorbed film. In all the systems studied the interfacial tension represents considerable interfacial free energy.

5.3.5.2 The interfacial barrier

It is evident from Section 5.1.2.3 that the oil phase can exert a considerable effect on the nature of an adsorbed film at the oil-water interface. For example, an adsorbed film of SDDS is more expanded at the aromatic hydrocarbon-water interface than if the oil is an alkane. These observations have been discussed in terms of the degree of oil-surfactant-water interactions within the interfacial region (Section 5.1.2.3). The aromatic hydrocarbon emulsions manifest low stability (Table 5-4) and a significant degree of coalescence is evident from the rapid separation of free oil (Table 4-11). It is reasonable to conclude that these emulsions are stabilized less effectively than those of alkanes as a result of the more expanded surfactant film. Not only does such a film afford less protection against coalescence but it should also be more easily displaced from the region of droplet contact. Similar observations have been recorded for dispersions of benzene stabilized with potassium laurate (70) and anisole or chlorobenzene stabilized with non-ionic surfactants (37a).

The results obtained using different alkanes are more difficult to explain. Emulsion stability increases markedly as the alkane chain length is increased (Table 5-4). However, adsorption studies suggest that the surfactant film may become more expanded as hydrocarbon chain length increases, although this effect may arise as a result of impurities in the oil phase (Section 5.1.2.3). A number of authors have reported an apparent increase in the area per adsorbed SDDS molecule at an alkane-water interface with longer hydrocarbon chain length (71,237). More recently however, Buscall & Davis (240) have challenged such observations; no evidence was found to suggest that the degree of SDDS adsorption varied with the chain length of alkanes at highly purified oil-water interfaces.

Irrespective of whether the area per adsorbed molecule increases with the longer chain length alkanes, or remains constant, the relative stabilities of the alkane emulsions evidently cannot be explained simply in terms of the amount of surfactant adsorbed.

The most obvious explanation for the behaviour of emulsions of alkanes, or those containing long chain alkane as an additive, is that the longer chain length homologues are increasingly contaminated with surface active impurity. The contaminant could then be co-adsorbed with alkyl sulphate molecules to produce a more coherent interfacial film. Even small quantities of such an impurity can exert profound effects on interfacial properties such as film compressibility (117c), interfacial mobility (280a,306) and viscosity (125,126), all of which may influence the coalescence mechanism (Sections 1.2.3.2 and 5.2.3). Nevertheless, the results from interfacial tension studies do not suggest that a high emulsion stability in the presence of extremely small quantities of hexadecane results from impurities. The relative stabilities of emulsions containing various grades of aliphatic hydrocarbon, and the observation that purification of hexane and hexadecane samples failed to alter the properties of these emulsions appreciably (Section 4.3.3), support the conclusion that any contaminants present did not play a major role in determining stability.

Emulsions which manifest different stabilities must resist coalescence to varying degrees. Cockbain & McRoberts (104) suggested a mechanism of coalescence involving displacement of the interfacial film into the dispersed phase. High stability was therefore favoured by high resistance of the interfacial film to wetting by the dispersed phase. In this context Becher and others (1b,337) have correlated the spreading coefficient (Equation 1.8b) with emulsion stability for various oils dispersed in mixed surfactant systems. It was proposed that a negative oil-water spreading coefficient (s) was required for good emulsion stability. Furthermore, Rehfeld (173) found that the centrifugal stabilities of a series of alkane emulsions dispersed in SDDS solution was related to the respective spreading coefficients. Becher (1b) pointed out that droplets of non-spreading oils (ie. negative value of s) might tend to maintain a separate identity whilst a positive s value would allow the droplet to lose its identity at the emulsion surface. However, it was considered more probable that the spreading coefficient could be correlated with other properties of the system which are of significance in emulsion stability (see below). The measured coefficients for alkanes on water (Table 5-1) and 10^{-2} mol dm^{-3} SDDS solution (Table 5-4) decrease with an increase in hydrocarbon chain length. Spreading coefficients for the cyclic hydrocarbons are somewhat higher than those for alkanes. Qualitatively at least, there is some agreement with previous findings. However this theory certainly does not explain the enchanced stabilization caused by the presence of hexadecane where the spreading coefficient remains unchanged, or long chain alcohols where the spreading coefficient is increased (Table 5-5). It must be concluded that spreading behaviour is not a principal factor in emulsion breakdown in the present study.

Similar conclusions also apply to the numerous correlations between stability and oil phase properties which change monotonically with chain length (eg. density, viscosity), but which cannot explain the stabilizing effects caused by small quantities of long chain alkane.

Sumner (321) proposed that coalescence could occur through the penetration of the surfactant film by dispersed phase. Closely allied to this is the observation that the aqueous lamellae separating oil droplets can rupture at different thicknesses depending on the oil phase (134). It was shown, for example, that the critical thickness for film rupture of aqueous non-ionic films between oil phases varies from 18.5nm for octane, to 19.5nm for chlorobenzene and to 21.0nm for cyclohexane. Such behaviour could contribute to the differences in stability between cyclic and aliphatic hydrocarbon emulsions. However it is unlikely that slight differences in lamellar thickness can account for the widely variant stabilities of alkane emulsions.

It has been pointed out earlier that the structure of water near the surface of a solid or a liquid is different from that in the bulk phase (Sections 1.3.1 and 5.1.1). The hydration layers around a particle may differ in density and viscosity from bulk phase water. The general concept of interfacial water at the oil-water boundary is of several layers of molecules being oriented to form a layer of "soft ice" of a few nanometres thickness, the properties of which approach those of bulk water at an increasing distance from the surface (117a). The modifications in water structure are undoubtedly influenced by the nature of the other surface. For example, a mechanism has already been described whereby "icebergs" can form around non-polar groups such as hydrocarbon chains in water (Section 5.1.1). It is conceivable that similar structures may be formed around the surface of hydrocarbon droplets. This is in contrast to the opinion of MacRitchie

(138) that no orientation of water should occur at an interface with paraffins. There is no doubt that the presence of adsorbed surfactant molecules will further alter the interfacial structure. The water phase is involved in interactions with the polar "head" groups at the interface through ion-dipole or dipole-dipole attraction and through hydrogen bonding (117a,338). For example, ionic species adsorbed at the interface can produce polarization and orientation of water molecules; for long chain alcohols the hydroxyl group dipole may succeed in orientating the dipoles of water molecules to develop a structured layer.

Davies & Rideal (117a) suggested that oriented "hydration sheaths" might influence emulsion stability by preventing the close approach of oil droplets. They anticipated that ionic groups should orientate a considerable number of water molecules. Such a stabilizing mechanism could give rise to variations in stability depending on the chemical nature of the oil phase. It was further proposed that the inclusion of a long chain alcohol with an ionic surfactant would increase the water of hydration and hence improve emulsion stability. However de Vries (339) opposed this view, suggesting that alcohols of different chain lengths should be equally effective by this mechanism, whereas in practice long chain alcohols were the better stabilizers. In a review of emulsion stability Kitchener & Mussellwhite (45) explain the phenomena formerly ascribed to hydration sheaths by electrical forces or steric factors arising from the adsorbed molecules. One principal objection to stabilization by structured water is that the organized layers probably extend over only a short range insufficient to prevent the increasing van der Waals forces of attraction from bringing droplets into contact. Perhaps significantly, similar considerations of colloidal stability have suggested that a repulsion barrier arising from the structuring of water around particles may be important at very low surface potentials, but insignificant where electrical repulsion is large (340,341). By analogy with the micellar surface, a degree of structuring might be anticipated where SDDS is adsorbed; for a surfactant concentration not too far in excess of the cmc it has been suggested that only one or two layers of water molecules are orientated around the micelle (342). It remains unlikely that the observed variations in emulsion stability arise through differences in the amount of structured water at the oil-water interface. Such a conclusion is also suggested by the wide range of stabilities obtained with emulsions of alkanes or alkane mixtures. It is not anticipated that a slight variation in the degree of hydrocarbon-water interaction with alkane chain length (Section 5.1.1) would give rise to sufficient differences in interfacial structure to explain such results. In the presence of long chain alcohol there is some indication from electrophoretic measurements (Section 4.4.2) that the thickness of a structured layer may be increased slightly, although the contribution of such a factor to stability is unknown.

It has been established that the chemical nature of an oil gives rise to a specific emulsifier HLB necessary to produce a stable emulsion (Section 1.2.4). The so-called required-HLB (or critical-HLB) is therefore an empirical quantity which may usefully describe the behaviour of dispersions of various oils stabilized by a particular surfactant. Although the available number of required-HLB values is limited those compiled by Lo _et_ _al_ (170) enable some degree of comparison with the present stability data (Table 5-4). For example, values for the alkanes fall from a required-HLB of 11.0 for hexane to 8.5 for tetradecane, whilst further values for cyclohexane (12.0) benzene (>12), and toluene (>12) are also listed.

The relationship between empirical required-HLB values and other properties of the oil phase have been the subject of much speculation (1f). In a detailed study Lo et al (170) measured the required-HLB by employing various blends of non-ionic surfactant. For aliphatic hydrocarbons (C_6 to C_{14})the required-HLB could be inversely related to dielectric constant, whereas for hydrocarbons with the same carbon number but of different chemical types (hexane, cyclohexene and benzene) the required-HLB increased with dielectric constant. The latter result supports the correlation between dielectric constants of various oil phases and the required-HLB observed by Gorman & Hall (169). It is noteworthy that HLB value has long been considered to be related directly to polarity and therefore, it should be a function of any parameter which is some measure of polarity. In this context, a striking correlation between the spreading coefficient and required-HLB has been noted (1f, 337). The present emulsion stability results do in fact show a similar dependance (Table 5-4) upon the required-HLB and the spreading coefficient (see above). For the case of mixed oils the concept of an additivity rule for required-HLB has been questioned, therefore, it is difficult to predict the effect of a small quantity of additive on its value, although the required-HLB varies by only 2 units throughout the alkane series from C_5 to C_{14} and only slight effects would be expected when, for example, 0.04 mol dm^{-3} of dodecane or hexadecane was included in a hexane emulsion. It is important to note that some doubt has been cast on the validity of required-HLB by the observations that stable emulsions can often be prepared over a wide range of emulsifier HLB (170,343), and more significantly, that many surfactants giving an optimum HLB failed to maintain even moderate stability (170). Lo et al (170) were forced to conclude that more fundamental properties determined stability, and that an interaction between emulsifier molecules and those of the oil was probably the important factor. The use of surfactants of structure and polarity adapted to the structure and polarity of the oil was considered necessary, whilst the use of emulsifier mixtures with HLB equivalent to a required-HLB value for the oil was found not to be an adequate index.

Hallworth & Carless (71,92,126) have reported that emulsions of various petroleum fractions exhibit differing stabilities when dispersed in SDDS solution. Long chain length oils gave far more stable emulsions than the short chain fractions. This behaviour was attributed to the ease with which surfactant could be displaced from the region of droplet contact. It was postulated that alkyl sulphate molecules can associate with the long chain length oil molecules to form a more coherent film, and thus provide a more effective barrier against coalescence. The stabilizing effect of long chain length additives (alcohol or alkane) was also observed (91,92,126) and was presumed to result from the interaction of additive with surfactant molecules at the interface. This theory provides a plausible and attractive explanation of the relative stabilities of alkane emulsions as observed in the present work and consequently it has been examined in detail. One obvious reservation is that, even assuming that each of the twelve alkyl groups of the surfactant penetrates into the oil phase, a maximum interaction (and therefore maximum stability) should be achieved with dodecane as the oil phase. However, the stability of the C_{14} and C_{16} alkanes was found to be greater than dodecane (Table 5-4). The suggestion that as many as four or five alkyl groups of the surfactant may in fact be drawn into the alkane (heptane) medium by the polar head-group (344) must also detract from the interaction theory.

Further doubts arise in applying this theory when the effect of various additives is considered. It is known that in the presence of aliphatic alcohols the interfacial film becomes more condensed and should provide a more coherent and effective barrier to coalescence (Section 1.2.5). The suggestion that long chain alkane will behave in a similar manner (92,126) is open to question. Intuitively such behaviour would be expected to result in an increase in the interfacial free energy of the system. The argument for "adsorption" of the long chain alkane is not convincing from a strictly thermodynamic viewpoint. When an alkanol is dissolved in an alkane the activity coefficient of the solute at high dilution (j) is essentially independent of its chain length; therefore, the non-ideality of alkanols as solutes in alkanes ($j \simeq 15$ at 25°C) can be attributed wholly to the hydroxyl moiety (345a). The adsorption of an alkanol from an alkane to the oil-water interface is a result of the polar nature of the hydroxyl group whilst the contribution of the methylene groups to the free energy of adsorption is negligible (345b,346). In contrast, it can be supposed that a long chain alkane will behave almost ideally when dissolved in a shorter chain length homologue and there should be no tendency for the long chain component to concentrate at the interface (203b). The present results indicate that the inclusion of a long chain aliphatic alcohol in the oil increases the stability of a hexane emulsion, the effect becoming more pronounced as the alkanol chain length is increased (the C_{12} additive is less effective than the C_{16} on a molar concentration basis). Surprisingly, alkane additives are more effective in enhancing stability than the corresponding alkanols although the dependence on chain length is still apparent. Neither of these observations (the chain length effect above C_{12} or the better stabilization with alkanes) can be adequately explained on the basis of a simple "interaction" theory of stabilization.

It is known that normal hydrocarbons exhibit an increasing degree of crystallinity between the C_8 and C_{18} homologues (347b). This phenomenon or the resultant effect on oil phase viscosity (see below) could explain the relative stabilities of the alkane emulsions. However, such a mechanism would also require the preferential adsorption of long chain alkane to the interface. Furthermore, there is no evidence from interfacial viscosity measurements (125,126) to suggest that crystallinity is significant in saturated hydrocarbons at $25^{o}C$.

A possible explanation of the observations on emulsion stability, related to that just described, is that droplets are stabilized by a liquid crystalline phase (Section 1.2.5). Liquid crystal posesses almost gel-like physical properties and when formed at an oil-water interface in emulsions this phase tends to surround the dispersed droplets and prevent coalescence. Furthermore, the formation of liquid crystal in this way is known to be highly dependent on the chemical nature of the oil phase. Mixed surfactant systems such as the anionic surfactant-long chain alcohol or Span-Tween combinations tend to favour liquid crystal formation, particularly at high concentrations, and may exert a stabilizing effect on emulsions in this way (183-185,338,348). However, Hallworth & Carless (91) considered that the concentration of added alcohol (octadecanol) would have to be considerably higher than 0.015 mol dm^{-3} in order to permit a liquid crystalline phase to form. If this were so the concentration of added C_6 to C_{16} alcohols used in the present investigation (0.04 mol dm^{-3} in the oil phase) may also be insufficient. Again, the stabilizing effect obtained with long chain alkane as an additive can only be accounted for by the participation of a high proportion of these molecules in the interfacial structure. Furthermore, the surfactant film at interfaces of SDDS solution against the alkanes or alkane mixtures (without alcohol) remain in an expanded state which will reduce the probability of liquid crystal formation in these systems. Nevertheless, this aspect of emulsion stabilization cannot be discounted entirely without confirmative data from phase relation studies on the systems involved. Ekwall et al (338) has pointed out that types of liquid crystal can form even when the surfactant concentration is not great. It is also known that long chain alcohol is adsorbed strongly at the oil-water interface, even from dilute solution in the oil. It is concluded, therefore, that liquid crystal formation represents a possible but unlikely explanation for the present results.

The significance of hydrocarbon chain interactions (between oil and surfactant molecules) and the incidence of liquid crystal in promoting emulsion stability may yet be resolved by measuring the rheological properties of the interface (348,349). At present, however, measurements of the required exactitude are difficult to obtain (Section 1.2.3.2). Carless & Hallworth (125,126) have investigated this aspect of emulsion stabilization in some detail. The argument for an increased condensation of an adsorbed alkyl sulphate film by long chain alcohol (octadecanol) was supported by the observation of an increase in interfacial viscosity in the presence of alcohol and an associated increase in emulsion stability. The enhancement of stability was attributed to an increase in the visco-elasticity of the adsorbed film, thus preventing the displacement of alkyl sulphate ions and maintaining a high degree of electrical repulsion between adjacent or colliding droplets. However, it was also found that a small quantity of impurity in the oil can exert a quite considerable effect on interfacial visco-elasticity without any apparent influence on emulsion stability, and conversely, that a small amount of long chain paraffin can enhance the stability of an emulsion without a corresponding influence on the rheological properties of the interface. It is worth noting that the above study revealed no general correlation between the rheological properties of the interface and stability for various paraffin emulsions stabilized with SDDS. More recently Boyd et al (348) have investigated the rheological behaviour of various interfaces at low shear rates and have succeeded in demonstrating that the occurence of liquid crystal at an interface does give rise to visco-elastic interfacial films.

It seems appropriate at this point to review the role of rheological properties at the interface in emulsion stabilization. A complete description of the rheological behaviour of an interface must account for the resistance to shear at constant area (shear viscosity) and the resistance of the interface against changes in area (dilational viscosity). In addition, two elasticity coefficients, representing a shear modulus and a dilational elastic modulus are required (350). The significance of each of these parameters in determining emulsion stability remains somewhat obscure (Section 1.2.3.2).

Gibbs and Marangoni effects, which give rise to dilational elasticity (Section 1.2.3.2), are believed to promote the regular thinning of a draining film by opposing the lateral displacement of surfactant and extension of the interface. The presence of a high degree of elasticity is believed to play a positive role in the stabilization of foams (131, 140,350). In the same way elasticity may maintain the liquid lamella, and hence a barrier to coalescence, between contacting emulsion droplets although its precise contribution to emulsion stability is as yet unknown. It has been shown that dilational elasticity can give rise to immobilization in the interface of individual oil droplets in surfactant solutions and hence decrease the rate of drainage from lamellae (Section 5.2.3). It might be postulated that the more expanded surfactant film at a benzene-water interface (for example) should manifest a lower degree of elasticity than a film at an alkane-water interface. Such a mechanism could contribute to the lower stability of benzene and other cyclic hydrocarbon dispersions in relation to alkane emulsions. Furthermore, Mysels et al (139) have shown that the presence of small quantities of dodecanol cause a measurable increase in the dilational elasticity of SDDS films in air. Support for this observation has come from other workers (137, 140). Similar changes may occur at the oil-water interface in the presence of alcohol. Again, film elasticity could contribute to the higher stability of emulsions containing long chain alcohol. On the other hand it is difficult to envisage appreciable differences in the dilational elasticity of SDDS films at the various alkane-water interfaces, where the physical state of the film is similar in each case (Section 5.1.3) and the degree of interaction between film molecules should not vary significantly. However, wide differences in emulsion stabilities have been observed in these systems.

Of the four rheological parameters mentioned above, only the shear viscosity has been investigated experimentally to a significant extent. A high interfacial shear viscosity has the effect of retarding film drainage and surfactant displacement. The stability of foams has been partly attributed to a film viscosity effect (349,350). If conditions of shear prevail at the interface during coalescence the shear moduli of viscosity and elasticity should be important. It should be noted that mixed films of SDDS and hexadecanol (351) or octadecanol (126), which are known to enhance emulsion stability, have been found to give a measurable increase in interfacial viscosity. However various investigators (45,55,125,126,349) have failed to show conclusively that a relationship does exist between interfacial viscosity and emulsion stability. Films of "pure" SDDS at oil-water interfaces are generally found to posess low shear viscosity (125,349,350), whilst emulsion stability varies considerably.

Interfacial films frequently develop visco-elastic behaviour, which can be studied by analysis of the deformation-time relation of the film when subjected to a small stress. Sherman (124) has discussed the role of the various rheological moduli in preventing droplet coalescence. From a consideration of the net forces acting on contacting droplets he points out that a visco-elastic interfacial film will begin to rupture when the compressive force acting on a droplet exceeds a critical value. Provided that this rupture is sufficient, the adsorbed emulsifier becomes displaced and coalescence will occur. Consequently, in the absence of interfacial visco-elasticity the adsorbed film should rupture more readily when a compressive stress operates. There is some experimental evidence that high film visco-elasticity correlates with an enhanced emulsion stability (124,348). The investigation of SDDS films at air-water interfaces has indicated a low order of interfacial viscosity which increases with surfactant concentration. Some visco-elasticity develops only after a lengthy period of ageing (349). The inclusion of dodecanol has been shown to cause visco-elasticity in the film (137, 140) and appreciable yield value(the tension that the monolayer will sustain before flowing) (352). Brown _et al_ (352) found that yield value is reduced above the cmc of SDDS, presumably through solubilization of alcohol in the surfactant micelles. In the stabilization of paraffin emulsions by SDDS it has been postulated that the film becomes increasingly visco-elastic with the addition of octadecanol (and to a lesser extent, hexadecanol) and that this resulted directly in an increase in emulsion stability (91,92,126). However, in the same study some paraffin emulsions stabilized with SDDS showed high stability without evidence of visco-elastic interfacial films (126).

5.3.5.3 Electrical stabilization

The repulsion between two electrically charged spheres arises from the surface potential, Ψ_o (Equation 1.5). The measurement of electrophoretic mobility provides information regarding the magnitude of the electrostatic repulsive forces between such spheres, although the subsequent accurate determination of Ψ_o is not possible (Section 1.2.3.2). The substitution of Ψ_o by the zeta potential (Z) at the plane of shear is generally considered to give rise to little error. Further problems arise in predicting the energy barrier to close approach of charged bodies, particularly in emulsion systems where the effects of a distribution of droplet sizes, overlapping double layer, the magnitude of the Hamaker constant and the possible change in surface potential lead to uncertainty in the determination of overall interaction energy. The variation of surface potential during droplet approach is particularly important. The estimation of the repulsive potential VR from Equation 1.5 assumes that the droplets maintain constant potential as their double layers overlap. This can be achieved by rapid desorption or displacement of surfactant molecules (see below), which is likely if the surfactant film is expanded. More condensed films may maintain a constant surface charge during droplet contact or collision, and this may increase VR considerably (153).

The electrophoretic mobilities and estimates of zeta potential (from Equation 3.20) are given in Table 4-14 for a range of oils dispersed in SDDS (10^{-2} mol dm^{-3}) solution. For convenience the relevant values are also listed in Table 5-4. Droplets of the alkane emulsions carry the highest zeta potential (-115 to -130 mV) whilst that of cyclic hydrocarbons is somewhat similar (cyclopentane -131 mV; cyclohexane -125 mV). The introduction of unsaturation into either type of molecule causes a reduction in zeta potential (decene -118 mV; cyclohexene -116mV;

benzene −114 mV).

In general it appears that the mobilities and zeta potentials of the oil droplets can be related to the degree of surfactant adsorption at the interface (Section 5.1.2.3). Consequently, there is no striking correlation between the magnitude of Z and emulsion stability; some of the differences in stability can be explained in terms of a greater degree of adsorption, leading to increased repulsion between the droplets (see below), but there are notable exceptions. For example, the relation between alkane chain length and zeta potential is an interesting one. The observed decrease in Z with increasing alkane chain length (and stability) could arise from a lesser degree of adsorption at longer chain length (see Sections 1.3.3.3 and 5.1.2.3). An alternative possibility is that the faster coarsening of short chain alkane emulsions produces a more closely packed interfacial film, either by better molecular packing after coalescence (Section 5.3.4) or through the concomitant increase in SDDS concentration in the aqueous phase with a reduction in interfacial area (Section 5.3.5.1).

Notwithstanding the cause of differences in zeta potential with alkanes as the oil phase, there is an inverse correlation between changes in Z with chain length and emulsion stability for these systems. Furthermore, the inclusion of a small quantity of long chain alkane into the oil phase of a hexane emulsion has no significant effect on droplet charge but the stability of the dispersion is markedly enhanced. Even more remarkable is the measured fall in Z for emulsion droplets comprising or containing long chain alkanol, since this is also accompanied by an increase in stability. In the latter case the reduction of SDDS adsorption as a result of the adsorption of alcohol molecules is the most obvious explanation for a fall in Z. This possibility has been discussed in a previous section (Section 5.1.2.4) and was considered improbable. A change in the measured electrophoretic mobility, and therefore zeta potential, can arise in two ways, by a change in the charge density at the droplet surface or a change in the thickness $(^1/K^{i})$ of the double layer (see Figure 1). In this case it seems more likely that the fall in zeta potential results from an outward shift of the shear plane caused by adsorption of the alcohol, possibly through an increase in the thickness of structured water around each droplet (Section 5.3.5.2).

The range of zeta potentials measured varies from approximately -100 mV for the stable alcohols, to -120 mV for unstable cyclic hydrocarbons, to -130 mV for the alkanes. These potentials should give rise to energy barriers sufficient to maintain moderate or good stabilization against coalescence (113,158). Nevertheless, the poor correlation between the magnitude of Z and emulsion stability is supported by several previous observations (37a,71,91,153-155). When two droplets approach the ionic "head" groups of the surfactant tend to repel each other. In an expanded or mobile interfacial film the surfactant molecules may be dispelled from the region of closest approach by desorption into the aqueous phase or displacement around the droplet surface. The latter mechanism, originally proposed by Robinson (153), has been suggested as the main cause of discrepancies between zeta potential measurements and emulsion stability (48,65c). Robinson (153) postulated that a closely packed film which cannot be compressed easily would prevent coalescence through displacement of surfactant. The close approach of droplets should inhibit desorption of surfactant from the interface into the aqueous phase (104). Davies & Rideal (117c) have discussed the compressibility of interfacial films in some detail. The concept of two-dimensional compressibility (C_s) was introduced, the reciprocal of which was termed the surface compressional modulus (C_s^{-1}). The latter assumes the value of the surface pressure for ideal films, but increases progressively for more condensed films.

The stability results for the cyclic hydrocarbons relative to alkanes can be explained in terms of the lower repulsive potential and ease of displacement of SDDS films. The lower charge density on the droplets will allow thinner lamellae to form between benzene droplets than alkanes for example. The displacement of surfactant will be opposed by high elasticity and/or low compressibility in the film. The more expanded film should be less effective in opposing the displacement of surfactant, particularly if the proposed alkyl chain interaction of dodecyl sulphate ions in cyclic oils (Section 5.1.2.3) occurs, since this will further increase the compressibility. The relative stabilities for many of the systems can be explained on this basis, emulsion stability would be expected to increase in the order benzene < cyclohexane < hexane for example. The lower stability of unsaturated oils (eg. decene or cyclohexene) might also be due to a slightly greater expansion of the surfactant film and the lower zeta potential. Although the adsorption data in Section 4.1.1 do not confirm this view it may be that these are insufficiently accurate to detect the differences involved.

The high stability of emulsions containing alkanols suggest that resistance to displacement and compression are the important factors in stabilization. Despite carrying a slightly lower charge the emulsion droplets are more stable and the visco-elastic properties (Section 5.3.5.2) and lower compressibility of the more condensed film (117c) presumably resist film displacement and maintain the electrical barrier to coalescence. In the case of emulsified alkanes such a mechanism can describe the observed differences in stability through the increased interaction of surfactant with long chain oil molecules, as discussed previously (Section 5.3.5.2). Where a long chain alkane is present as an additive it is necessary that the minor component concentrates at the interface. The compressibility of SDDS films at any alkane interface should be similar, whilst the role of long chain alkane in producing enhanced viscous or elastic properties in the interface is in some doubt.

It is interesting to compare the stabilizing effect of hexadecane (0.04 mol dm^{-3}) on droplets of hexane or benzene. In the former case the emulsion assumes a high degree of stability. With benzene the stability increase is also very considerable but free oil separates more readily. Here the adsorbed film is probably more expanded, electrical stabilization is less and the elasticity and compressibility of the film favour coalescence. However, the droplet size distribution remains quite narrow! It is postulated that the largest droplets cream to the emulsion surface where they coalesce. Some evidence that coalescence is favoured at the surface where droplets remain in close proximity was introduced in Section 4.3.4. The short duration of a droplet collision in the bulk emulsion may reduce the probability of coalescence, there being insufficient time for the necessary rearrangement of surfactant to take place (65c). The creaming rate of emulsions containing hexadecane is considerably reduced, owing to the increased stabilization of small droplets. However, the prevention of creaming in unstable systems does not appear to influence the coarsening rate to any significant extent (Section 5.3.2.2).

Such observations provide some indirect evidence for the molecular diffusion route of emulsion degradation. Further correlations between this theory and the observed emulsion stabilities are discussed below (Section 5.3.6). It may also be significant that the proposed theory for coalescence describes the behaviour only of those systems which exhibit coalescence to a marked degree (by separation of free oil) relative to those which do not.

5.3.6 Influence of dispersed phase on molecular diffusion

5.3.6.1 General principles

The "molecular diffusion" theory of emulsion degradation was first presented in a semi-quantitative form by Higuchi & Misra (49). The possible importance of this process in emulsion coarsening had been mooted previously (88,353), whilst its significance in solid/liquid dispersions ("Ostwald ripening") was well established (354-355).

The theoretical argument for molecular diffusion is presented in Appendix IV. Its basis is that small particles demonstrate deviations in their physical properties as compared to larger particles or plane surfaces. Specifically, the vapour pressure, and therefore solubility, of small droplets is increased. Higuchi & Misra (49) concluded that this increase in solubility will make small droplets thermodynamically unstable with respect to larger ones; thus the small droplets will tend to dissolve as the larger ones tend to grow at their expense.

It is important to realize that a great number of factors will affect the rate of such a process in emulsion systems. It is evident that molecular diffusion depends upon the presence of very small droplets. As these disappear from the system the rate of coarsening will slow progressively. A significant increase in solubility of the oil phase will occur only for very small droplets. It has been reported, for example that the solubility of benzene will increase by about 5% (at 25°C) for droplets of 0.1 μm (357a). Similar values have been reported for the vapour pressure and solubility of small crystals (358). A distribution of sizes may cause small droplets to aggregate around large ones, a factor which should strongly assist diffusion. Creaming or a decrease in droplet size should have similar effects due to a reduction in droplet separation. On the other hand, it has been shown that attempts to reduce the diffusion rate by narrowing the droplet size distribution would probably affect the rate of coarsening only slightly (49).

It is assumed in the theory (49) that the emulsion degradation process is diffusion controlled in the external phase. Factors which affect the diffusion coefficient, such as the viscosity of the external phase, should affect the degradation rate (Appendix IV). Small velocity gradients, however, are unlikely to affect the degradation rate (49, 359). The diffusion coefficient will be markedly affected by any barrier to interface mass transfer. Higuchi & Misra (49) supposed that interfacial films, unless of the viscous polymeric or the polymolecular type, probably do not significantly affect the overall diffusion rate. However, adsorbed films of low molecular weight surfactants are particularly important in inhibiting interfacial turbulence (360) and the internal circulation of droplets (357b) both of which would promote diffusion. Recent investigations suggest that the presence of reversibly adsorbed molecules at an interface may, after all, reduce the rate of interfacial mass transfer (26,357b).

Another important aspect of the molecular diffusion theory is that the rate of transfer of solute from an oil droplet into water is dependent on the interfacial tension (Appendix IV). A reduction in tension will result in a slower rate of diffusion. However, the presence of small quantities of water dissolved in the droplet should have no appreciable effect on the diffusive rate (49).

5.3.6.2 Effect of oil phase

Molecular diffusion theory predicts that the greater the solubility of the oil phase in the continuous medium, the greater the instability due to droplet dissolution and growth. For a hypothetical system comprising droplets of 0.5 and 1.0 μm, in equal number concentrations, Higuchi & Misra (49) calculated the approximate limit at which the oil solubility would prevent degradation by the molecular diffusion route. It was shown that a solubility of 3×10^{-8} kg dm^{-3} will lead to only a 10% change in the radius of small droplets in one year if interfacial tension $\gamma_{ow} = 1.0$ mN m^{-1}. However, for a mixture of 0.05 and 0.10 μm droplets the corresponding changes will occur over one thousand times faster, through the stability being proportional to the cube of particle radius. Calculations show that for a solubility of approximately 10^{-3} kg dm^{-3}, submicron particles in the presence of larger particles should disappear within an hour !

It appears that molecular diffusion can contribute significantly to the instability of emulsion systems under certain conditions, even at surprisingly low oil solubility. Since instability by this process depends upon the solubility of the oil, molecular diffusion could provide an explanation for the observed effects of dispersed phase on stability. In Figure 37 the stability factor f (Table 5-4) is plotted against water solubility (271,361ab) for the hydrocarbon oils. It should be noted that the relevant parameter for stability in emulsion systems ought to be the oil solubility in the aqueous medium (SDDS solution). In this case solubility values will be higher than for water but the range of values required are not documented. It is assumed, for the purpose of evaluating the molecular diffusion process that the relative magnitudes and order of solubility will not be altered significantly in surfactant solution. The order of stability for the hydrocarbon oils follows their respective solubilities (Figure 37). Similar conclusions can be drawn from correlations between the changes with time of mean volume diameter or viscosity and solubility (347a). The molecular diffusion theory also predicts that the rate of coarsening of an emulsion will decrease with time, as was found in the present work (Section 5.3.4). The slight deviations arising in Figure 37 for the xylenes can be explained since the stability has been assessed from rather limited data.

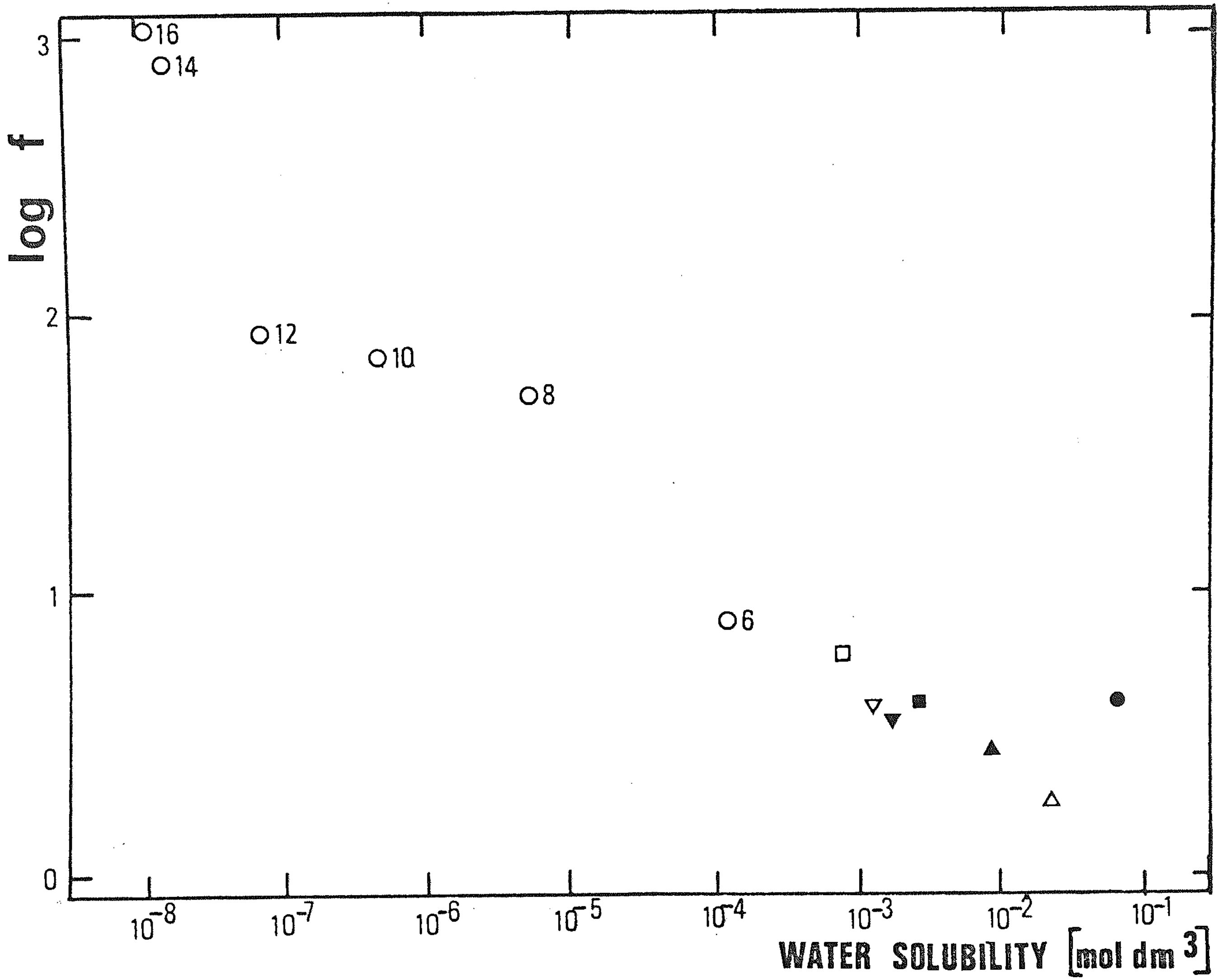
From Figure 37 it can be seen that emulsion stability is low when the oil solubility in water is somewhat greater than that of hexane (9.5×10^{-6} kg dm^{-3}). Stability is moderate for octane (6.6×10^{-7} kg dm^{-3}) and high for oil solubilities less than that of dodecane (8×10^{-9} kg dm^{-3}). For droplets in the micron size range with an interfacial tension (γ_{ow}) of 1.0 mN m^{-1} Higuchi & Misra (49) predict that emulsions should exhibit a high stability (10% increase in the radius of larger fraction of droplets in one year) if the solubility is less than 3×10^{-8} kg dm^{-3}). A similar calculation for interfacial tensions of 5 and 10 mN m^{-1} gives the limit of solubility as 6×10^{-9} and 3×10^{-9} kg dm^{-3} respectively. Corresponding changes would occur within a day (low stability) if the oil solubility was greater than 10^{-5} kg dm^{-3} for $\gamma_{ow} = 1.0$ mN m^{-1} (ie. 5×10^{-6} and 10^{-6} kg dm^{-3} where γ_{ow} is 5.0 and 10.0 mN m^{-1} respectively). From the particle size data in Table 4-5 it seems reasonable to compare these data to the present systems. The measured γ_{ow} values fall between 5 to 10 mN m^{-1} for the alkane systems in 10^{-2} mol dm^{-3} surfactant and the oil solubilities predict emulsion stabilities which are in good agreement with those measured.

These observations are by no means conclusive evidence for molecular diffusion, since several of the oil properties described previously (Section 5.3.5.2) give approximate correlations with the stability of hydrocarbon emulsions. Furthermore, the alkanol dispersions show an unexpectedly high degree of stability although the mean droplet size is extremely small (Table 4-5), and despite considerable droplet aggregation and a relatively high oil phase solubility. For example, the water solubility of hexanol is almost a hundred times greater than that of cyclohexene, yet the measured stabilities are almost identical.

FIGURE 37

RELATIONSHIP BETWEEN EMULSION STABILITY AND OIL PHASE SOLUBILITY FOR EMULSIONS STABILIZED WITH 10^{-2}mol dm^{-3} SDDS SOLUTION.

○ alkanes (carbon number shown), □ cyclohexane, ■ cyclohexene, △ benzene, ▲ toluene, ▽ o-xylene, ▼ p-xylene, ● hexanol.



This may well be due, at least in part, to the error involved in measuring d_v for fresh hexanol emulsions whose interfacial area may well be greater than that measured. Other factors which could account for an enhanced stability in alkanol emulsions are discussed below.

5.3.6.3 Effect of additives

According to molecular diffusion theory (Appendix IV) the inclusion of a component which is soluble in the dispersed phase, but with extremely low solubility in the continuous medium, can exert a profound effect on stability. The rate of emulsion breakdown will be retarded by a factor (F_d) given by the ratio of partition coefficients (K_d) for the components of the oil phase. Thus,

$$F_d = K_d(y) \; / \; K_d(x) \quad , \qquad 5.11$$

where $K_d(x)$ and $K_d(y)$ are the partition coefficients for the major and minor components respectively. As F_d increases the stabilization against molecular diffusion should increase. Higuchi & Misra (49) predict that about 1% of additive should normally be sufficient for emulsions in the micron size range if F_d is large. As droplet size decreases a larger quantity of additive or one with a higher F_d value must be employed to maintain stability. As interfacial tension falls correspondingly less additive is required.

The principal problem in relating the present stability results for hexane emulsions containing additives to molecular diffusion theory is in obtaining hexane-water partition coefficients for the determination of F_d values.

Provided that effects due to solute dimerization and/or ionization are negligible a relationship between partition coefficient and activity coefficient (j) can be used to advantage:-

$$K_d = j_w \; / \; j_o \quad , \qquad 5.12$$

where j_w and j_o are the respective activity coefficients of solute in water and oil at infinite dilution. It is reasonable to assume that a solution of an alkane in hexane is almost ideal, and therefore j_o (alkane) can be estimated without significant error (362) (Table 5-7). Also, the activity coefficient of an alkane in water is approximately equal to the reciprocal of its mole fraction solubility (346), which enables j_w to be estimated from the available solubility data (296, 361ab). The relevant values for j_o, j_w and K_d for the alkanes used are given in Table 5-7.

The partition coefficients for alkanols present a somewhat greater problem. Several measurements on K_d have been carried out on short chain length alkanols (345a), but values for the less water soluble higher homologues are difficult to obtain experimentally. Aveyard & Mitchell (345a) have determined the free energy of transfer from oil-water partition data for various alcohols (C_4,C_5,C_6 and C_7 n-alkanols) in C_8,C_{12} and 6_{16} alkanes. The K_d (alcohol) values were not affected by alkane chain length. By calculating log K_d values and plotting these against alkanol chain length a linear relation can be obtained. By assuming that the linear relation between log K_d (alcohol) and carbon number holds for longer chain alkanols (up to C_{16}) the values of K_d for octanol, dodecanol and hexadecanol have been determined graphically. These values are given in Table 5-8.

An alternative approach is to utilize the group contribution approach of Davis (363abc). By the subtraction of one -OH group value from the corresponding K_d (alkane) a theoretical value of K_d (alcohol) can be obtained. The conversion of a terminal methyl group to a methylene (363b) and the addition of an -OH group (363c) results in an overall change of approximately -3.66 in $\log K_d$ (363c). The K_d (alcohol) values calculated in this way are listed in Table 5-8.

The theory of group contribution can also be applied to estimate K_d (alcohol) from the activity coefficient values of lower homologues. The most useful data found cited in the literature was for octanol in the heptane-water system (318). The activity coefficients at 25°C were reported as $j_w = 1.23 \times 10^4$ and $j_o = 3.35 \times 10^1$, which gives $K_d = 3.7 \times 10^{-2}$ according to Equation 5.12 . The activity coefficient j_o will increase as the alkane chain length is decreased and K_d will be somewhat lower for the partition of octanol from water into hexane. Approximate values of K_d for higher alcohols can be obtained using the increment in log K_d per methylene group which is +0.62 (363a). The calculated partition coefficients are again listed in Table 5-8.

The K_d (alcohol) values obtained from activity coefficient and partition data for lower alcohols show reasonable agreement (Table 5-8). Not surprisingly the data obtained by group contribution considerations for the addition of an -OH terminal grouping to the alkane series shows some disparity, although K_d still increases significantly with hydrocarbon chain length. The difference arises because solubility values used to calculate K_d (alkane), and hence K_d (alcohol) do not increase in a regular fashion with carbon number. The solubilities of alkanes with chain length $> C_{11}$ appear to be greater than would be expected if the log solubility-carbon number relationship was a continouous function (361b). This behaviour has been attributed to a probable aggregation of alkane molecules (304,361b). No comparable behaviour has yet been reported for long chain alcohol molecules at high dilution in water although thisis possible. In the circumstances it was decided to proceed using the K_d (alcohol) values extrapolated from partition coefficients for lower alcohols. Although, inevitably, these are approximate, the qualitative conclusions relating molecular diffusion theory and emulsion stability should remain valid.

Table 5-7

Partition coefficient data for alkane hydrocarbons in the hexane-water system.

Solute	Mole fraction water solubility	Activity coefficients		Partition coefficients
		j_w	j_o	K_d
Hexane	2.0×10^{-6}	5.0×10^{5}	1.0	5.0×10^{5}
Octane	1.3×10^{-7}	7.7×10^{6}	1.0	7.7×10^{6}
Decane	7.0×10^{-9}	1.4×10^{8}	0.95	1.3×10^{8}
Dodecane	8.5×10^{-10}	1.2×10^{9}	0.95	1.1×10^{9}
Tetradecane	6.4×10^{-10}	1.5×10^{9}	0.9	1.4×10^{9}
Hexadecane	5.0×10^{-10}	2.0×10^{9}	0.9	1.9×10^{9}

Table 5-8

Partition coefficient data for alkanols in the hexane-water system

Solute	Partition coefficient (K_d)		
	(1)	(2)	(3)
Octanol	3.5×10^{2}	1.7×10^{3}	3.0×10^{2}
Dodecanol	1.1×10^{5}	2.5×10^{5}	1.0×10^{5}
Hexadecanol	4.0×10^{7}	4.2×10^{5}	2.5×10^{7}

NOTES:

(1) Extrapolated from data of Aveyard & Mitchell (345a).

(2) Group contribution from K_d (alkane) (Table 5-7)

(3) Group contribution from activity coefficients (318).

The values of K_d (y) and F_d for the range of additives employed in this work are collected in Table 5-5. The correlation between stabilizing effect of a minor component and its partition coefficient is striking. Both the effect of increasing the chain length of an additive and the greater stabilizing effect of alkanes than alkanols are predicted by Equation 5.11 .

In the presence of hexadecane as an additive the stabilization obtained is perhaps more noteworthy than is suggested by the specific interfacial area data and therefore by the stability factor in Table 5-5 (see Section 5.3.4). An initial fall in specific interfacial area occurs which was not observed with hexadecane alone (compare Figures 20 and 25), suggesting that the amount of added hexadecane is insufficient to stabilize the smallest hexane droplets. After the initial period, corresponding to only a small change in the measured d_v (from 2.0μm to about 2.5μm), the system assumes a stability almost as high as that of a hexadecane emulsion. Hexane emulsions containing an equivalent amount of decane or dodecane (0.04 mol dm^{-3} in the oil phase) display a gradually decreasing rate of coarsening as predicted by molecular diffusion theory. Octane exerts a barely perceptible stabilizing effect on hexane emulsion, an observation not inconsistent with predictions from the molecular diffusion concept of stability.

In contrast, the stabilizing effects of the aliphatic alcohols show some anomalous behaviour. When hexadecanol (0.04 mol dm^{-3} in the oil phase) is present in hexane emulsion the stability is slightly less than that obtained when decane is the minor component. This behaviour would be expected from the relative F_d values of the two additives. The initial rapid change in specific interface is significantly more pronounced in the presence of hexadecanol than with decane, possibly owing to the occurrence of a larger number of small droplets when alcohol is present (Table 4-8). In the presence of octanol or dodecanol a hexane emulsion coarsens at a rapid initial rate, as expected from their F_d values. The dependence of the rate of change in d_v or specific interface upon alcohol chain length in this region could arise from the original degree of dispersion (through a different interfacial tension for example). However, contrary to the predictions of molecular diffusion theory, a definite stabilizing effect has been obtained with octanol or decanol as additives to a hexane emulsion at longer storage times (Figures 24 and 25, Table 4-8). Similar behaviour has been noted earlier for emulsions of the alcohols as the oil phase (Section 5.3.6.2). The stability was found to be far greater than that which would be predicted through molecular diffusion and inspite of a greater incidence of small droplets.

Such behaviour may be partly due to the lowering of interfacial tension, and therefore molecular diffusion rate, in the presence of alcohol (49). For example, the tension shows a tenfold variation from about 10 mN m^{-1} for alkanes to 1.0 mN m^{-1} for alcohols, the effect of which corresponds to a tenfold decrease in solubility. It is also possible that adsorbed SDDS + alcohol films provide a greater barrier to interfacial mass transfer than does SDDS alone (Section 5.3.6.1). The mechanism of such an action is not well understood although it appears that several processes could be responsible. The suppression of interfacial turbulence and internal circulation in the droplet probably play a part but in addition the "blocking" of a greater area of the interface by adsorbed molecules is possible (357b). Also, more specific effects such as the mutual interaction of film molecules (234e) or interaction with the oil (91,92) could conceivably operate in reducing the rate of transfer of hexane across the interface (357b). The presence of a more condensed film when alcohol is present will also reduce any contribution of coalescence to instability (Section 5.3.5), which could account for the stabilizing effect of the shorter chain length alcohols.

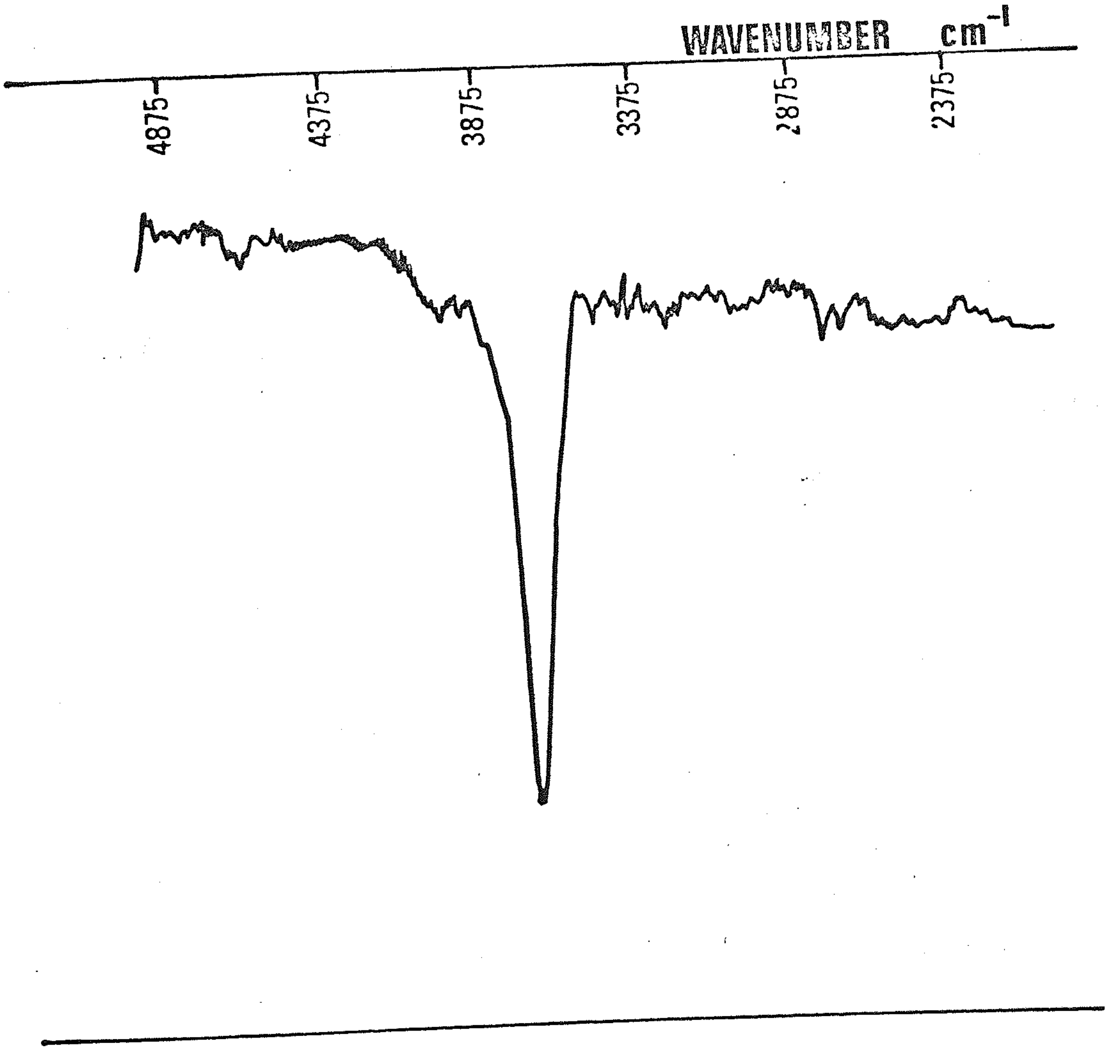
The alkanols are known to undergo appreciable self-association even at low concentration levels in alkane solvents (345a,364-366). The partition coefficient K_d (alcohol), and therefore F_d, will be increased if the alcohol associates in hexane (345a,357b). Such behaviour would offer an alternative explanation for the unexpectedly higher stability of hexane emulsions containing octanol or dodecanol.

Liddel & Becker (364) showed that dimerization of butanol in carbon tetrachloride could be detected at concentrations as low as 0.05 mol dm^{-3} at 25^{0}C. The association in alkane would probably be greater (365). More recent work on the C_4 alcohol has suggested that self-association in octane can be detected by infra-red spectroscopy at about 0.06 mol dm^{-3} and above (345a). Fletcher & Heller (365) detected association of octanol in decane at concentrations as low as 10^{-4} mol dm^{-3}. Both octanol and dodecanol have been found to associate above 0.02 mol dm^{-3} in octane by infra-red and osmometric techniques (366).

Solutions of 0.04 and 0.08 mol dm^{-3} dodecanol in hexane have been prepared and examined at 25^{0}C by infra-red spectroscopy using a Grubb-Parsons IR spectrophotometer with 10mm silica cells. The spectrogram for the most concentrated sample is presented in Figure 38. For both solutions a sharp absorption peak was obtained in the wave number region of 3660 cm^{-1}. This can be attributed to the O-H stretching mode of alcohol monomers (345a,364,366). However, no broad band was observed in the region 3350 to 3500 cm^{-1}. The absence of absorption at these slightly longer wavelengths indicates that no O-H stretching in hydrogen bonded alcohol could be detected.

FIGURE 38

INFRA-RED SPECTROGRAM FOR HEXANE CONTAINING 0.08 mol dm^{-3} DODECANOL



5.3.6.4 Evidence for molecular diffusion

Previous experimental evidence for the role of molecular diffusion in emulsion breakdown is notably sparse, although the diffusion process has been implicated in this respect on several occasions (32,41,42,88, 90). The same phenomenon can be observed more readily in solid dispersions (354-356) or foams (45). Kitchener & Mussellwhite (45) presumed that the effect was less evident in emulsions where the oil solubility is usually low, giving slow diffusion rates, and because of the difficulty of observing droplets of the relevant size.

Twenty years ago Kremnev & Ravdel (353) argued in favour of "isothermal distillation" of small droplets into larger ones. It was estimated that benzene droplets of less than 0.1 μm in water would distill into larger droplets in a few seconds whilst those of 1.0 μm and 5.0 μm would take several minutes and hours respectively. They proposed that in the presence of a surfactant the reduced interfacial tension, and to a lesser extent the formation of an adsorbed film, were responsible for a slower rate of distillation. Nevertheless it was considered that distillation contributed significantly to the observed rapid disappearance of droplets with radius 1 μm or less from benzene emulsions.

Higuchi & Misra (49) have followed a very similar course in their work, but expanded the theory to predict the behaviour of a hypothetical system consisting of an equal number of droplets with radius 0.5 and 1.0 μm. The general conclusions from this simple case were considered to be approximately applicable to more complex systems such as a log normal distribution of sizes. The theory was seen to explain the behaviour of carbon tetrachloride emulsions in various concentrations of surfactant (Aerosol OT) and in the presence of small quantities of Nujol or hexadecane.

A somewhat more quantitative study by Kahlweit (367) revealed that the breakdown of an isoamyl alcohol dispersion, measured as a change in the size distribution with time, was predicted reasonably by Ostwald ripening during the initial period of coarsening. Nixon & Beerbower (324) have explained a sharp fall in the yield value of kerosene emulsions with a high content of dispersed phase in terms of a rapid disappearance of small droplets through molecular diffusion.

On the other hand Hallworth and Carless (71,92) have calculated the expected rate of degradation for light petroleum and chlorobenzene emulsions stabilized with SDDS. The demulsification rates of the petroleum emulsions were found to be much faster than those expected from the disappearance of 1.0 and 2.0μm droplets by molecular diffusion. Molecular diffusion could only account for the instability of chlorobenzene emulsions or systems in which paraffin solubility was enhanced by solubilization of the oil in surfactant micelles. However, no account was taken of the rapid increase in the calculated rate of molecular diffusion which would arise if submicron sized droplets were considered. Similarly, the increase in stability due to adding octadecanol (91,92) was found to be several times greater than could be explained by the effect of a lower interfacial tension on molecular diffusion. A similar observation has been made in the present work. Hallworth & Carless (91,92) considered that an interfacial barrier to diffusion, caused by the condensed mixed film could explain this discrepancy, but that coalescence was the more likely demulsification process. The possibility of an additional stabilizing effect preventing molecular diffusion, which can arise from the F_d value of octadecanol in paraffin (Section 5.3.6.3), was apparently overlooked.

From the present work it has been noted that the stability of hydrocarbon dispersions in SDDS solution is highly dependent on the chemical nature of the oil. The presence of C_8, C_{12} or C_{16} alkanols and especially C_{12} or C_{16} alkanes enhance the stability of hexane emulsions. The C_{16} alkane has been shown to exert a similar effect on benzene and cyclohexane emulsions. The small droplets in the emulsions seem to be particularly affected by the inclusion of long chain alkane. The process of molecular diffusion is dependent on the solubility of the oil phase in the continuous medium but the presence of a less water soluble component in the oil will retard emulsion degradation through this mechanism. Good correlation has been observed between the water solubility of the range of oil phases and emulsion stability and between the effectiveness of an alkane or alkanol additive in stabilizing hexane emulsions and its oil-water partition coefficient. In the absence of any evidence for interfacial effects in many of these systems it is concluded that a major route for the change in interfacial area and increase in droplet size with time is the dissolution of smaller droplets and the growth of larger ones.

The coalescence of oil droplets will also occur and its rate will be affected by the extent to which molecular diffusion gives rise to large droplets and accelerates creaming. The alkane and alkanol emulsions in 10^{-2} mol dm^{-3} SDDS appear to be quite well stabilized with respect to coalescence and will undergo changes principally through molecular diffusion whereas in the breakdown of aromatic oil emulsions both mechanisms will contribute. This is best shown by comparing the stability results of benzene and benzene + hexadecane emulsions. In both cases the separation of free oil is significant but in the latter a far greater stability of small droplets can be observed both visibly and microscopically.

Summarizing, it has been found that wide differences in emulsion stability result from varying the nature of the oil phase whilst using a particular surfactant (SDDS). According to Schulman & Cockbain (175a) the most effective conditions for stability should be the presence of a closely packed and electrically charged interfacial film. In some instances the degree of expansion of the film at the oil-water interface correlates with stability. However, in other cases wide differences in stability arise when the expansion of the film and electrical charge on droplets are not significantly different. These observations can be explained either through differences in the ease with which the surfactant film can be displaced, or by the effect of oil phase solubility on molecular diffusion. The former mechanism has been used previously to describe the stability of paraffin emulsions (71,92,126) and the stabilizing effect of long chain alcohols (91,92) in terms of the interaction of adsorbed species with oil molecules. A number of the present observations cannot be accounted for in this way and suggest that molecular diffusion may give rise to significant differences in emulsion stability when the system is well stabilized against coalescence. It should prove possible to elucidate the relative importance of the interfacial and diffusion mechanisms through measurements on the rheological properties of interfaces. Alternatively, a more precise analysis of the changes in the shape of droplet size distribution curves during ageing may prove to be informative (347c). The principal problem is of course that the rate of molecular diffusion is largely dependent upon particles in the submicron size range which cannot be measured by light microscopy. The examination of a wider range of oil phases may also give some indication as to the importance of molecular diffusion. An obvious choice would be to include isomeric alkanes as oil phases and particularly as additives (347d). For example, a branched isomer with high carbon number and low water solubility would be expected to enhance the stability of a hexane emulsion if molecular diffusion was the main route of breakdown, but should have no effect or even reduce the stability (by impairing the interfacial packing of surfactant molecules) if film effects and coalescence were important.

5.3.7 The effect of surfactant concentration

A number of observations have been made on the changes in stability for hydrocarbon emulsions as SDDS concentration is varied (Section 4.3.4). An increase in concentration from 10^{-4} to 10^{-3} and to 10^{-2} mol dm^{-3} results in a progressive increase in stability.

Below a concentration of 10^{-2} mol dm^{-3} SDDS substantial amounts of free oil separated from all the systems studied. The area per adsorbed molecule increases extremely rapidly as the surfactant concentration is decreased from 10^{-2} to 10^{-4} mol dm^{-3}. The increase in area per adsorbed molecule represents a decrease in the surface charge density on emulsion droplets, which is reflected in a sharp fall off in electrophoretic mobility and zeta potential (Figure 30). Thus, the potential energy barrier to close approach of colliding or contacting droplets is reduced. It is suggested that as the area per molecule increases the electrical stabilization is further reduced since surfactant molecules can be displaced more readily from droplet contact points (Section 5.3.5.3). Therefore, an increase in film expansion as the surfactant concentration falls results in a progressive increase in the coalescence rate. It is noticeable that free oil appears relatively rapidly in those systems where the area per molecule exceeds about 0.60 nm^2. This is illustrated by the instability of a benzene emulsion, even in 10^{-2} mol dm^{-3} SDDS (area$\simeq$ 0.70 nm^2 molecule^{-1}).

Rowe (58) reported that there was a minimum concentration of SDDS, in the region of the cmc, below which emulsions of mineral oil exhibited rapid separation of free oil. Rehfeld (173) made a similar observation for SDDS stabilized hydrocarbon emulsions under centrifugation. It was suggested that the cmc corresponds to the highest degree of molecular packing for adsorbed molecules and the greatest mechanical stability in the interfacial film. Additional reports confirm the progressive increase in stability with surfactant concentration up to the cmc, under gravity (86,105) and centrifugation (368).

Increased stability can also be ascribed in part to the increased resistance to molecular diffusion (Section 5.3.6) through a lower interfacial tension and possibly an increased barrier to interfacial mass transfer (Section 5.3.6.3). However the contribution of molecular diffusion to emulsion breakdown below a concentration of 10^{-2} mol dm^{-3} assumes somewhat less significance owing to the considerable changes in the rate of coalescence.

The systems studied show an excellent correlation between the fall in interfacial tension and increase in electrophoretic mobility as the surfactant concentration is increased below the cmc. Similar observations have been reported for the adsorption of SDDS (369) and other anionic surfactants (370) at paraffin-water interfaces. Earlier studies suggested certain anomalous behaviour (ie. a maximum in electrophoretic mobility in the absence of appreciable interfacial activity) for various anionics including alkyl sulphates (143). No such behaviour was observed in the present work.

As the concentration of surfactant is increased further, from 10^{-2} to 10^{-1} mol dm^{-3} the limited number of observations give inconclusive results. A small fall in the stability of a hexane emulsion is indicated although experimental variations in the measurement of the rapid changes taking place could account for this. Alternative explanations for a fall in stability are outlined below. No significant fall in stability was found with a hexadecane emulsion. It seems that an examination of the effect of surfactant concentration on systems exhibiting moderate stability may be more informative.

The raising of the surfactant concentration from 10^{-2} to 10^{-1} mol dm^{-3} produces a negligible fall in interfacial tension. Previously this behaviour has been interpreted as evidence for little or no further adsorption above the surfactant cmc. Significantly, the measured zeta potential falls slightly over the same concentration range, indicating the absence of micellar adsorption (Section 1.3.3.2). The fall in zeta potential occurs because the mobility of the droplets is a function of both surface charge density and the thickness $1/K^1$ of the electric double layer. Both these factors are dependant on surfactant concentration. As the concentration is raised an increasing excess of counter-ions in the medium tend to reduce the double layer thickness (see Table 3-9) (371). Increased penetration of counter ions into the Stern layer will tend to reduce the surface potential slightly. A fall in the electrophoretic mobility (and zeta potential) above the cmc can be explained as a thinning of the double layer, leading to a steeper drop of the repulsive potential in the aqueous phase, without a compensating increase in the number of adsorbed ions.

It has been reported previously that emulsion stability is maximized at about the cmc of surfactant (see above). Osipow <u>et al</u> (105) proposed that the presence of micelles between adjacent droplets would favour desorption of surfactant and reduce stability. At high ionic strengths, as when there is a high concentration of surfactant (or in the presence of added electrolyte), a reduced surface potential and thinning of the double layer enhance the aggregation of droplets (87c). A high ionic strength also favours a reduced thickness of the aqueous lamellae between contacting droplets (45,88). According to Davies & Rideal (117a) the net effect may be a large increase in the coalescence rate.

Alternatively, if the oil droplets are well stabilized against coalescence changes might be expected in the rate of molecular diffusion as the surfactant concentration increases. In section 5.1.2.1 a mechanism was discussed whereby dissolved oil reduced the cmc of SDDS by its incorporation in the hydrocarbon core of surfactant micelles. The degree of cmc depression was apparently related to the water solubility of the oil. The solubilization of oil molecules within SDDS micelles can cause relatively large increases in the water solubility of slightly soluble substances (372), and provides a potential mechanism for the acceleration of molecular diffusion. However, the change in molecular diffusion need not necessarily parallel the apparent increase in solubility since the availability of solubilized oil for transfer to large droplets is open to question. Probably more important is the effect of increased droplet aggregation on molecular diffusion as the surfactant concentration is increased (Section 5.3.6.1).

5.4 CONCLUSIONS

Over the years many aspects of emulsion stability have been studied in detail. However, the importance of the chemical nature of the dispersed phase in determining stability has received little attention. In the present work four main techniques, namely the measurement of interfacial tension, the stability of oil droplets at an oil-water interface, emulsion stability and electrophoretic mobility, have been used to study the effect of dispersed phase composition on emulsion stability.

The molecular structure of an oil-water interface is affected by the nature of the oil phase when the latter is significantly polar (228ab). Evidence has been presented to support the view that different non-polar oils also affect interfacial structure, possibly enough to influence the process of surface adsorption.

Samples of sodium dodecyl sulphate (SDDS) were carefully characterized for use throughout this work.

The adsorbed film of SDDS at a plane air-water interface was found to be of the non-ideal gaseous type at concentrations between 10^{-4} mol dm^{-3} and the cmc. Considerable deviation from ideality is caused by the ionic repulsion between surfactant molecules. This deviation is reduced as the film becomes more expanded.

At any given area per adsorbed molecule it was shown that the surfactant exerts greater surface pressure at the oil-water interface than at the air-water interface, owing to a reduction in interaction between hydrocarbon chains of surfactant molecules. There was some indication that surface pressure may depend upon the effectiveness of the oil phase in preventing this interaction.

At a given surfactant concentration the adsorbed film was invariably more expanded at oil-water rather than air-water interfaces.

It was concluded that the area per molecule of adsorbed surfactant can be affected by the chemical nature of the oil phase. The more polar oils resulted in more expanded films. Slight differences were detected for the adsorption at various alkane-water interfaces. These were probably due to impurities in the oil phase although other possible explanations have been discussed.

The inclusion of a small amount of alkyl alcohol into a particular oil resulted in a considerable lowering of the interfacial tension owing to the adsorption of a mixed surfactant film. The surface pressure arising from SDDS in the mixed film was apparently lower than when alkyl sulphate was used alone. This may have been due to the reduced adsorption of SDDS and/or a lowering of the effective repulsion between the ionic species in the film.

The presence of an alkane mixture as the oil phase gave rise to predictable surface pressure and molecular area data for the adsorption of SDDS.

In general electrophoretic mobility measurements closely reflected changes in the degree of adsorption. Slight differences in mobilities were observed with alkanes, the shorter chain length oils producing droplets with a higher charge. This may have been due to differences in SDDS adsorption. Alternatively the more rapid coalescence in emulsions of lower alkanes may have led to a closer packing of surfactant at the interface. No significant changes in electrophoretic mobilities were observed when emulsions were aged from one to fifty days. A small amount of alkane added to the oil phase produced no significant change in droplet charge. The presence of alkanol in the oil caused a slight decrease in mobility, either as a result of reduced SDDS adsorption or through an outward shift of the shear plane.

The stability of oil-in-water emulsions was found to be highly dependent on the nature of the oil phase . Those oils which produced expanded interfacial films of SDDS gave rise to unstable emulsions. Systems containing alkanol as the oil or as an additive manifested enhanced stability because of the presence of the mixed film. In some cases differences in stability could not be accounted for by differences in interfacial adsorption. For example, alkane emulsions were found to have widely different stabilities although the properties of their interfacial films were apparently similar. Also, small quantities of long chain alkane were shown to exert a considerable stabilizing effect when added to unstable systems. The possible explanations for such observations have been discussed. It was concluded that emulsion breakdown may be due, at least in part, to the preferential dissolution of small droplets and "condensation" of oil onto larger droplets (molecular diffusion).

The coalescence rate of droplets at a plane interface is dependent on a great number of experimental factors including temperature, vibrations, droplet size and interface curvature. These factors have been investigated and a standard procedure for droplet stability measurement has been developed. Under controlled conditions droplet coalescence rates showed the stabilizing effect of increasing concentrations of SDDS. The presence of added alkanol in hydrocarbon oil led to a greater stability than when SDDS alone is present in the system. This was no doubt due to the formation of a mixed surfactant film.

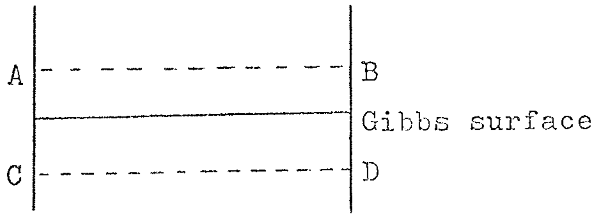
The stability of droplets at the plane interface was dependent on the nature of the oil phase used. However, the correlation with emulsion stability was poor. It has been concluded that differences in stability parameters for various oils were attributable largely to differences in film drainage in the systems investigated and that the droplet stability measurements did not provide a sensible *a priori* indication of emulsion stability.

APPENDIX

APPENDIX I

The Gibbs Adsorption Equation for a strongly dissociating electrolyte at the oil-water interface

At any interface there is a region of finite distance across which the properties change gradually from those of one bulk phase to those of the other (see diagram). The "interface" may be considered as a dividing surface (Gibbs surface) of zero thickness and volume, positioned somewhere between the two planes AB and CD. The two bulk phases are considered to be homogeneous up to the two planes.



From free energy considerations at the Gibbs surface it can be shown that

$$S_e \; dT \; + \; A_e \; d\gamma \; + \; \sum n_i \, du_i \; = \; 0,$$

where S_e is the surface entropy, T is the temperature (Kelvin), A_e is the surface area, γ is the surface tension, n_i is the number of molecules of the i th component in the surface and u_i is the surface chemical potential.

Thus at constant temperature

$$A_e \; d\gamma \; + \sum n_i \, du_i \; = \; 0.$$

Dividing by the surface area:-

$$d\gamma \; + \; \Gamma_i \; du_i \; = \; 0,$$

where $\Gamma_i = n_i/A_e$ which may be defined as the surface excess of the adsorbed species in molecules per unit area.

For the adsorption of a univalent electrolyte ($A^+ \, B^-$) at the oil(L)-water interface six molecular and ionic species must be considered, A^+, B^-, H^+, OH^-, H_2O and L. Hence,

$$-d\gamma = \Gamma(A^+)\ du\ (A^+) + \Gamma(B^-)\ du\ (B^-) + \Gamma(H^+)\ du\ (H^+) + \Gamma(OH^-)\ du\ (OH^-) + \Gamma(H_2O)\ du\ (H_2O) + \Gamma(L)\ du\ (L)$$

It is usually assumed that dissociation of water with respect to dissociating solute is negligible (though this may not be so in very dilute solutions). Furthermore the Gibbs surface is defined so that the excess or deficit of both oil and water is zero. This condition is only physically reasonable for an adsorbed monolayer (117d) when the two liquids exhibit low mutual solubility (203b).

Thus in terms of the surface excess of solute relative to the bulk phases:-

$$-d\gamma = \Gamma(A^+)\ du\ (A^+) + \Gamma(B^-)\ du\ (B^-).$$

Since the surface phase is defined as being electrically neutral

$$\Gamma(A^+) = \Gamma(B^-) = \Gamma(AB) ,$$

and therefore

$$-d\gamma = \Gamma(AB)\ du\ (A^+) + \Gamma(AB)\ du\ (B^-)$$

The chemical potential of any component may be represented by

$$u = u^0 + RT\ \ln\ a ,$$

where u^0 is the standard chemical potential of the component and is constant for a given substance at a given temperature, and a is the activity of the component.

Now, $du\ (A^+) = RT\ \ln\ a\ (A^+)$

and $du\ (B^-) = RT\ \ln\ a\ (B^-)$,

therefore

$$-d\gamma = \Gamma(AB)\ RT\ \ln\ a\ (A^+) + \Gamma(AB)\ RT\ \ln\ a\ (B^-)$$

or

$$-d\gamma\ /\ 2RT = \Gamma(AB)\ d\ \ln\ a^{\pm}$$

where $a^{\pm}$ is the mean activity given by $a^{\pm 2} = a\ (A^+)\ a\ (B^-)$.

NOTES

(1) This form of the Gibbs equation differs from the usual form by a factor of two. Thus the variation in surface tension with activity for a 1:1 electrolyte is twice as large as for a non-electrolyte. The alternative form is derived in the same way but with one less component in the original summation term. The latter form may also be used in the presence of a high concentration of inorganic electrolyte (eg. A^+C^-). Here the adsorption of A^+B^- does not produce an appreciable change in the surface concentration of common ion; $du(A^+)$ and $du\ (C^-)$ may be neglected in comparison with $du\ (B^-)$.

(2) The precise physical significance of "excess" concentration (Γ) requires some clarification. In the above argument the amount adsorbed is measured by its surface excess, defined as the extra amount of component in the interfacial region by virtue of the presence of the interface. By applying the alternative convention of a surface phase of finite thickness (210) rather than Gibbs surface, the total surface concentration may be calculated (203a). For strongly adsorbed monomolecular films there is no appreciable difference between excess and total concentrations at the interface.

APPENDIX II

EASTMAN KODAK COMPANY
ROCHESTER, NEW YORK 14650

Dear Mr. Smith:

We wish to acknowledge your recent letter concerning the difficulties you experienced using our Dodecyl Sodium Sulphate, chemical 5967.

When this chemical was originally prepared, our analysis showed 95+ percent C_{12}. We have now retested the material by hydrolyzing the ester and analyzing the alcohol portion by G.C. Our tests agree with your findings. This analysis indicated 71 percent of C_{12}, 17 percent of C_{14}, 8 percent of C_{16}, and 4 percent unknown. Under the circumstances, we have removed this material from stock and we are starting a new batch which should be available shortly.

By a copy of this letter we are advising Kodak Limited of your findings and we are sure they will contact you concerning proper adjustment.

If we can be of further assistance, please let us know.

Yours very truly,

(Mrs) Dorothy K Brophy

Eastman Organic Chemicals

DKBrophy:MC

AIR MAIL

APPENDIX III PROGRAM FOR ANALYSIS OF DROPLET REST-TIME DATA

```
 10/53/23          18/06/74         COMPILED BY XALV MK.  3A
 LINE STATEMENT
    0     0        'INPUT' 0=CR0
    1     0        'OUTPUT' 0=LP0
    2     0        'SPACE' 20000
    3     0        'EXTENDED'
    4     0                    'BEGIN'  'COMMENT'  DROP STABILITY ANALYSIS MARKS;
    5     1                 'REAL' MAX,TIME,LIMIT1,LIMIT2,SX,SY,SXSQ,SYSQ,SXY,
    6     1             A,B,C,VAR,DEN,RATE,LIM;
    7     1                'INTEGER' NUM,CODE,I,SUM,L,K,M,N,P,Q;
    8     2                'ARRAY' DROPS,TIMECYCLE,TIMES,TIMEREG,CORR,NOTCOALREG[1:1000];
    9     3                'INTEGER''ARRAY'NOTCOALES,SUMS[1:1000];
   10     4               CODE:=READ: 'COMMENT' SYSTEM CODE;
   11     6               NEWLINE (2);
   12     7               WRITETEXT('('SYSTEM%CODE')');
   13     8               PRINT(CODE,3,0);
   14     9               NEWLINE (1);
   15    10               L:=0;
   16    11               NUM:=READ: 'COMMENT' NUMBER OF DROPS MEASURED ;
   17    12               MAX:=READ: 'COMMENT'   MAXIMUM LIFETIME SECONDS;
   18    13                    NEWLINE(1);
   19    14                    WRITETEXT('('NUMBER%OF%DROPS%MEASURED ')');
   20    15                    PRINT(NUM,3,0);
   21    16                    NEWLINE (1);
   22    17                    WRITETEXT('('MAXIMUM%LIFETIME%(SECS)')');
   23    18                    PRINT(MAX,2,2);
   24    19                    NEWLINE(2);
   25    20                    WRITETEXT('('LIFETIMES%(SECS)')');
   26    21              'FOR'I:=1 'STEP'1 'UNTIL' NUM 'DO' 'BEGIN'
   27    22             DROPS[I]:=READ; 'COMMENT' INDIVIDUAL DROP TIMES IN SECONDS;
   28    24                    NEWLINE(1);
   29    25                    PRINT(DROPS[I],2,2);
   30    26                  'END';
   31    27                PAPERTHROW;
   32    28                  'COMMENT' CALCULATE NUMBER OF DROPS NOT COALESCED

   33    28                      AT GIVEN TIME;
   34    28                 'FOR'TIME:=0 'STEP' 0.1 'UNTIL' MAX 'DO'
   35    29                   'BEGIN'  SUM:=0 ;L:=L+1;
   36    32                   'FOR'I:=1 'STEP' 1 'UNTIL' NUM 'DO'
   37    33                     'BEGIN'  'IF' DROPS[I]  'GE' TIME 'THEN'
   38    34                       SUM:=SUM+1; 'END';
   39    36                    SUMS[L]:=SUM; TIMECYCLE [L]:=TIME;
   40    36                 'END';
   41    39                 SUMS[0]:=500;    M:=0;
   42    41                    'COMMENT' SQRT DATA  TO GIVE TIMES AT WHICH  DROP
   43    41                      NUMBER DECREASES BY INTEGRAL AMOUNTS;
   44    41                 'FOR' K:=1 'STEP' 1 'UNTIL'L 'DO'
   45    42                  'BEGIN'  'IF'  SUMS[K] < SUMS[K-1] 'THEN''BEGIN'
   46    43                    M:=M+1;
   47    45                    NOTCOALES[M]:=SUMS[K];
   48    46                    TIMES[M]:=TIMECYCLE[K];  'END';
   49    48                  'END';
   50    49                   NEWLINE(1);
   51    50                    NEWLINE(3);
   52    51                  WRITETEXT('('TIME(SECS)%%%NO%NOT%COAL%%%%LN%NOT%COAL')');
   53    52                   NEWLINE(1);
   54    53                 'FOR' N:=1 'STEP' 1 'UNTIL' M 'DO'
   55    54                 'BEGIN'
   56    54                   PRINT(TIMES[N],0,4); SPACE(6);
```

continued overleaf :-

APPENDIX III : continued

```
   57   57            PRINT(NOTCOALES[N],2,0); SPACE(6);
   58   59              CORR[N]:=LN(NOTCOALES[N]);
   59   60              PRINT(CORR[N],0,4);SPACE(6);
   60   62             NEWLINE(1);
   61   63          'END';
   62   64             'FOR'N:=1 'STEP' 1 'UNTIL'M'DO'
   63   65               'COMMENT' VALUES OF TIME AND LOG NOT COALESCED ARE
   64   65               OBTAINED OVER THE LIMITS 5% TO LIM% TIME MAX;
   65   65  *            LIM:=0.3;
   66   66  *        LAB2:     LIMIT1:=0.05*MAX;
   67   67               LIMIT2:=LIM*MAX;
   68   68      PRINT(LIMIT2,0,2);
   69   69              P:=0;
   70   70             'FOR' N:=1 'STEP' 1 'UNTIL' M 'DO'
   71   71             'BEGIN' 'IF' TIMES[N] < LIMIT1 'THEN' 'GOTO' LAB1;
   72   73             'IF' TIMES[N] > LIMIT2 'THEN' 'GOTO' LAB1;
   73   74               P:=P+1;
   74   75               TIMEREG[P]:=TIMES[N];
   75   76              NOTCOALREG[P]:=CURR[N];
   76   77             LAB1:'END';

   77   78                'COMMENT' START REGRESSION ;
   78   78              SX:=SY:=SXY:=SXSQ:=SYSQ:=0;
   79   79                'FOR' Q:=1 'STEP' 1 'UNTIL' P 'DO'
   80   80                'BEGIN'  SX:=SX+TIMEREG[Q];
   81   82                        SY:=SY+NOTCOALREG[Q];
   82   83                        SXY:=SXY+(TIMEREG[Q]*NOTCOALREG[Q]);
   83   84                        SXSQ:=SXSQ+TIMEREG[Q]↑2;
   84   85                        SYSQ:=SYSQ+NOTCOALREG[Q]↑2;
   85   86                       'END';
   86   87                A:=SXY-SX*SY/P;
   87   88                DEN:=SQRT((SXSQ-SX↑2/P)*(SYSQ-SY↑2/P));
   88   89                'IF'DEN<1*10↑(-5)'THEN''GOTO' LAB3;
   89   90                C:=A/DEN;
   90   91                NEWLINE(1);
   91   92                NEWLINE(1);
   92   93               WRITETEXT('('LIMIT%2')');
   93   94                PRINT(LIM,1,2);
   94   95                WRITETEXT('('CORRELATION%COEFFICIENT')');
   95   96                PRINT(C,0,4);
   96   97                B:=A/(SXSQ-SX↑2/P); 'COMMENT'GRADIENT OF REGRESSION LINE;
   97   98                VAR:=SYSQ-P*(SY/P)↑2-B*B*(SXSQ-P*(SX/P)↑2);
   98   99                VAR:=VAR/(P-2);
   99  100                VAR:=SQRT(VAR);
  100  101                WRITETEXT('('STANDARD%DEVIATION')');
  101  102                PRINT(VAR,0,4);
  102  103                NEWLINE(1);
  103  104                'COMMENT' CALCULATE RATE CONSTANT FROM GRADIENT;
  104  104                RATE:=-B;
  105  105           NEWLINE(1);
  106  106         WRITETEXT('('RATE CONSTANT-SEC-1')');
  107  107                PRINT(RATE,0,4);
  108  108        WRITE TEXT ('('HALF %LIFE%SECS')');
  109  109         PRINT(0.693/RATE,0,4);
  110  110   NEWLINE(1);
  111  111           NEWLINE(1);
  112  112          LAB3:      LIM:=LIM+0.05;
  113  113                'IF'LIM<1.05'THEN''GOTO'  LAB2 ;
  114  114           'END';
 SEGMENT AXXX         LENGTH  828
 NO OF BUCKETS USED     24

 COMPILED   #AXXX           EC
```

* LIM:=0.1 and LIMIT2:=0.01*MAX where $t_{max} > 100s$.

APPENDIX IV MOLECULAR DIFFUSION

The basis of the molecular diffusion theory is that very small particles exhibit deviations in their physical properties as compared to larger particles or plane surfaces. Lord Kelvin showed that the vapour pressure of a liquid droplet is greater than the saturation vapour pressure over a plane surface (355). In terms of fugacity (f_1) one can write

$$RT \ln (f_1^d / f_1^\infty) = 4 \gamma V / d, \qquad \text{IV.1}$$

where f_1^d is the fugacity of a small droplet of diameter d and f_1^∞ is the fugacity of the flat surface, γ is the surface tension and V is the molar volume.

For the case of a single droplet of a sparingly soluble oil in water, assuming Henry's Law to hold, Equation (1) can be written

$$RT \ln (C^d / C^\infty) = 2 \gamma_{ow} M / rp, \qquad \text{IV.2}$$

where C^d and C^∞ are the respective solubilities of droplets with radius r and radius infinity, γ_{ow} is the interfacial tension, M and p are respectively the molecular weight and density of the oil. This equation may be simplified to

$$C^d = C^\infty \exp (K^a / r) \qquad \text{IV.3}$$

provided that γ_{ow} and p remain constant for small particles. (To a first approximation K^a is assumed to be a constant although there is evidence to suggest that γ_{ow} and p change with particle size (347a).

Higuchi & Misra (49) suggested that an increase in solubility will result in small emulsion droplets being thermodynamically unstable with respect to larger ones. An analysis of the rates of the dissolution of small droplets and growth of larger droplets was presented. The rate of growth or dissolution for a spherical particle can be expressed by the following equation when the process is controlled by diffusion through the external phase:-

$$G \quad = \quad 4\pi \, D \, r \, (C^s - C^o) \quad , \qquad \text{IV.4}$$

where G is the rate, D is the molecular diffusion coefficient of the particle material in the external phase, C^s is the solubility of the growing or dissolving phase and C^o is the concentration of the material in the external phase at a point remote from the particle (353,359).

From Equation IV.3 ,

$$G \quad = \quad 4\pi \, D \, r \left[C^{\infty} \exp \, (K^a \, / \, r) - C^o \right] \quad , \qquad \text{IV.5}$$

From Equation IV.5 and a consideration of the total mass of the particle material dissolved in the system the rate of change of radius of a droplet can be estimated (49,353). For a mixture of particles of two different radii r_1 and r_2, which grow at rate G_1 and dissolve at rate G_2 respectively, the rate of decrease of r_2 will be

$$dr_2/dt \quad = \quad \frac{D \, C^{\infty} \, K^a}{r_2^{\,2}} \left[\frac{n_2 \, (r_2 - r_1)}{n_1 r_1 - n_2 r_2} \right] \quad , \qquad \text{IV.6}$$

where n_1 and n_2 are the respective numbers of particles with radius r_1 and r_2. Higuchi & Misra (49) calculated how small C^{∞} would have to be to give only a 10% change in the size of small droplets in a year (ie. a "stable" system), where r_1 = 1.0 μm and r_2 = 0.5 μm and with equal number concentration of the two sizes. Using D - 5x10^{-6} cm^2 s^{-1}, γ_{ow} = 1.0 mN m^{-1}, M = 100 and p = 10^3 kg m^{-3}, they found that C^{∞} was 3x10^{-8} kg dm^{-3}. This low value for C^{∞} was taken to indicate that molecular diffusion may be important even for sparsely soluble oils.

The presence of dissolved external phase in the droplet has a negligible effect on the molecular diffusion rate (49).

The addition of a third non-interacting component (y) to a disperse phase (x) has also been considered (49). From Equation IV.3 :-

$$C^{d}(x) = C^{\infty}(x) \exp(K^{a}(x)/r) \qquad \text{IV.7}$$

and

$$C^{d}(y) = C^{\infty}(y) \exp(K^{a}(y)/r) , \qquad \text{IV.8}$$

where $K^{a}(x)$ and $K^{a}(y)$ represent $2\gamma_{ow}\bar{V}/RT$ and $\bar{V}$ is the partial molal volume of component (x or y) in the droplet.

The C^{∞} terms can be related to the partition coefficients (K_d) of the two components by

$$K_d = C^{\infty}_{oil} / C^{\infty}_{water} , \qquad \text{IV.9a}$$

so that

$$C^{\infty}_{water} = C^{\infty}_{oil} / K_d , \qquad \text{IV.9b}$$

From Equations IV.7 and IV.8:-

$$C^{d}(x) = \frac{C^{\infty}(x)_{oil}}{K_d(x)} \exp(K^{a}(x)/r) , \qquad \text{IV.10}$$

and

$$C^{d}(y) = \frac{C^{\infty}(y)_{oil}}{K_d(y)} \exp(K^{a}(y)/r), \qquad \text{IV.11}$$

Higuchi & Misra (49) concluded that the presence of the y component will give rise to a pseudo-steady state situation where the rate of degradation depends on the diffusive rate of x or y or both. If the diffusion coefficients D (x) and D (y) are similar and $K_d(x) \gg K_d(y)$ then the degradation rate will be similar to that of component x alone. However, if $K_d(x) \ll K_d(y)$ then the diffusion rate of component y will govern the degradation of the particle, the changes in the system proceeding only as fast as the changes in distribution of the slowest diffusing component. It was suggested that the degradation rate will be retarded by a factor F_d given by:-

$$F_d = K_d(y)/K_d(x) \qquad \text{IV.12}$$

According to this theory, the higher F_d becomes, the more stable the system is with respect to molecular diffusion degradation.

APPENDIX V

Glossary of symbols and abbreviations

A	area of interface available to each adsorbed ion or molecule
A_{cmc}	area of interface available to each adsorbed ion or molecule at the surfactant cmc
A_e	cross sectional area of electrophoresis capillary
A_H	Hamaker constant
A_o	cross sectional area of adsorbed ion or molecule
A'	total area of a plane interface (Equation 1.12)
a_o, a_1, a_2	coefficients of polynomial equation (Equation 3.5)
a'	frequency of droplet collisions resulting in aggregation (Equation 5.9)
$a^{\pm}$	mean thermodynamic activity of a solute
b	cell constant for conductivity measurement
b'	coalescence rate for emulsion droplets (Equation 5.10)
C_n	carbon number (where n is an integer)
c	surfactant concentration
d	droplet diameter
d_{av}	mean (length-number) droplet diameter of emulsion = $\frac{\Sigma nd}{\Sigma n}$
d_v	mean (volume-number) droplet diameter of emulsion $=\left(\frac{\Sigma nd^3}{\Sigma n}\right)^{\frac{1}{3}}$
d_{vs}	mean (volume-surface) droplet dimaeter of emulsion = $\frac{\Sigma nd^3}{\Sigma nd^2}$
dt/do	ratio of mean volume diameter (d_v) at a particular time to the initial mean volume diameter of emulsion
E	strength of applied electric field in electrophoresis cell
e	end correction for Wilhelmy plate
F	force acting on Wilhelmy plate
F_c	fraction of droplets coalescing with plane interface in a given time = $N_o - N/N_o$
F_d	emulsion stability factor (Equation 5.11)

f	emulsion stability factor (Equation 5.8)
G	conductance
g	acceleration due to gravity (9.81 m s^{-2})
H	distance of separation between two interacting particles
h	distance of separation between droplet and plane interface
$j(\ )$	activity coefficient of a solute (specified in brackets) at infinite dilution
j_w	activity coefficient of a solute at infinite dilution in water
j_o	activity coefficient of a solute at infinite dilution in oil
K	conductivity (formerly specific conductance)
$K_d(\ )$	partition coefficient of a solute (specified in brackets)
K'	reciprocal thickness of electrical double layer
k	Botzmann constant (1.380 54 x 10^{-23} J K^{-1})
k_c	rate constant for droplet coalescence at plane interface (Equation 3.7)
L	length of Wilhelmy plate
L_e	length of electrophoresis capillary
L'	thickness of Wilhelmy plate
M	geometric mean rest-time for droplets at a plane interface (Equation 4.1)
N	number of droplets not coalescing at a plane interface after a given time
N_o	number of droplet rest-times measured
N_v	number of droplets in 1cm^3 of emulsion
N_v^o	number of oil droplets in 1cm^3 of freshly prepared emulsion
N_v^t	number of oil droplets in 1cm^3 of emulsion after time t
n	constant (Equations 1.14 , 3.10 , 3.11) ; number of emulsion droplets of a particular diameter (d) (in definition of mean diameters)
n_D^{25}	refractive index at 25°C and at the average D-line of sodium
n_i	excess number of molecules if ith. component in an interface
n_z	charge number (Equation 3.19)

P	gas pressure (Equation 1.9a)
p	density
p_e	distance of stationary level from outer wall of electrophoresis capillary
p_o	density of dispersed oil
q	mean separation distance between emulsion droplets
R	gas constant (8.314 $J\ k^{-1}\ mol^{-1}$)
R_e	electrical resistance in electrophoresis capillary
r	droplet radius
r_e	radius of electrophoresis capillary
S	specific interface of emulsion
S_o	specific interface of freshly prepared emulsion
s	spreading coefficient
T	Absolute temperature
$T_{\frac{1}{2}}$	first order half-life from droplet rest-time data
t	time (droplet rest time or emulsion age)
t_d	drainage time for film between single droplet and plane interface
t_{max}	maximum rest-time
t_{mean}	mean rest-time
t_o	minimum rest-time
t_h	time required for film to drain evenly to thickness h
t_1, t_2	respective flow times of phases 1 and 2 through U tube viscometer
t'_1	age at which emulsion creaming becomes apparent
t'_2	age at which emulsion cream volume reaches minimum (negligible coalescence)
t'_3	age at which emulsion serum becomes clear
t'_4	age at which free oil separates from emulsion
u	electrophoretic mobility
V	volume of gas (Equation 1.9a)
VA	attractive interaction between two particles

VR	repulsive interaction between two particles
VT	total interaction between two particles
v	velocity of particle migration in electrophoresis capillary
$\bar{v}$	sedimentation velocity of suspended particles
WA	work of adhesion
WC	work of cohesion
Z	zeta potential

a-w	air-water (interface)
cmc	critical micelle concentration
CTAB	cetyl trimethyl ammonium bromide
DLVO	Derjaguin-Landau and Verwey-Overbeek theory
DTAB	dodecyl trimethyl ammonium bromide
GLC	gas-liquid chromatography
HLB	hydrophilic-lipophilic balance
o-w	oil-water (interface)
o/w	oil-in-water (emulsion)
rpm	revolutions per minute
SDS	sodium decyl sulphate
SDDS	sodium dodecyl sulphate
SHDS	sodium hexadecyl sulphate
w/o	water-in-oil (emulsion)

α	coalescence constant for droplet rest-time data (Equations 3.10 , 3.11 and 3.12)
Γ	surface excess of solute
γ	surface or interfacial tension
γ_c	critical interfacial tension for spreading
γ_o, γ_w	respective surface tensions of oil and water phases

γ_{ow}	interfacial tension between oil and water phases
γ_1, γ_2	respective surface tensions of phases 1 and 2
γ_{12}	interfacial tension between phases 1 and 2
γ^d	dispersion force contribution to surface tension
γ^p	polar force contribution to surface tension
$\Delta\gamma^p$	excess polar interaction at interface
Δm	apparent increase in weight of Wilhelmy plate when in an interface
Δp	density difference between two phases
δ	solubility parameter
ε	dielectric constant
η	viscosity
η_r	relative viscosity
η_r^T/η_r^o	ratio of relative viscosity at a particular time to initial relative viscosity of emulsion
η_1, η_2	respective viscosities of phases 1 and 2
μ_i	surface chemical potential of adsorbed species
Π	surface or interfacial pressure (film pressure)
Π_a	film pressure due to adhesion between surfactant molecules
Π_b	kinetic film pressure
Π_r	film pressure due to repulsion between surfactant molecules
Π_1	film pressure due to adsorbed SDDS
Π_2	film pressure due to adsorbed aliphatic alcohol
Π_{12}	film pressure due to mixed (SDDS + alcohol) surfactant
Π_1	film pressure due to SDDS in mixed film
σ	geometric standard deviation (Equation 4.1)
ϕ	volume fraction of oil dispersed in emulsion
ϕ_c	ratio of cream volume to total emulsion volume
ϕ_G	Girifalco-Good constant (Equation 5.2)
ϕ_{max}	maximum volume fraction of dispersed phase
ψ	surface potential

APPENDIX VI

Addresses

B.D.H. Chemicals Ltd., Poole, Dorset, BH12 4NN.

Bellingham & Stanley Ltd., 61 Marksfield Road, South Tottenham,
London, N.15.

C.I. Electronics Ltd., Brunel Road, Churchfields, Salisbury,
Wiltshire.

Ciba-Geigy (U.K.) Ltd., 42 Berkley Square, London, W1X 5DB.

Fisons Scientific Apparatus Ltd., Bishop Meadow Road, Loughborough,
Leicestershire, LE11 0RG.

Griffin & George Ltd., 285 Ealing Road, Alperton, Wembley, Middlesex.

Grubb-Parsons, Walkergate, Newcastle-upon-Tyne, NE6 2YB.

Hopkin & Williams Ltd., Freshwater Road, Chadwell Heath, Essex.

A.R. Horwell Ltd., Grangeway, Kilburn High Road, London, N6 2BP.

Ilford Ltd., 23 Roden Street, Ilford, Essex.

International Equipment Company, Needham Heights, Massachusetts, U.S.A.

Johnson Matthey Metals Ltd., 73-83 Hatton Garden, London, EC1P 1AE.

Koch-Light Laboratories Ltd., Poyle Estate, Colnbrook, Buckinghamshire.

Kodak Ltd., Chemical Division, Kirkby, Liverpool, L33 7UF.

Kodak Ltd., Photographic Division, Station Road, Hemel Hempstead,
Hertfordshire, HP1 1JU.

May & Baker Ltd., Dagenham, Essex, RM10 7XS.

Measuring & Scientific Equipment Ltd., 25-28 Buckingham Gate, London, SW1.

Perkin Elmer Ltd., Post Office Lane, Beaconsfield, Buckinghamshire.

Rank Brothers, High Street, Bottisham, Cambridge, CB5 9DA.

Townson & Mercer Ltd., Beddington Lane, Croydon, CR9 4EG.

Wayne Kerr Co. Ltd., Roebuck Road, Chessington, Surrey.

Wellcome Reagents Ltd., Temple Hill, Dartford, Kent, DA1 5AH.

APPENDIX VII

PUBLICATIONS

The following publications have arisen from the work described in this thesis :-

Davis, S.S. and Smith, A. "Effect of the nature of the disperse phase on the stability of oil-in-water emulsions." J. Pharm. Pharmacol. 24 Suppl., 155P (1972).

Davis, S.S. and Smith, A. "The interpretation of droplet coalescence data using the log normal distribution." Kolloid-Z. Z. Polym. 251, 337-342 (1973).

Smith, A. and Davis, S.S. "The role of molecular diffusion in determining emulsion stability." J. Pharm. Pharmacol. 25, Suppl., 117P (1973).

Davis, S.S. and Smith, A. "The influence of the disperse phase on the stability of oil-in-water emulsions." "Theory and practice of Emulsion Technology", Chapter 19 (Academic Press, in press).

Davis, S.S. and Smith, A. "The stability of hydrocarbon oil droplets at the surfactant / oil interface." Kolloid-Z. Z.Polym., in press.

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