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A DIELECTRIC STUDY OF SYSTEMS

EXHIBITING MOLECULAR ASSOCIATION

BY

MICHAEL HUGH BOYLE

This thesis has been submitted in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy of the Council for National Academic Awards.

Sheffield City Polytechnic
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ABSTRACT

A dielectric study of systems exhibiting molecular association by Michael H Boyle.

Time domain spectroscopic methods have been developed and in combination with bridge methods have provided interpretable data on selected alcohol-water systems and micellar solutions of nonionic surfactants.

Dielectric relaxation studies have shown that addition of water to an alcohol causes a reduction in the relaxation time of the principal dispersion which for all compositions is Debye-type. The relaxation behaviour has been interpreted using a model based on hydrogen-bond rupture and subsequent dipole reorientation. The possibility of relaxation times being modified by the formation of associated species has been examined.

Static permittivities of the polyoxyethylene dodecyl ether surfactants C_{12}E_n (n = 4, 6 and 8) and Brij 30 in binary mixtures with water are interpreted as originating from normal micelles at all compositions. In C_{12}E_4 and Brij 30 mixtures, the behaviour at higher surfactant concentrations is most successfully described by heterogeneous mixture equations for spherical dispersions; deviations at low surfactant concentration are attributed to either oblate spheroidal micelle shape or secondary aggregation of micelles. Axial ratios for oblate spheroids have been calculated using equations derived in this work. In mixtures containing higher n-ethylene oxides, the heterogeneous mixture approach becomes progressively less applicable because of smaller micelle size and an increasing contribution of molecular association between surfactant headgroups and water.

Static permittivities of C_{12}E_4 and Brij 30 in ternary mixtures with water and an n-alkane are attributed to normal micelles at some compositions and inverted micelles at others. Results for microemulsions of C_{12}E_4 have been interpreted as indicating micellar inversion in which normal spherical micelles change to oblate spheroidal with increasing temperature and then invert to form prolate spheroidal and finally spherical inverted micelles. Axial ratios for both types of spheroidal shape have been calculated.
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Chapter 1 Introduction

1.1 Alcohol-water mixtures – Introduction

Since the explicit recognition of the existence of the hydrogen bond, there has appeared a very extensive number of papers dealing with such bonding (1). In alcohols, H-bonding frequently leads to the association of molecules into clusters ranging from dimeric complexes up to large chain-like structures. In pure alcohols, complex equilibria exist between single, unassociated molecules commonly referred to as monomers, and a large number of H-bonded species, both of the open linear and closed cyclic type referred to as multimers (2). A number of authors have suggested specific association complexes for the pure alcohols involving small sized clusters such as the tetramer (3, 4) but the weight of evidence is now in favour of association involving long chains (5, 6). Studies of alcohol-water mixtures have led to the suggestion of small complexes involving four alcohol molecules and one water molecule in some alcohol-water mixtures (7, 8). In contrast to alcohol-water mixtures, molecular association in binary and ternary mixtures involving surfactants leads to micelle formation involving aggregation of a large number of molecules (9, 10, 11, 12).
This thesis describes an attempt to gain more information on molecular association using dielectric methods, where the associated mixtures under investigation have been:

1. Alcohol-water mixtures,

1.1.1 Alcohols

A variety of techniques including dielectric methods have been applied to the study of liquid alcohols. In dielectric studies, information on molecular association has been obtained from two basic aspects, namely:

1. Static permittivity, and
2. Dielectric relaxation.

1.1.1.1 Static Permittivity

Association between molecules arises from short range interactions due to H-bonding with near neighbours. Such interactions were neglected in the earlier theories of Debye (13) and Onsager (14), but were included in the later theory of Kirkwood (15).

In order to account for short range interactions, Kirkwood introduced a dimensionless correlation parameter 'g', the so called g-factor, which indicates an average parallel orientation of
neighbouring dipoles when \( g > 1 \), whereas an average anti-parallel orientation is indicated by \( g < 1 \).

An open linear chain will give \( g > 1 \) whereas a closed structure will give \( g < 1 \).

Chain dimer structures for alcohols are illustrated in Figure 1.

The Kirkwood-Fröhlich equation (Chapter 2 equation [2.3]) has been used to determine \( g \)-values for alcohols. The values obtained will be subject to some error due to uncertainty concerning the appropriate value of \( \varepsilon_{\infty} \). In the extensive early determinations of Dannhauser and Cole (16), a "somewhat arbitrary" choice of \( \varepsilon_{\infty} = 2.4 \) was adopted as a "reasonable compromise" between the value given by the high frequency limiting value of the principal dispersion, and that given by
n^2 (n = refractive index). In later works, the value selected has ranged between 1.0 n^2 (17) and 1.1 n^2 (18).

Garg and Smyth (19) studied C_3 to C_{10} n-alcohols over a range of frequencies up to 136 GHz. Comparison of the interpolated ε_∞ values with refractive index data by the same authors indicates that the assumption that ε_∞ = kn^2 where k lies between 1.0 and 1.1 is justified, although the scarcity of high frequency data points gives some uncertainty. In contrast, results for the secondary alcohol cyclohexanol (20) suggest a rather higher value for ε_∞, and in the absence of detailed experimental relaxation data for alcohols other than the normal type, it is possible that the ε_∞ values for such alcohols may be significantly in error. However, despite this uncertainty, it is well established that for the n-alcohols g is significantly greater than unity, being typically within the range 2.5 to 3.1 at room temperature (16, 18, 21), indicating extensive self-association of the open linear type.

Similarly high g-values have been reported for other alcohols such as the secondary alcohol cyclohexanol (17) indicating similar association.
Tertiary butanol has $g = 2.12$ at $25^\circ$ C (18) indicating some degree of steric hindrance to linear association. In contrast, for more sterically hindered alcohols such as the octanol isomers 2 methyl- and 3 methyl 4 heptanol values of $g = 1$ and $g < 1$ have been reported (22), indicating the presence of closed structures.

Many authors have suggested that the behaviour of the n-alcohols and other unhindered ones such as the secondary alcohol cyclohexanol is most satisfactorily explained on the basis of association involving long chains of indefinite length (eg 6, 16, 17).

Using a method for calculating the $g$-factor which was an extension of the earlier work of Oster and Kirkwood (23), Dannhauser and Cole (16) considered a model of infinite chains of doubly H-bonded molecules.

It was assumed that there exists a distribution of chains of varying lengths governed by the association equilibria:

$$\text{(ROH)}_n + \text{(ROH)} \rightleftharpoons \text{(ROH)}_n + 1$$

with equilibrium concentrations governed by an equilibrium constant $K$ given by

$$K = \frac{C_n + 1}{C_n C_1} = \frac{1}{C_0} \exp \left( \frac{\Delta H - T\Delta S}{RT} \right)$$
where $C_n = \text{concentration of polymer}$
$C_0 = \text{gross monomer concentration}$
$\Delta H = \text{activation enthalpy}$

and $\Delta S = \text{activation entropy}$

The authors obtained the following approximate expression for the mean $g$-value of an $n$-membered chain, $\bar{g}_n$, in which the group moments along the O-H and O-R bonds were 1.55 D and 1.20 D respectively with the ROH bond angle $= 105^\circ$:

$$\bar{g}_n = 2.40 + \frac{2.00}{n} \quad (n > 1)$$

and $g_1 = 1$

The mean $g$-factor $\bar{g}$ was then given by

$$\bar{g} = \frac{1}{C_0} \sum_{n=1}^{\infty} n \bar{g}_n C_n = 2.39 - 2.00a^{\frac{1}{2}} + 0.61a$$

where $a$ is defined by $\frac{C_1}{C_0} = (1 - KC_0 \alpha)^2$

For $\Delta H$ in the range 25 to 35 k J mol$^{-1}$ and $\Delta S$ in the range 65 to 105 J mol$^{-1}$K$^{-1}$, they reported that the temperature dependence of $g$ in butyl alcohols was satisfactorily accounted for, but the low temperature value of $g = 2.39$ for 1 butanol was too low, even when the uncertainty in the experimental value of $g$ due to uncertainty in $\varepsilon_\infty$ was included.

They suggested that this discrepancy in $g$ was at least partly due to the "crude assumptions" of the
model with the assumption that $K$ is independent of $n$ being particularly doubtful.

In a subsequent paper, Dannhauser and Bahe (18) reported $g$ values for $C_1$, $C_2$ and $C_3$ alcohols in addition to the $C_4$ data and values for all the alcohols were given for a wide range of temperatures. For MeOH, the values of $\Delta H$ and $\Delta S$ were rather lower than for the other alcohols and for all the alcohols, the authors noted that the $\Delta S$ values were considerably more negative than those given by Pimentel and McClellan (1). Although this discrepancy was noted, it was not discussed. The success in giving the correct temperature dependence of $g$ is considered significant but the discrepancies between both the low temperature values of $g$ with experimental values and that of $\Delta S$ with literature data reveals limitations in the approach.

An alternative approach favoured by some authors has been one based on a smaller association complex of specific size. Fletcher (4) favoured an open tetramer and Bordewijk et al (3) favoured a closed tetramer where the $g$ value is greater than unity because the hydroxyl groups are not all in the same plane. It should be noted that, in contrast with the chain association model, neither
Fletcher nor Bordewijk et al calculated g-values for these specific sized complexes. In addition, the more recent work of Bordewijk et al (24) favoured a large open structure of unspecified size for pure alcohols.

As dilution of alcohols in non-polar solvents reduces the self-association of the alcohol, such studies have been extensively performed in order to gain information on possible association complexes. The experimental data for diluted alcohols appears to be adequately accounted for by association models involving equilibria of monomers, dimers, trimers and possibly tetramers. (4, 24, 25, 26).

It is considered that whilst there is much detail concerning association complexes in alcohols still to be resolved, the weight of evidence is essentially in favour of the long chain model for unhindered alcohols, whereas when steric hindrance is significant, association is often limited to small closed complexes such as dimers, trimers and tetramers. Further, dilution of unhindered alcohols in non-polar solvents also reduces association to similar small size complexes.

1.1.1.2 **Dielectric Relaxation**

Relaxation studies have revealed that the dielec-
tric dispersion of unhindered alcohols may be described by three relaxation times, $\tau_1$, $\tau_2$ and $\tau_3$ where $\tau_1 > \tau_2 > \tau_3$ (19, 20). The principal dispersion is due to the $\tau_1$ process and if $A_1$, $A_2$ and $A_3$ represent the amplitudes of each dispersion, it is generally assumed that these three regions describe the entire dipolar relaxation behaviour of the alcohol, ie

$$A_1 + A_2 + A_3 = \varepsilon_s - \varepsilon_\infty$$

where $\varepsilon_\infty$ is the high frequency limiting value of the dispersion. The highest frequency dispersion region (ie $\tau_3$) is generally attributed to reorientation of the OH groups in free monomers around the C-O bond (19).

There is some disagreement concerning the cause of the $\tau_2$ dispersion. Garg and Smyth (20), Jakusek and Sobczyk (27) and Crossley (28) have suggested that it is due to monomer rotation but Glasser et al (29) suggested that $\tau_2$ is a mean of monomer values with either small multimers or a polymer chain segment such as an -OR group rotating about its bond.

By far the most pronounced dispersion is that associated with the $\tau_1$ process and at present the interpretation is the least clear. For the n-alcohols $\tau_1$ increases regularly with increasing alkyl chain length, ranging from
54.4 ps for MeOH (30) to 2.019 ns for 1 decanol at 20° C (19) and the dispersion is Debye-type (single relaxation time). Sterically-hindered alcohols such as 3 methyl 4 heptanol do not exhibit the $\tau_1$ relaxation and it is thus sensitive to the steric environment of the OH group.

There are two basic approaches in the explanation of the $\tau_1$ dispersion. The first is based on chain like association following the model of Kauzmann (31 -33) which considered dielectric relaxation in terms of H-bond rupture followed by rotation of monomers, where H-bond rupture is the rate determining step. Dannhauser and Flueckinger (5) studied isomeric methylheptanols and observed Debye-type relaxation for all the liquids studied but the activation energies for the dispersion were found to be sensitive functions of the isomer structure. This led them to conclude that H-bond rupture is not the rate determining step but rather a prerequisite for dipolar reorientation. They suggested that, because the local structure remains on average chain-associative, dipolar reorientation is, of necessity, co-operative and occurs relatively infrequently; but when it does occur they suggested that the orientation rate is dependent on both the shape and size of the molecule since both of these properties will
affect the interaction between a molecule and its near neighbours. Campbell et al (34) suggested that on the basis of the Dannhauser and Fleuckinger model (5), a monotonous shortening of $\tau_1$ on dilution would be expected due to reduced molecular association but for C$_2$ to C$_6$ alcohols in cyclohexane, these authors observed an initial lengthening of $\tau_1$ on dilution. They added that co-operative effects by the solvent would not be expected since in cyclohexane solute - solvent interactions were minimal. An initial increase of $\tau$ on dilution was also reported by Sagal (35) for ethanol in cyclohexane, Hanna (36) for 1 butanol in tetralin and decalin, van den Berg et al (37) for 1 butanol in hexane and tetrachloromethane and Komooka (38) for 1 hexanol in cyclohexane. In contrast, both 1 propanol and 1 butanol exhibited a monotonous fall in $\tau_1$ on dilution in the more electron donating solvents 1, 4 dioxane, benzene, chlorobenzene and pyridine (39). Sagal (35) suggested that the observed behaviour could be explained on a model where $\text{H}$-bond rupture and dipole reorientation occur when a monomer molecule approaches the associated chain with its oxygen favourably orientated for a 'switch', where the oxygen may be present in a monomer or at the end of a chain structure.
The initial lengthening of $\tau_1$ was attributed to a solvent-screening effect giving increased resistance to rotation due to the presence of more bulky cyclohexane molecules.

A similar 'switch' interpretation was suggested by Campbell et al (34), but these authors suggested that in the pure alcohol, the linearly associated chains become entangled which thus increases the proximity of all molecular species enabling the switch to be more rapid. With initial dilution, the chains become less entangled without becoming shortened, thus increasing $\tau_1$. On further dilution, there is an increase in the fraction of unbonded oxygen atoms as the chain structure is broken thus again reducing $\tau_1$.

The results of van den Berg et al (37) revealed
an increase in $\tau$ on dilution to approximately 0.5 mf of alcohol and that over the range of concentrations in which $\tau$ increased, the g-factor remained constant at the pure alcohol value. Below 0.5 mf of alcohol, both $\tau$ and g decreased. The authors suggested that the close correspondence between $\tau$ and g indicated that the dielectric relaxation was due to linear multimers, but the authors did not make proposals concerning the size of such multimers.

Campbell et al (34) made no reference to the data of van den Berg et al but the observed relation between g and $\tau$ could be accounted for on the "entangled-chain" model if the behaviour over the range of concentrations from pure alcohol down to 0.5 mf is attributed to chains becoming less entangled in such a way that the net association between entangled chains is such that the g-factor is unaffected. This is not an unreasonable proposal since entangled chains would not be expected to produce a highly ordered lattice-type structure, thus in some regions an increase in g will occur, whereas in others there will be a reduction in g so that, on average, the net change in g is zero. Further, since the g-values of pure alcohols can be adequately accounted for without reference to entangled chains, it seems reasonable
to assume that such entangled chains do not affect the measured average g-factor.

The 'solvent screening' proposal of Sagal (35) is considered more difficult to reconcile with the data of van den Berg et al (37) since if such screening is the cause of the observed initial increase in $\tau$ on dilution, it would be reasonable to expect that the g-factor would be affected due to reduced association which is not in accord with the experimental data.

The other approach in explaining the $\tau_1$ dispersion has been due to Bordewijk et al (3) who suggested that the only associated species in the pure alcohol is a highly polar cyclic tetramer which is retained during reorientation. This model satisfactorily accounts for the Debye-type relaxation of the $\tau_1$ process but it was disputed by Campbell et al (34) on the basis of observed similar relaxation times for $C_2$ to $C_{10}$ n-alcohols diluted to below 0.3 mf in a non-polar solvent (34, 19) where the principal dispersion was Debye-type down to quite low concentrations. These authors suggested that, since several associated polar species are likely to exist in similar proportion at these low concentrations, their observations "throw considerable doubt" on
Bordewijk's hypothesis.

It should be added that the presence of similar proportions of several associated polar species at low concentrations has been confirmed by infrared data (4).

It is considered that, although the mechanism of the $\chi_1$ dispersion is not yet fully accounted for, since the existence of self-association involving long chains is reasonably firmly established, a mechanism of H-bond rupture, and thus chain breakage, followed by reorientation is at present the most satisfactory. A model based on the 'switch' proposal of Sagal seems particularly suitable with the entangled-chains suggestions of Campbell et al (34) rather than solvent screening being preferred.

1.1.2 Water

The dielectric properties of water have been extensively studied and have been considered in detail in recent treatises by Hasted (40) and Grant et al (42).

1.1.2.1 Static Permittivity $\varepsilon_s$

The static permittivity of water is accurately described by the expression

$$\varepsilon_s = 87.740 - 0.4008T + 9.398 \times 10^2T^2 - 1.410 \times 10^5T + 4.305 \times 10^7T^5$$
where $T$ is the temperature in °C (43).

It is well established that liquid water has a high degree of short range order and thus, since $\varepsilon_s$ is high, the Kirkwood g-factor would be expected to be substantially higher than unity. Determination of $g$-values using the Kirkwood-Fröhlich equation [2.3] has posed considerable difficulty however, since at present the appropriate value of $\varepsilon_\infty$ is still unresolved. If the value corresponding to the high frequency limit of the principal dispersion is adopted following Hill (44), a value of $g = 1$ at $25^0$ C is obtained which, as Grant et al (42) noted, is rather unlikely.

Zafar et al (45) proposed that a second relaxation process occurs in the far infra-red region which had a value of $\varepsilon_\infty$ of 1.8 ($= n^2$). When equation [2.3] is applied, a value of $g = 2.8$ is obtained. However, Afsar and Hasted (46) have suggested that the dielectric behaviour in the far infra-red region is better explained in terms of a resonance absorption process, rather than one of relaxation, thus the value of $\varepsilon_\infty$ must be regarded as still undetermined.

Theoretical approaches to account for the magnitude of $\varepsilon_s$ and its temperature dependence,
together with g-factor estimations, have been applied by a number of authors.

X-ray studies by Bernal and Fowler (47) established that water molecules, like ice, are tetrahedrally H-bonded. Two basic types of approach commonly adopted to describe liquid water behaviour have been
(i) the bond bending model (47, 48), and
(ii) characterisation of water by a significant number of broken bonds together with the presence of some zero bonded molecules (49, 50).

Pople (48) developed a model in which the majority of H bonds were regarded as distorted rather than being broken. He assumed that all molecules in liquid water are H-bonded to 4 neighbours each at a fixed distance \( R_q \). The nearest neighbour was thus constrained to be \( R_q \) distant from the central molecule, but the distances from the central molecule to the second, third and further neighbours will be dependent on the extent of bond-bending. This is illustrated in figure 3.
Each lobe represents either an O-H bond or a lone pair of electrons. He further assumed that each water molecule is exactly tetrahedral so that the angles between O-H bond directions and lone pair directions are all \( \text{arc cos} \left( -\frac{1}{3} \right) \). On this model an H-bond is considered undistorted when both the O-H of a donor water molecule and the lone pair to which it is H-bonded lie along the oxygen-oxygen line of the two molecules, giving zero bond-bending energy when all the \( \text{H}_2\text{O}-\text{H}_2\text{O}-\text{H}_2\text{O} \) angles are tetrahedral as in ice I. When either the lone pair direction or the O-H bond direction depart from the oxygen-oxygen line by an angle \( \phi \) the bond is distorted, giving an increase in the energy of the system \( \Delta U \) given by:

\[
\Delta U = k_\phi (1 - \cos \phi)
\]

where \( k_\phi \) is called the H-bond bending force constant. The radial distribution function of
the second and third neighbours was derived by statistical mechanics and analytical geometry and the value of $k_9$ which gave the best fit with X-ray diffraction data was selected. Application of the Kirkwood theory to this model predicted a temperature dependence of $\varepsilon_S$ in close agreement with experiment but the absolute values of $\varepsilon_S$ were too low. This discrepancy has been attributed to neglect of the field contribution from further neighbours and revised calculations by Eisenberg and Kauzmann (51) have given $\varepsilon_S$ values in close agreement with the experimental ones. Pople also obtained satisfactorily high g-factor values of 2.60 at 0° C falling to 2.46 at 83° C.

Using a model of water characterised by a significant proportion of broken bonds, Haggis et al (50) considered water as a statistical assembly of molecules forming 0, 1, 2, 3 and 4 bonds with surrounding neighbours. By assuming that the probability of H-bond forming or breaking is the same for all bonds, with the probability of a given type of bond, $i-j$, being given by

$$m_{ij} f_1(T) \exp \left( -\frac{\Delta H}{RT} \right)$$

where $f_1(T)$ is a function of temperature only, and $m_{ij}$ is the number of bonds of type $i-j$ between two water aggregates.

The probability of a given bond being formed at the same time was given by

$$n_{i-1} n_{j-1} f_2(T, p)$$

where $f_2(T, p)$ is a function.
both of the temperature and the condition of the water molecules. Under equilibrium:

\[ \frac{-\Delta H}{RT} = n_{i-1} \cdot n_{j-1} \cdot f(T, p) \]

Following Pauling (52), the authors considered that the latent heat of vaporisation, \( L \), is made up of two parts, the heat necessary to overcome the van der Waals forces (\( W \)) and the heat required to break the remaining H bonds, of which there are two molecule giving:

\[ p = 100 \left( 1 - \frac{L - W}{2\Delta H} \right) \]

The value of \( p \) at \( 0^\circ C \) was obtained using dielectric data and assuming the van der Waals forces were temperature invariant, using \( \Delta H = 19 \text{ kJ mol}^{-1} \), both the value of \( \varepsilon_s \) and its temperature dependence could be accounted for. G-factor values were calculated for the four types of associated structures with a value of \( g = 2.8 \) of \( 0^\circ C \) being obtained for the four molecule complex.

Recent developments have been molecular dynamics calculations by Rahman and Stillinger (53) on a sample of water containing 216 rigid molecules with the assumption that each oxygen atom is surrounded by a tetrahedral arrangement of four point charges. At the single temperature of \( 34.3^\circ C \), these authors obtained a value of \( g = 2.72 \).
All the theoretical approaches considered here give g-values substantially higher than unity as expected from the well-established high degree of correlation in the liquid. The values are also notably similar to the value of 2.8 at 25°C obtained from equation \[ 2.3 \] when the value of \( \varepsilon_\infty \) of 1.8 given by Zafar et al (48) is used.

1.1.2.2 Dielectric Relaxation

The dielectric relaxation of water is characterised by a relaxation time \( \tau \) of 9.3 ps at 20°C which exhibits a small distribution of values with the relaxation time spread parameter \( \alpha = 0.013 \) (equation \[ 2.8 \]) at this temperature (41).

Grant et al (42) suggested that the value of \( \tau \) indicates that it is related to the movement of individual molecules rather than clusters. These authors added that the molecular dynamics calculations of Rahman and Stillinger (53), which used a model based on individual molecules, gave a value of \( \tau = 6.7 \) ps at 34.3°C, which compares very favourably with the experimental value of 5.6 ps thus giving further support to the monomer reorientation interpretation.

Grant and Sheppard (54) have suggested that the small distribution of relaxation times could be explained using a bond breaking model in which
the distribution is attributed to different H bond strengths between symmetrically and asymmetrically two-bonded water molecules, where in the symmetrical case the H-bonding involves either both protons or both orbitals associated with lone pair electrons whereas in the asymmetrical case the H-bonds are one of each type. The dielectric relaxation was attributed to the rate formation of one-bonded molecules from two-bonded molecules.

1.1.3 Alcohol-water Mixtures

1.1.3.1 Static Permittivity $\varepsilon_s$

Since the static permittivity of water is higher than that of any of the alcohols, using simple additivity rules, it would be expected that the addition of water to alcohols would result in a steadily increasing value of $\varepsilon_s$ as the water content is increased. This behaviour was observed by Akerlof (55) and Decrooocq (56) in methanol, ethanol and n-propanol-water mixtures. However, work on longer alkyl chain alcohols has revealed a fall in permittivity with increasing water content and, in some cases, the presence of a minimum value for $\varepsilon_s$.

This effect was observed by Brown and Ives (7) in t-butanol water mixtures, Lawrence et al (8) in cylvohexanol-water mixtures, and D'Aprano (57)
in 1-pentanol-water mixtures. Brown and Ives suggested that the effect was due to the formation of a relatively long life water-centred aggregate in which four alcohol molecules are H-bonded to one water molecule (4A/W). This interpretation was also favoured by Lawrence et al from viscosity, nmr and dielectric data. The latter authors reported dipole moment calculations based on the assumption of free rotation of the alcohol molecules about the H-bonds connecting them to the central water molecule which revealed that a decrease in \( \varepsilon_S \) occurs with addition of water, when linear multimers larger than tetramers are present in the anhydrous alcohol; but if the multimers are cyclic, the formation of the 4A/W complex leads to an increase in \( \varepsilon_S \). Using this approach, these authors were able to satisfactorily account for the variation of \( \varepsilon_S \) with water content for a number of alcohols, together with its temperature dependence. The water-centred 4A/W complex model was also favoured by Lippold and Adel (58) from dielectric, viscosity and nmr studies of n-octanol-water mixtures.

Tjia (59) disputed the 4A/W complex model and suggested that the divergence of the behaviour of \( \varepsilon_S \) upon the addition of water to different alcohols was due to differences in the structure
of the corresponding complexes. In contrast to the monotonous increase in $\varepsilon_s$ when water is added to ethanol, Tjia observed that, at low temperatures, the addition of water to mixtures of ethanol with the non-polar solvent methylcyclopentane caused an initial reduction in $\varepsilon_s$. This was interpreted as indicating that the type of complex is highly sensitive to the density of hydroxyl groups of alcohol molecules and that allowance should be made for the existence of at least two kinds of complex. It was suggested that one complex gave rise to a relatively high dipole moment and the other a relatively low dipole moment where the former dominates at high densities of hydroxyl groups of alcohol molecules. This dominance of the former at high densities led Tjia to conclude that it contains more alcohol molecules than the low moment type.

Tjia suggested that the high dipole moment complex was one containing two $\alpha$ multimers (ie multimers with $g > 1$) joined by one water molecule with their dipole moments aligning. He added that proposed forms of the association complexes were highly speculative due primarily to uncertainty concerning the structure of the $\alpha$ multimers.
In the absence of a proposed structure for the \( \alpha \) multimers, the suggestion of an aggregate in which two such multimers are joined by one water molecule is considered unsatisfactory.

Hasted (40, 41) has calculated \( g \)-values for a number of alcohol-water mixtures by assuming that \( g_1 = g_2 = g \) in equation \([2.6]\) and using early experimental values for the static permittivity, refractive index and gas-phase dipole moment data. He noted that the theory had limitations due to neglect of cross-correlation terms arising from the correlation of dipoles of species 2 with those of species 1.

The calculations revealed that for methanol-water mixtures, as the alcohol content is increased from zero, the \( g \)-factor increases to a maximum at approximately 0.4 mole fraction (mf) of alcohol at \( 20^\circ C \) with a shift to lower mf at higher temperatures. N-propanol-water mixtures exhibited a minimum in the \( g \)-factor at approximately 0.5 mf whereas t butanol-water mixtures exhibited a progressive fall in \( g \) with added alcohol to 0.6 mf above which \( g \) remained almost constant.

The results for methanol-water mixtures were interpreted as indicating a structure-making effect
which maximises the g-factor. Conversely for the propanol-water mixtures, a structure-breaking effect which is most pronounced at about 0.5 mf was suggested.

In view of the fact that alcohol-water mixtures contain two highly associated components, neglect of cross-correlation terms is probably an unjustified assumption which makes the results of the calculations open to some doubt. This view is strengthened by the proposals given by various authors for the existence of a 4A/W complex which indicates the importance of cross-correlation effects.

1.1.3.2 **Dielectric Relaxation**

The relaxation behaviour of mixtures of polar liquids has been discussed by Davies (60). The author suggested that, if the relaxation process consists in single molecule reorientation, a binary polar mixture should show separate absorption centres corresponding to the relaxation times of the two components. Further, if the volume participating in the molecular relaxation was sufficiently large to have a composition indistinguishable from the overall average, then only a single absorption effect would be observed. This interpretation was proposed by
Schallamach (61) from dielectric dispersion studies of a number of binary mixtures of polar liquids.

Only one relaxation process was observed if both components were associated or if both were unassociated whereas mixtures of an associated with an unassociated liquid exhibited two separate relaxations. Davies (60) noted that the results conformed to a general pattern in that the more compatible pairs of liquids, eg two alcohols, two ethers, bromide and aldehyde, appeared to merge molecularly, thus giving the observed single relaxation whereas the less compatible mixtures of an alcohol with a bromide or an alcohol with an ether could exhibit molecular segregation due to the strong self-association of the alcohol molecules thus giving two separate relaxations.

However, Schallamach's results were obtained only for a restricted frequency range and in order to traverse the dispersion region, the measurements were performed over a range of temperatures. This procedure was rightly criticised by Davies (60) on the basis that varying temperature also varies permittivity, viscosity and solubility values. In particular, it was suggested that the range of temperatures used would have probably exceeded the
solubility limit for mixtures such as 1 propanol with isooamy bromide, thus causing phase separation effects.

Daumezon and Heitz (62) studied binary mixtures of an alcohol with an alkyl halide at temperatures between 120 and 160 K and similarly observed two separate relaxations, thus confirming the observations of Schallamach for such mixtures. These authors attributed the Debye-type lower frequency dispersion to relaxation of the alcohol and the higher frequency dispersion, which was not Debye-type, was attributed to a co-operative process between a weakly associated species involving alkali halide molecules and alcohol monomers.

Studies of mixtures of alcohols by Denney and Cole (63) and Bordewijk et al (3) did not reveal resolution of component features but simply a progressive shift from characteristics of the one alcohol to those of the other, thus indicating that these mixtures could be considered to have effectively provided a single environment.

If such behaviour were exhibited by alcohol-water mixtures, the principal dispersion should exhibit a progressive decrease in relaxation time with increasing water content. This behaviour has
been reported by Chekalin and Shakhparonov in methanol and 1 propanol-water mixtures (64, 65). Similarly, Peyrelasse (66) observed the effect in methanol-water mixtures. Chekalin et al attributed the relaxation to two single Debye-type dispersions and interpreted the dielectric behaviour using a chain association model where water molecules replaced alcohol molecules in the H-bonded chain. Their chain model for the alcohol-water mixture exhibited the unusual feature of an alcohol oxygen atom being involved in H-bonding to the hydrogen atoms of two other molecules. These results of Chekalin et al also showed that addition of water produced an increase in the relaxation time of the higher frequency $\tau_2$ dispersion. This effect was not commented upon.

Peyrelasse (66) considered that the principal dispersion was more accurately described by a Cole-Cole arc relation (equation [2.8]) with parameter $\alpha$ exhibiting a maximum value of 0.083 at about 65% by weight of alcohol (corresponding to about 0.5 mf). The author noted that this peak in $\alpha$ occurred at a similar composition to the peak at 0.4 mf of alcohol in the g-factor for methanol-water mixtures calculated by Hasted (41).

This approximate correlation of the peak in $\alpha$
with the peak in $g$ led Peyrelasse to conclude that addition of methanol to water increases the molecular association. In the absence of other data in which a maximum in the spread of relaxation times, $\alpha$, is related to molecular correlation, $g$, this proposal is considered unacceptable.

Tjia (59) observed a fall in relaxation time for alcohol-water mixtures of 1, 2, 3 and 4 heptanol on the addition of water up to 0.15 mF. The principal dispersion for 1 heptanol-water mixtures was Debye type but the 2, 3 and 4 heptanol-water mixtures exhibited Cole-Davidson skewed-arc behaviour where the $\beta$-parameter decreased monotonously with increasing water content. In order to interpret the relaxation behaviour, Tjia suggested two possibilities. In the first case, he considered his results could be explained on the basis of cyclic alcohol-water complexes of varying size. Alternatively, the results were considered to be due to dielectric friction effects associated with dipole-dipole interactions in linear structures based on a proposal that in alcohol-water mixtures which exhibit a fall in static permittivity $\varepsilon_s$ on addition of water, such as the heptanols at higher temperatures, a decrease in the energy of the
dipole-dipole interaction also occurs. This was suggested as being quite plausible on the basis that the dipole-dipole interaction energy contributes to the activation energy $\Delta G$ and using a Kauzmann type relation (31): 
\[ \tau = \tau_0 \exp \left( \frac{\Delta G}{kT} \right) \]
a decrease in $\Delta G$ would be accompanied by a fall in relaxation time $\tau$ which is in agreement with Tjia's experimental observations. He considered that a fall in $\varepsilon_S$ is likely to cause the dipolar reorientation to be less hindered, giving a reduction in friction on the dipole. It was pointed out that this approach would also account for the observed properties of ethanol-water mixtures where addition of water causes a monotonous increase in $\varepsilon_S$ and Hassion and Cole (21) had reported a monotonous increase in relaxation time $\tau$ on addition of water to ethanol up to 5% by mass.

An increase in $\tau$ on addition of water was also reported by Sarojini (67) in methanol-, ethanol-, 2 propanol- and 1 butanol-water mixtures up to approximately 4% by volume of water, with the effect being most pronounced in the 1 butanol mixtures. These mixtures also exhibit a monotonous increase in $\varepsilon_S$ on addition of water, giving further support for Tjia's dielectric friction interpretation.
However, the relaxation data of Sarojini for methanol-water mixtures is in disagreement with the more recent data of Chekalin et al (64) and Peyrelasse (66). Further, more recent measurements by Buck (68) revealed a decrease in $\tau$ as water is added to ethanol which is in disagreement with the results of Hassion and Cole (21) and Sarojini (67). More recent measurements have thus established that addition of water to both methanol and ethanol reduces the relaxation time. Since it is well established that for both of these alcohols, addition of water also increases the static permittivity $\varepsilon_s$, it would appear that the relationship between $\tau$ and $\varepsilon_s$ proposed by Tjia on the basis of dielectric friction is incorrect.

The more recent measurements on methanol and ethanol-water mixtures, in which addition of water causes a reduction in relaxation time, are in accord with those of Chekalin and Shakhparonov for 1-propanol-water and Tjia for 1, 2, 3 and 4 heptanol-water mixtures and it appears that addition of water to alcohols causes a reduction in relaxation time regardless of whether the static permittivity increases or decreases on addition of water.

The only exception to this trend is the data of
Tjia (59) on 3 heptanol-water mixtures at the low temperatures - 60° and - 70°C, particularly the - 70° data. At these temperatures, Tjia observed a minimum in \( \varepsilon_s \) and obtained values of \( \tau \) which remained almost constant with water content over the range 0.02 to 0.15 mf of water. In contrast, at higher temperatures where a minimum in \( \varepsilon_s \) was not exhibited, a steady decrease in \( \tau \) with increasing water content was observed. The author suggested that the different relaxation behaviour of the 3 heptanol-water mixtures at low temperatures could have been due to the mixture being no longer homogeneous, which is clearly a possibility at temperatures of - 60° and - 70° C.

1.1.3.3 **Summary**

Since particularly strong support for a specific association complex (4A/W) arose from studies of t butanol- and cyclohexanol-water mixtures in which a minimum in \( \varepsilon_s \) is observed (7, 8), it was considered that dielectric relaxation studies on aqueous mixtures of these two alcohols might give further information on the proposed (4A/W) complex.

In addition, since it has been suggested that steric factors limit the association in t butanol to small size complexes (69), which is in contrast with cyclohexanol for which chain-like association
has been proposed (17), it was considered that the dielectric relaxation of aqueous mixtures of these two alcohols might exhibit significantly different behaviour.

It was therefore decided to study the dielectric relaxation of alcohol-water mixtures of both t-butanol and cyclohexanol. Since the experimental data of Sarojini (67) for both methanol- and ethanol-water mixtures appears to be in error, it was considered possible that her data for 1-butanol-water mixtures might also be erroneous. In view of this, it was decided to include some studies of the relaxation of 1-butanol-water mixtures. In addition, some measurements on 1-heptanol-water mixtures have been included in order to confirm or otherwise the trend revealed in the lower temperature studies of Tjia (59).

1.2 Micellar solutions of non-ionic surfactants in binary mixtures with water and ternary mixtures with water and hydrocarbons

1.2.1 Introduction

In dilute aqueous solution, the behaviour of non-ionic surface active agents (surfactants) often resembles that of simple organic molecules, but at higher concentrations of surfactant, pronounced deviation from this simple behaviour occurs (9, 10). Examples of physical properties which have been
found to be exhibiting these deviations are interfacial tension, viscosity, electrical conductivity and specific heat (9).

The well-defined, but not abrupt, changes are attributed to the association of molecules into micelles and the concentration of surfactant at which micelles appear is known as the critical micelle concentration (CMC). The micelle may be anionic, cationic, zwitterionic or non-ionic, depending on the chemical structure of the surfactant.

Non-ionic surfactants are characterised by CMC values that are typically about a factor of 100 lower than ionic surfactants containing comparable oleophilic groups. This is due to the absence of the counterion layer which reduces the electrostatic repulsion between the charged surfactant headgroups at the micelle-solvent interface in ionic surfactants. Commercial non-ionic surfactants such as those with a polar headgroup based on ethylene oxide contain a range of ethylene oxide group sizes and are thus termed polydisperse in contrast to the monodisperse pure surfactant.

Becher (11) has pointed out that, although a large number of non-ionic surfactants prepared by
commercial processes are polydisperse, "it is to be expected that their properties will be close to that of the homogeneous compound having the composition of the mean". However, Shinoda et al (10) have pointed out that impurity and polydispersity effects introduce a certain degree of ambiguity into the determination of surfactant properties and suggested that experiments with pure materials or mixtures of known composition would be "highly desirable". Further, Shinoda and Kunieda (70) have shown that solubilisation of oil (or water) is higher when the surfactant is monodisperse than when it is in a polydisperse form.

1.2.2 Micellar Structure
Surfactants are characterised by a polar headgroup which has hydrophilic properties, and is thus at the micelle-water interface in an aqueous solution of a surfactant and, further, these headgroups will be hydrated by a number of water molecules. The other part of a surfactant molecule is typically a hydrocarbon chain which will therefore have oleophilic properties.

It would be thus expected that in an aqueous mixture containing a small proportion of surfactant which is in excess of the CMC, a representative spherical micellar structure would be as in
The hydrocarbon (oily) portion of the surfactant is inside the micelle which may be thus referred to as an oil-in-water (O/W) structure. Such a micellar structure is called a normal micelle, whereas an arrangement in which the polar headgroups are at the centre is called an inverted micelle. Whilst an inverted micelle would not be expected in a binary mixture of surfactant and water at low surfactant concentration, in ternary mixtures with a hydrocarbon as the third component such inverted structures would be possible. In non-ionic surfactants, reduced H-bonding causes the hydrophilic behaviour of the polar headgroup to decrease rapidly at higher temperatures and is accompanied by dehydration. This causes an increase in the aggregation number of the micelle and produces "giant" micelles (10, 11). Above a certain temperature known as the cloud point, the mixture turns turbid and at a somewhat higher temperature it
begins to separate into two phases (11). This turbidity is generally attributed to reorganisation, growth and eventual bursting of the micelles associated with dehydration of the polar headgroup (71) which is followed by the formation of a separate surfactant-rich phase.

1.2.3 Micellar Shape

Although many authors have assumed that micelles are spherical in shape (eg 9, 10, 72, 73), Tanford et al (74) have reported that for aqueous solutions of polyethylene glycol dodecyl ethers (C_{12}E_n) where n \geq 8, comparison of calculated and observed Stokes radii revealed an oblate spheroidal shape with axial ratios ranging from 1.5:1 for C_{12}E_{23} up to 2.5:1 for C_{12}E_8. Theoretical calculations of micellar free energy by Tanford (75) also favoured an oblate spheroidal shape.

Tanford et al (74) also suggested that for aqueous solutions of C_{12}E_n where n < 8, a distinctly different mode of association believed to be the result of secondary aggregation occurs. These authors reported the work of Elworthy and Macfarlane (76) and Attwood (77) in support of this interpretation. Tanford et al (74) added that this secondary aggregation effect was strongly temperature dependent since C_{12}E_6, which formed
large aggregates at 25° C or above only formed single micelles at 5° C (78, 79).

Secondary aggregation effects rather than an increased aggregation number as the cloud point is reached were suggested by Staples and Tiddy (80) from nmr studies of C₁₂E₆ micelles. The authors differed in respect of whether or not the secondary aggregation involves association of polyoxyethylene chains between different micelles. Such association was favoured by Tanford et al but Staples and Tiddy reported that calculations of the average distance between micelles gave a figure which was too large for association to occur. These authors instead suggested an interpretation based on the change in the balance between hydration forces and van der Waals forces. The hydration force arises due to the attraction between the polar headgroups and water and gives a repulsive force between the oily aggregates whereas the van der Waals force causes an attraction between the oily aggregates. The authors suggested that since dehydration of non-ionic surfactants occurs when the temperature is increased, the hydration-repulsion force will also decrease with increasing temperature. This change of hydration-repulsion force was suggested as causing a balance between this force and the van der Waals force at the cloud point, resulting in
secondary aggregation. It was added that similar
effects should occur in all pure non-ionic
surfactants with water just below the cloud point.

Bostock et al (81) have shown, from nmr studies of
self diffusion in aqueous solutions of C_{12}E_6 with
mass fractions of surfactant between 0.1 and 1,
that normal micelles are present at all compositions
including the pure surfactant. In contrast,
Friberg et al (86) reported that in surfactant-rich
aqueous solutions of C_{12}E_4, no micelles had been
detected. In the absence of details of the
experimental methods used, it is difficult to
evaluate the assertion of an absence of micelles.
It is possible that failure to identify micelles
could have been due to the micellar structures
being of small size and thus outside the
measurement limits of the technique used by
Friberg et al.

In contrast to possible small micelles in
surfactant-rich solutions, Bostock (83) has
reported that, in water-rich solutions of the
surfactant C_{12}E_4 and its commercial counterpart
Brij 30, which has an average alkyl chain length
of twelve and an average ethylene oxide chain
length of four, large micelles occur. In addition,
some marked differences between C_{12}E_4 and Brij 30
have been reported in both binary mixtures with water and ternary mixtures with heptane.

1.2.4 **Microemulsions**

Ternary mixtures containing a surfactant, water and an oily component often form an optically transparent liquid phase. With non-ionic surfactants, the clear phase is often observed over appreciable composition ranges (82, 84, 85, 86, 87). A representative phase diagram is given in figure 5.

Figure 5

![Diagram of microemulsion phase diagram](image)

Some of the clear phases contain normal micelles (W/O) and others contain inverted micelles (O/W). In ternary systems containing appreciable proportions of both oil and water where the micelles become very large, these clear phases are frequently referred to as microemulsions, following the proposal of Schulman (88). Although microemulsions of both ionic and non-ionic surfactants
are currently attracting much interest, there is still "disagreement, confusion and controversy" (89) concerning use of the title microemulsions. Shah et al (89) suggested that this is due to a lack of complete characterisation of the molecular association and aggregation in such systems. In order to show the relative order of the size of the dispersed phase in various systems, the authors proposed a classification of droplet size as follows:

Molecular solutions : size 0 to 1 nm
Micellar solutions : size 1 nm to 10 nm
Microemulsions : size 10 nm to 100 nm
Colloidal dispersions : size 100 nm to 1 µm
Macroemulsions : size 1 µm to 10 µm

For microemulsions, Friberg (90) proposed that the droplet sizes be in the range 20 to 80 nm, whereas Prince (91) proposed 10 nm to 200 nm. Thus, although there is some disagreement about the precise upper and lower limits for the size of the dispersed phase, there is a consensus that droplet sizes are substantially larger than those of micellar solutions.

There have been two basic approaches in the theory of microemulsion stability, and these have been discussed in the review by Prince (91). One theory considers a microemulsion as a two phase
system, resembling an emulsion in being thermodynamically unstable (92), where the surfactant is adsorbed between two mutually insoluble liquids causing one liquid to be spontaneously dispersed in the other due to transient interfacial forces (93, 94). The other theory considers a microemulsion to be a thermodynamically stable one phase system of swollen micelles where the surfactant organises itself into colloidal aggregates which, under appropriate conditions, can bind water or oil (95, 96). A recent article by Crooks (97) suggested that, at present, the experimental evidence favours the swollen micellar approach. Prince (91) noted that either theory "can and is being used" to formulate microemulsions.

Emulsions stabilised with non-ionic surfactants such as polyethylene glycol alkyl ethers generally form O/W emulsions at low temperatures and W/O emulsions at higher temperatures (87, 98), and there is thus a temperature at which the emulsion type changes. This temperature is usually referred to as the phase inversion temperature (PIT). Phase inversion effects have also been reported in microemulsions (84, 86, 87). In addition to O/W and W/O micellar structures, Shinoda et al (70, 87, 99-102) have reported that, at temperatures close to the PIT, another isotropic liquid phase may be obtained.
This phase is called the surfactant phase and is observed as an isolated region, corresponding to about 10% by mass of surfactant, in the three component phase diagrams (82, 84, 85). Shinoda and Kunieda (87) suggested that the surfactant phase consists of lamellae of water and hydrocarbon with the surfactant as the continuous phase. From studies of ternary mixtures of the surfactants polyethylene glycol dodecyl ether (C₁₂Eₙ), Friberg et al (86) suggested that the presence of spherical micelles, in addition to planar structures, in the isotropic surfactant phase could not be ruled out. These authors considered that their results could be broadly accounted for by considering that in both normal and inverted micellar solutions, the micelles were spherical. However, the authors also observed anomalous hydrocarbon solubilisation behaviour and this was attributed to deviations from spherical shape.

1.2.5 Dielectric Properties

1.2.5.1 Ionic Surfactants

In contrast to alcohols and water, the dielectric properties of aqueous mixtures of surfactants have received very little attention and where studies have been reported, they have been primarily on ionic surfactants (103, 104, 105, 106, 107). Due to the presence of the counterion layer between
the polar headgroup of the surfactant and the continuous aqueous phase, substantial differences between the dielectric behaviour of ionic and non-ionic surfactant micellar mixtures would be expected.

In micellar solutions of anionic surfactants, a typical structure will be as given in figure b,

Figure 6

Aqueous
Bulk Phase

core 10
28

Stern layer 0
up to a few A

Gouy-Chapman
double layer

hundred A

Counterions

The thick double layer would be expected to give an important and possibly dominating contribution to the dielectric properties. The electrical properties of counterion layers have been considered in detail by O’Konski (108) who showed that such layers can cause pronounced dielectric dispersion effects.

1.2.5.1.1 Binary Mixtures with Water

Kaatze et al (103) studied aqueous solutions of n-alkyl amine hydrochlorides as ionic
surfactants above the CMC at 25° C in the frequency range 5 to 37 GHz with surfactant concentrations typically in the range 0.2 to 2.7 mol l⁻¹. The extrapolated static permittivity, εₛ, decreased with increased surfactant concentration, falling from 76.1 at 0.2 mol l⁻¹ to 34.0 at 2.71 mol l⁻¹ for OctACl. The authors reported that with concentrations below about 1.5 mol l⁻¹, the εₛ values agreed with the "commonly expected" respective ε values for the mixture but the mixture relation used was not quoted except that it was stated as being applicable to "non-polar, spherically shaped solute particles which do not strongly interact with the solvent".

However, from the later works of Kaatze et al (109, 110) on the dielectric properties of aqueous solutions of polyethylene glycols where n = 1 to 14,000, it is evident that the mixture equation used was a modified form of the Rayleigh equation for a heterogeneous mixture, (equation [2.14] in Chapter 2), in which an adjustable empirical parameter was included. It should be noted that these heterogeneous mixture equations assume complete absence of molecular association between the two or more components of the mixture. In the binary
mixture case, such a mixture is considered as a dispersion of globules of one component in the continuous medium formed by the other component. In the general case in which the two components differ from each other in terms of permittivity and conductivity, polarisation occurs due to accumulation of charge at the interface between the two components. This interfacial polarisation is often called the Maxwell-Wagner effect.

At higher concentrations of all the surfactants and, in addition, for all solutions of DoTACl which was studied at concentrations down to 0.4 mol l\(^{-1}\), Kaatze et al. (103) reported that the measured \(\varepsilon_s\) values were lower than the calculated values. Using an approach based on the heterogeneous mixture equation of Polder and Van Santen (equation [2.49] in Chapter 2), the authors reported that the experimental values agreed with theoretical values if an oblate spheriodal shape of axial ratio approximately 3:1 was assumed. The authors reported that other data on DoTACl (111, 112) supported the 3:1 value. The adjustable parameter used in the more recent reports of Kaatze et al (109, 110) was not referred to and so it is presumed that it was not applied to this experimental
The dielectric relaxation data was considered to be most accurately described by a model based on two Debye-type relaxations with times $\tau_p$ and $\tau_q$. The $\tau_q$ value was approximately four times longer than that of free water, whereas the $\tau_p$ value was slightly smaller than that of free water. The authors reported that extensive earlier studies of aqueous solutions of monomers had not revealed $\tau$ values similar to $\tau_q$ and they attributed it to the porous structure of the micellar surface producing a relatively long bound water dispersion. The $\tau_p$ dispersion was attributed to effects of weak electric fields acting near the micellar surface modifying the free water relaxation.

It is worthy of note that Kaatze et al (109, 110) favoured use of a heterogeneous mixture equation in studies of aqueous solutions of polyethylene glycols. Since such solutions are not micellar and, in the case of ethylene glycol particularly, association between individual molecules would be expected, description based on a heterogeneous mixture equation is surprising. Nevertheless, since the authors reported good agreement with experimental values when the adjustable parameter
had the same value of 0.728 for all polymers (n = 1 to 600,000), the use of such an approach does seem to be justified.

Cavell (107) studied cationic micelles in aqueous solutions of tetradecyl trimethyl ammonium bromide (TTAB) with TTAB concentrations in the range from zero up to 800 mol m$^{-3}$ at 20° C in the frequency range 0.35 to 35 GHz. The static permittivity $\varepsilon_s$ exhibited anomalous effects in giving a maximum value of 92.0 at 200 mol m$^{-3}$. This effect was not commented upon.

The dielectric relaxation was analysed in terms of two relaxation times $\tau_1$ and $\tau_2$ where the faster $\tau_1$ dispersion contained a small distribution of relaxation times which remained constant around 9.5 ps for all concentrations of TTAB. The $\tau_2$ dispersion was Debye-type and decreased with increasing concentration of TTAB above 50 mol m$^{-3}$ from 596 ps at 50 mol m$^{-3}$ to 202 ps at 800 mol m$^{-3}$. The $\tau_1$ dispersion was attributed to relaxation of the slightly bound solvent water and the $\tau_2$ dispersion was interpreted using a model of Schwarz (113) based on a frequency dependent surface admittance of the assumed spherical counterion layer. Using micellar size values for TTAB given by Tartar
(114) and known mobilities of bromide ions, the equation of Schwarz was found to give a value for $\tau_2$ which was a factor of two lower than the experimental value at the highest concentration.

The reduction of $\tau_2$ with increasing water content was attributed to an increase in the thickness of the electrical double layer, which in the model of Schwarz had been assumed to be of negligible thickness compared with that of the radius of the dispersed globule. The author used his experimental data to calculate a value for the radius, $r$, of the micelle which included the double layer and obtained a small fall in $r$ with increasing TTAB content where the values of $r$ were approximately 50% higher than the value given by Tartar.

Beard et al (105) studied micellar solutions of SDS (sodium dodecyl sulphate) in water with SDS concentrations of up to 12 g l$^{-1}$ at 25$^\circ$ C in the frequency range 500 kHz to 1.5 GHz. The static permittivity increased with increasing SDS concentration following an approximately linear relationship. The dielectric relaxation revealed Cole-Cole arc type behaviour with parameter $\alpha = 0.19$ and a relaxation time, $\tau$, of approximately $1 \times 10^{-9}$ s. Both $\alpha$ and $\tau$ remained
constant over the range of concentrations studied.

The variation of $\varepsilon_S$ with concentration was discussed in the context of the observed linear increase of the dielectric increment $\Delta \varepsilon (=\varepsilon_S - \varepsilon_\infty)$ with SDS concentration. The authors stated that the observed dielectric properties were characteristic of a heterogeneous dielectric relaxation for an inhomogeneous boundary of bound water between the hydrocarbon core of the micelle and the bulk water. The measured $\alpha$ value was noted as being close to the value of 0.2 obtained by Grant (115) for bound water in bovine serum albumen, where in the SDS solutions the heterogeneous relaxation was not handicapped by the much larger dipolar relaxation of the core.

The authors considered a number of approaches to the dielectric properties of spherical particles surrounded by a shell and found the approach of O'Konski (108) to be of particular interest. The O'Konski model enabled the dielectric increment to be satisfactorily accounted for but gave $\tau$ values approximately a factor of 100 larger than the measured ones. The authors suggested that this could be due to a contribution by the
reactive component of the conductive shell which was neglected in O'Konski's theory. In this case, since the shell contained both ions and water with a permittivity greater than that of the core, it was considered that an analysis based on bound water would be useful. Two such approaches were used. The first followed a model by Grant (115) for protein hydration based on a dielectric mixture formula. The second followed a shell model after Schwan (116) where the behaviour of the hydrocarbon core, water shell and surrounding electrolyte were considered in terms of a Maxwell-Wagner type dispersion. Using the experimental data for $\tau$ and $\Delta\epsilon$ in the approach following Schwan and assuming that the radius of the spherical micelle core did not exceed that of the straight dodecyl chain, the authors obtained a value of 6.6 g H$_2$O/g SDS for the number of grams of bound water per gram of SDS in the micelle, compared with a value of 25 g H$_2$O/g SDS given by the Grant model. It should be noted that even with the lower figure of 6.6 g H$_2$O/g SDS, a rather high figure of 100 water molecules per molecule of SDS is obtained.

1.2.5.1.2 Ternary Mixtures with Water and a Hydrocarbon

Eicke and Christen (117) studied micellar solutions of the ionic surfactant Aerosol AY
(sodium di 2 pentyl sulphosuccinate) in benzene containing solubilised water. They reported that studies using a number of techniques indicated that the Aerosol AY with benzene micellar solution involved aggregations of similar size and that the micelles contained sub-units of trimer complexes. Eicke and Shepherd (104) studied the dielectric relaxation of Aerosol AY in benzene with solubilised water at 20° C in the frequency range 200 kHz to 10 MHz. The static permittivity increased from 5 without water up to 27 at 6.3% by volume of water and followed an approximately quadratic relationship
\[
\left( \frac{\Delta \varepsilon}{\Delta \phi} \right) = 2 \text{ where } \phi = \text{ volume fraction of water}. 
\]
Dielectric relaxation was observed exhibiting Cole-Davidson type dispersion with parameter $\beta$ increasing from 0.33 without water up to 0.45 at 6.3% of water. The relaxation time $\tau$ fell from $3.8 \times 10^{-7}$ s to $6.3 \times 10^{-8}$ s at 2.7% of water and then remained constant up to the 6.3% value. At higher water content, both the permittivity and conductivity become unstable.

The authors used an approximate equation derived from the equation of Kirkwood where the dielectric increment ($\varepsilon_S - \varepsilon_\infty$) was considered to be proportional to the product of the concentration and square of the dipole moment of the polar
units, in order to obtain an aggregation number, n, for the hydrated micelles. From the experimental data, a value of n = 2 was obtained, indicating aggregation of micelles into pairs.

This aggregation of micelles into pairs was suggested as being the cause of the observed variation of $\varepsilon_s$ with increasing water content. The instability above 6.3% by volume of water was attributed to further aggregation of micelle pairs into higher aggregates. The authors added that approximate confirmation of the micelle pair interpretation was given by apparent molecular weight data.

The dielectric relaxation was attributed to orientation of the micelle and the authors reported that when viscosity data was substituted into the Debye equation for relaxation time, a micelle size of comparable value to that determined from both geometrical considerations and from partial specific volume and diffusion coefficient data was obtained.

The reduction of $\tau$ on addition of water was attributed to stabilisation of the micelle by water causing denser packing and thus allowing faster reorientation in the applied field. This interpretation is open to dispute since it would
not be expected that addition of water to an inverted micelle would cause a reduction in micellar size.

The observed Cole-Davidson type dispersion was simply attributed to micellar aggregation and deviation from spherical shape without further justification. Eicke et al (118) reported that high field studies on Aerosol OT (sodium di 2 ethyl hexyl sulphosuccinate) at 22° C revealed two superimposed relaxation processes. These were attributed to separate orientation polarisation effects with the higher frequency relaxation due to the trimer sub-units of the micelle and the lower frequency one due to whole micelles. In view of the sparse high frequency data of Eicke and Shepherd (104), it could easily be argued that their results were due to separate Debye-type dispersions rather than the Cole-Davidson type and thus the interpretation based on aggregation and non-spherical shape must be treated with some caution.

Clausse et al (119) used the ionic surfactant potassium oleate with 1 hexanol as co-surfactant in dielectric studies of microemulsions of water in hexadecane. Temperatures were not stated. The authors reported that microemulsions could be
prepared for mass fractions of water, p, up to 0.32 above which turbidity and instability was observed. The static permittivity increased linearly from approximately 4 at p = 0 to 8 at p = 0.2 above which it increased rapidly to approximately 80 at p = 0.3 and giving values in excess of 100 at concentrations close to p = 0.32. The one dielectric relaxation curve given in the report was for p = 0.308 for which the static permittivity was approximately 90. Although the measurement temperature was not stated, it is evident from a study of the report that it was approximately room temperature, for which pure water has a permittivity of less than 80.

For values of p < 0.2, dielectric dispersion was not observed but at higher values of p a pronounced dispersion occurred. The dielectric relaxation parameters were not quoted but from inspection of their results a value of \( \tau = 5 \times 10^{-8} \) s has been calculated by this author. The dielectric behaviour for p > 0.2 did not agree with predicted values given by equations due to Hanai (120) for water in oil emulsions. The authors suggested that for p < 0.2, the dispersed water could be considered as solubilised within the polar headgroups of the surfactant molecules and that the solutions should be called
hydrated micelles, rather than microemulsions. The concentration dependence of $\varepsilon_s$ in the range $p = 0$ to 0.2 was not commented on.

For $p > 0.2$, the authors suggested that most of the water molecules gathered into minute droplets surrounded by an interfacial film which was dispersed within the system and could thus be defined as a water-in-oil (W/O) microemulsion.

The dielectric relaxation was attributed to interfacial polarisation effects "similar to those observed in emulsions". They added that high conductivity observed in the microemulsions indicated that some of the water remained "free".

This interpretation of the dielectric behaviour on the basis of similarity to interfacial polarisation effects observed in emulsions is open to dispute since the literature data for emulsions reveals static permittivity values that are lower than those for pure water (120 to 127) with the only exception being a W/O dispersion in which the volume fraction of the dispersed phase was greater than 0.6 (121).

In order to account for the observed high static permittivity values on the basis of interfacial polarisation, it would be necessary to use an
approach based on that of Schwarz (113) where the dielectric behaviour is related to counterion effects. The observed high conductivity of the microemulsions is compatible with such a model.

Sjoblom and Friberg (128) studied W/O microemulsions of potassium oleate with potassium ethylate in ethanol as co-surfactant in hexadecane using light scattering and electron microscopy methods. They reported that, in the concentration range corresponding to the $p < 0.2$ range studied by Clausse et al (119), no micelles were present and it was suggested that this absence of micelles was the reason for the absence of dielectric relaxation in such mixtures.

More detailed studies of water in hexadecane microemulsions using the same surfactants as those used by Clausse et al (119) at mass fraction of water $p = 0.310$ have been reported by Peyrelasse et al (106). The dielectric behaviour was studied at a number of temperatures between $20^\circ$ and $32.5^\circ$ C in the frequency range 5 kHz to 2 GHz. The static permittivity data exhibited anomalous effects, giving a maximum $\varepsilon_S$ value of 69.1 at $25^\circ$ C. Further, the lowest $\varepsilon_S$ value obtained was 40.0 at $20^\circ$ C.
Anomalous relaxation behaviour was also observed in that a maximum value in the relaxation time $\tau$ was obtained at $25^\circ C$. Thus at the temperature where $\epsilon_s$ was a maximum, $\tau$ was also a maximum. The dielectric dispersion was Cole-Cole arc type with parameter $\alpha$ falling from 0.36 at $20^\circ$ to 0.27 at $32.5^\circ$ C.

The authors suggested that since the dielectric dispersion was of a Cole-Cole arc type, it arises from interfacial polarisation phenomena similar to those observed in emulsions. They added that the peculiar dependence of $\epsilon_s$ and $\tau$ upon temperature indicated that the dielectric behaviour could be more related to surface admittance effects associated with the surfactant/co-surfactant shell surrounding the water-swollen micelles.

It should be pointed out that conformation with a Cole-Cole arc representation of the dielectric dispersion does not of itself provide support for an interfacial polarisation interpretation, but in view of the presence of the counterion layer, such polarisation effects are to be expected.

Senatra and Guibilaro (129, 130) studied water in dodecane microemulsions using the same surfactant/
co-surfactant as Clausse et al (119). For mass fractions of water, p, up to \( \approx 0.3 \), stable isotropic solutions were obtained and for \( p > 0.3 \) turbidity and instability were observed in qualitative agreement with the observations of Clausse et al. However for \( p > 0.7 \) stable isotropic solutions were again obtained. The authors suggested that for \( p > 0.7 \), the microemulsions were of the O/W type, since they were characterised by high static permittivity and high conductivity. Further, at mass fraction \( p = p_c = 0.625 \), both \( \varepsilon' \) and \( \varepsilon'' \) diverged to infinity and at values of \( p \) close to \( p_c \) both W/O and O/W dispersions were reported as co-existing where only one dispersion was stable with the other being metastable with life-times of the order of a few days. The dielectric behaviour for \( p \) close to \( p_c \) revealed maxima in both the real and imaginary component of the permittivity (\( \varepsilon' \) and \( \varepsilon'' \)) where the magnitude of both \( \varepsilon' \) and \( \varepsilon'' \) exhibited a steady increase as the frequency was reduced to its lowest value of 16 kHz. The authors suggested that, since similar behaviour is observed in some nematic liquid crystals, the observation of such behaviour at values of \( p \) close to \( p_c \) could be due to a similar nematic liquid crystalline phase.
1.2.5.2 Non-ionic surfactants

1.2.5.2.1 Binary Mixtures with Water

The only literature data on the dielectric properties of mixtures of non-ionic surfactants with water is the relaxation study of dimethyl ethers of ethylene, diethylene and triethylene glycols reported by Kaatze (110). As in the studies of polyethylene glycols reported in the same paper, investigation was restricted to one composition only at a volume fraction of water of 0.93. The static permittivity values of these solutions were lower than those of the ethylene glycols but the relaxation times were very similar. The lower static permittivity values of the surfactant solutions were not commented upon, neither were the structural differences between the surfactants and the polyethylene glycols considered.

1.2.5.2.2 Ternary Mixtures with Water and a Hydrocarbon

There have been few investigations of ternary mixtures of non-ionic surfactants and these have all been with commercial products.

Clausse et al (131) used the non-ionic surfactants Tween 20 and Span 20 as emulsifiers in studies of benzene in water microemulsions. The dielectric properties were studied at 20° C in
the frequency range 100 kHz to 5 MHz. Dielectric dispersion was not observed. The dielectric behaviour was attributed to interfacial polarisation and the experimental data gave good agreement with theoretical values given by equations of Hanai (120, 121) for oil in water (O/W) emulsions. Deviations between theory and experiment were observed at low volume fractions of the dispersed phase when the mass fraction of the surfactants was 15% Tween and 1% Span, and also when the fraction was 10% Tween and 1% Span. When the mass fraction was reduced to 5% Tween and 1% Span, deviations were not observed. The authors suggested two possibilities for the observed deviations. There could be a contribution by the polar group of the surfactant in the shell of the dispersed globule, particularly when the size of the dispersed globule was small and this effect could be greater at higher surfactant concentration. The other possibility suggested was that in the continuous aqueous phase, micelles of the surfactant might be formed. Since the concentration of surfactant in the aqueous phase was kept constant, the authors pointed out that the concentration of surfactant molecules available for micelle formation would be greater
Fraction as the volume of the dispersed phase was reduced. It should be added that in the continuous aqueous phase, micelles of the surfactant must of necessity be formed. Possibly the authors were implying that in addition to swollen micelles which are oil (benzene) centred, there are other micelles present consisting solely of the surfactant alone. This is considered unlikely and indeed unnecessary to postulate, since the first proposal seems quite reasonable.

These authors suggested that extension of the studies to the higher frequencies utilised by Beard et al (105) could check the validity of the qualitative explanations proposed. How such an extension in frequency range would check the validity is not entirely clear but presumably such a study would confirm or otherwise the absence of dielectric dispersion in O/W microemulsions since the Hanai equations for O/W dispersions predict negligible dispersion, although Clausse et al appeared to imply that dielectric relaxation might well be observed at higher frequencies simply because such an effect occurred with the ionic surfactant SDS.
Peyrelasse et al (132) used the non-ionic surfactant Octarox, which is composed of blends of polyoxyethylene octyl phenyl ethers, as surfactant for microemulsions of water in undecane. The dielectric properties of a mixture containing 2.5 g of water, 15 g of undecane and 2 g of Octarox were studied in the temperature range 25° to 40° C in the frequency range 400 Hz to 3 MHz with an additional spot frequency measurement at 2.1 GHz. The authors published the dielectric data for the 30.2° C measurements. A static permittivity value of 17.5 was obtained and a pronounced dielectric dispersion was observed with $\varepsilon_\infty = 3.4$. Relaxation parameters were not quoted but inspection of the published data reveals that the dispersion was of the Cole-Cole arc type with parameter $\alpha$ approximately 0.5. The relaxation time $\tau$ was about $2 \times 10^{-7}$ s. The authors added that the dispersion was of the Cole-Cole arc type over the whole temperature range studied. Interpretation of the dielectric behaviour was not given.

1.2.5.3 Summary

Hanai (120) pointed out that, whilst solutions of simple molecules and some polymers are considered on the basis of the dielectric theory of polar
molecules, and emulsions are considered on the basis of the dielectric theory of heterogeneous systems, "there is no established approach to the dielectric properties of systems such as inverted micellar solutions and microemulsions". Although that assertion was made about a decade ago, a survey of more recent studies suggests that it is still applicable, as is indicated in the following summary of recent work.

Kaatze et al (103) have attributed the dielectric relaxation of binary mixtures of an ionic surfactant with water to orientation polarisation whereas Cavell (107) and Beard et al (105) have favoured an interfacial polarisation approach. Similarly in ternary mixtures of an ionic surfactant with water and a hydrocarbon Eicke et al (104) have proposed orientation polarisation, whereas Clausse et al (119) and Peyrelasse et al (106) have favoured an interfacial mechanism.

In non-ionic surfactants, the absence of the counterion layer should considerably simplify interpretation of dielectric properties but the very limited experimental data available precludes identification of the most suitable approach.

In binary mixtures with water, the only published data is for polyethylene glycol dimethylethers at one
composition (110) and the author made no reference to micellar behaviour. In ternary mixtures of a commercial non-ionic surfactant with water and benzene, Clausse et al (131) favoured an interfacial polarisation approach and the agreement between the experimental data at low proportions of surfactant with values given by the equation of Hanai for an O/W dispersion (120) is worthy of note.

It was considered that a study of the dielectric properties of binary mixtures of a non-ionic surfactant with water over a range of compositions would be instructive. In view of the proposals concerning micellar shape and size, together with secondary aggregation effects, for aqueous solutions of polyethylene glycol dodecyl ethers (74, 80, 81, 83, 85), these solutions seemed to be particularly worthy of investigation.

It was therefore decided to study the dielectric behaviour of aqueous solutions of the surfactants C12E4, C12E6, C12E8 and Brij 30 over the whole composition range. In addition, aqueous solutions of tetra ethylene glycol (E4) were studied over the whole composition range in order to gain information on the properties of a mixture which contains the E4 polar groups only.
and would thus not be expected to form micellar aggregates.

It was also decided to study the dielectric properties of ternary mixtures of the surfactants C$_{12}$E$_4$ and Brij 30 with water and a hydrocarbon since the results of phase diagram and electrical conductivity studies by Bostock (83) had revealed considerable complexity and suggested the occurrence of normal micelles in some compositions and inverted micelles in others.
Chapter 2  Theory
The dielectric properties of alcohol-water mixtures would be expected to be more satisfactorily described by molecular theories of homogeneous mixtures or solutions, whereas those of micellar and microemulsion systems may be more satisfactorily described by a macroscopic heterogeneous mixture approach. The theories of both homogeneous and heterogeneous mixtures are considered in this chapter. Existing theoretical equations for heterogeneous mixtures have been extended to concentrated spheroidal dispersions.

2.1  Dielectric theory of homogeneous mixtures
These have been reviewed by a number of authors. The treatise by Hill (60) is particularly worthy of note.

2.1.1  Static Permittivity $\varepsilon_s$
2.1.1.1  Pure Liquids
Debye (13) considered a microscopic spherical region surrounding a molecule in the dielectric which was large compared with molecular dimensions. By assuming that the field inside the sphere was zero and that local directional forces could be neglected, he obtained the equation

$$\frac{\varepsilon_s - 1}{\varepsilon_s + 2} = \frac{N_A}{3\varepsilon_0 \nu} \left( \alpha + \frac{\mu^2}{3kT} \right)$$

where $N_A$ is Avogadro's number
$\varepsilon_0$ is the permittivity of free space
$\nu$ is the molar volume
$k$ is the Boltzmann's constant
\( \mu \) is the dipole moment

and \( \alpha \) is the distortion polarisability

The later theory of Onsager (14) represented a molecule as a point dipole in a spherical cavity of molecular size, but local directional forces were again neglected. Subsequent theories of Kirkwood (15) and Fröhlich (133) included these local forces. Kirkwood treated unpolarisable point dipoles and obtained the equation:

\[
\frac{(\epsilon_S - 1)Q\epsilon_S + 1}{3\epsilon_S} = \frac{N_A}{\epsilon_0 v} \left( \frac{g\mu^2}{3kT} \right) \tag{2.2}
\]

where \( g \) is a dimensionless quantity called the Kirkwood \( g \)-factor which is included to take account of local directional forces.

Fröhlich (133) included the distortion polarisation contribution by considering the non-polarisable dipoles to be embedded in a medium of permittivity \( \epsilon_\infty \). Using the relation

\[
\mu_g = \left( \frac{3}{\epsilon_\infty + 2} \right) \mu
\]

where \( \mu_g \) is the gas phase dipole moment (60), the Kirkwood-Fröhlich equation was obtained:

\[
\frac{(\epsilon_S - \epsilon_\infty)(2\epsilon_S + \epsilon_\infty)}{\epsilon_S(\epsilon_\infty + 2)^2} = \frac{N_A g \mu_g^2}{4\epsilon_0 v kT} \tag{2.3}
\]

This is a standard equation applicable to single component liquids.
2.1.1.2 Extension of Kirkwood theory to liquid mixtures

Oster (134) used the original form of the Kirkwood equation [2.2] assuming that the net polarisation $P$ is given by the sum of the two components $P_1$ and $P_2$ according to the ideal mixing equation

$$P = x_1 P_1 + x_2 P_2$$

where $x_1$, $x_2$ are the respective molar fractions of components '1' and '2'. Application of the Oster approach gives:

$$\left( \varepsilon_s - 1 \right) (2\varepsilon_s + 1) v = \left( \varepsilon_{s1} - 1 \right) (2\varepsilon_{s1} + 1) x_1 v_1 + \left( \varepsilon_{s2} - 1 \right) (2\varepsilon_{s2} + 1) x_2 v_2$$

or

$$\varepsilon_s = \frac{\varepsilon_{s1} x_1 v_1 + \varepsilon_{s2} x_2 v_2}{x_1 v_1 + x_2 v_2}$$

Assuming additivity of volumes, the molar volume of the mixture, $v$, can be written as $v = x_1 v_1 + x_2 v_2$

and if $\varepsilon_s$, $\varepsilon_{s1}$ and $\varepsilon_{s2} >> 1$ then

$$\varepsilon_s = \varepsilon_{s1} \varphi_1 + \varepsilon_{s2} \varphi_2$$

where $\varphi_1$ and $\varphi_2$ are the volume fractions of components '1' and '2'.

The Oster approach can be similarly applied to the Kirkwood-Fröhlich equation by writing

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s} = \frac{N_A}{\varepsilon_0 \nu k T} (x_1 \varepsilon_1 \mu_1^2 + x_2 \varepsilon_2 \mu_2^2)$$

where the subscripts '1' and '2' refer to the components '1' and '2'.

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2.1.2 Dielectric Relaxation : Macroscopic Relaxation Time \( \tau \)

2.1.2.1 Debye-type dispersion

It is assumed that when an electric field \( E \) is applied, the distortion polarisation \( P_1 \) is established instantaneously compared with the dipolar reorientation and that the dipolar part of the polarisation \( P_2 \) obeys a rate equation of the form:

\[
\frac{dP_2}{dt} = \frac{P - P_1 - P_2}{\tau}
\]

where \( P \) is the equilibrium value of the total polarisation and \( \tau \) is the macroscopic relaxation time.

Writing \( P = \epsilon_0(\epsilon_\infty - 1)E \)

\[
P_1 = \epsilon_0(\epsilon_\infty - 1)E
\]

and \( P_2 = \epsilon_0(\epsilon^* - 1)E \)

the following expression for the complex permittivity \( \epsilon^* \), \((=\epsilon^\prime - j\epsilon^\prime\prime)\) is obtained:

\[
\epsilon^* = \epsilon_\infty + \frac{\epsilon_\infty - \epsilon_\infty}{1 + j\omega\tau}
\]

[2.7]

A plot of \( \epsilon^\prime\prime \) plotted against \( \epsilon^\prime \) produces a semi-circle of radius \( \frac{\epsilon_\infty - \epsilon_\infty}{2} \) with a centre at \( \left[ \frac{\epsilon_\infty + \epsilon_\infty}{2}, 0 \right] \).

Dielectric relaxation for which such a semi-circle is obtained is termed Debye-type.

2.1.2.2 Cole-Cole arc type dispersion

Many examples are found in practice which give a broader dispersion with a lower value of \( \epsilon^\prime\prime_{\text{max}} \) than the Debye-type.

For such dispersions, Cole and Cole (135) suggested the empirical equation:
where \( 0 < \alpha < 1 \)

This is termed Cole-Cole arc type dispersion and is attributed to a symmetrical distribution of relaxation times about a mean value.

### 2.1.2.3 Cole-Davidson skewed-arc type dispersion

Cole and Davidson (136) observed that the dielectric dispersion of glycerol gave a skewed-arc when \( \varepsilon^{\prime \prime} \) was plotted against \( \varepsilon^{\prime} \). These authors suggested the empirical equation:

\[
\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + (j\omega \tau)^{1 - \beta}}
\]

where \( 0 < \beta < 1 \)

The skewed-arc behaviour is attributed to a distribution of relaxation times with mechanisms of decreasing importance extending to the high frequency side of the dispersion.

In many liquids including the alcohols, the dielectric dispersion is best described by Debye-type relaxation involving more than one relaxation time, although in practice, distinction between multiple Debye-type relaxations and Cole-Davidson type dispersion is difficult due to sparseness of data points.

### 2.1.3 Molecular Relaxation Time

As the reaction field, which is set up in the Onsager cavity by the polarisation which the dipole induces in its
surroundings, does not follow precisely in phase with either the applied field or the dipole motion, the macroscopic relaxation time $\tau$ obtained from experimental measurements is not the same as the time constant for molecular dipole relaxation, $\tau^*$. 

A number of theoretical equations are available, giving relationships between $\tau^*$ and $\tau$. The simpler ones are listed below.

$$\tau^* = \left( \frac{\varepsilon_{\infty} + 2}{\varepsilon_S + 2} \right) \tau \quad [2.10] \tag{13}$$

$$\tau^* = \left( \frac{2\varepsilon_S + \varepsilon_{\infty}}{3\varepsilon_S} \right) \tau \quad [2.11] \tag{137,138}$$

and

$$\tau^* = \frac{3\varepsilon_S\varepsilon_{\infty}(2\varepsilon_S + \varepsilon_{\infty})}{2\varepsilon_S^3 + 6\varepsilon_S^2\varepsilon_{\infty} + \varepsilon_{\infty}^3} \tau \quad [2.12] \tag{139}$$

The above equations reveal that $\tau^*$ should be generally smaller than $\tau$ and thus care should be exercised when the macroscopic relaxation time $\tau$ is interpreted in terms of molecular orientation.

2.2 Dielectric theory of heterogeneous mixtures

In heterogeneous mixtures, it is assumed that there is no molecular association between the two or more components of the mixture.

A binary heterogeneous mixture is considered as a dispersion of globules of one component in the continuous medium formed by the other component, and it is usually assumed that the dispersed component contains spherical or, more generally,
The dielectric properties of heterogeneous mixtures have received much less attention than those of homogeneous liquids but extensive reviews have been given by van Beek (140) and Hanai (120). Of these two, the former is the more comprehensive.

2.2.1 Spherical dispersions: Static permittivity

Rayleigh (141) calculated the permittivity of a dispersion of spherical particles by considering the electrostatic field in a mixture where the spherical particles have uniform radius and are arranged regularly at the lattice points of a simple cubic lattice in a continuous medium.

For a volume fraction \( \vartheta \) of dispersed phase of permittivity \( \varepsilon_2 \) in a continuous phase of permittivity \( \varepsilon_1 \), Rayleigh derived an expression for the permittivity of the mixture, \( \varepsilon \), given by:

\[
\varepsilon = \varepsilon_1 \left[ 1 + \frac{3\vartheta}{\varepsilon_2 + \frac{2\varepsilon_1}{\varepsilon_2 - \varepsilon_1}} - \vartheta - 1.65 \left( \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \frac{4\varepsilon_1}{3}} \right)^{10/3} \right] \tag{2.13}
\]

For \( \vartheta \ll 1 \), \( \varepsilon \) in formal reduces to

\[
\frac{\varepsilon - \varepsilon_1}{\varepsilon + 2\varepsilon_1} = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} \vartheta \tag{2.14}
\]

This is sometimes referred to as Wiener's equation (142) but it is also one of the equations derived by Wagner (discussed later). In this work \( \varepsilon \) should be termed the Rayleigh equation. Rayleigh considered that \( \varepsilon \) should
be only applicable to low values of $\phi$ and van Beek has suggested that $[2.14]$ should be only applicable to volume fractions of dispersed phase $\phi < 0.2$.

Other forms of $[2.13]$ have also been reported. Runge (143) corrected for a factor $\left(\frac{1}{\pi}\right)^{f_{\text{full}}}$ in the Rayleigh equation by replacing the factor 1.65 by 0.525. Meredith and Tobias (144) used a different potential function for the electrostatic field and, by considering higher terms in the series expansion for the potential in the continuous phase, obtained the expression:

$$\varepsilon = \varepsilon_1 + 2\phi - 1.227 \frac{2\varepsilon_1 + \varepsilon_2}{4\varepsilon_1 + 3\varepsilon_2} \phi^{7/3} - 6.399 \frac{\varepsilon_2 - \varepsilon_1}{4\varepsilon_1 + 3\varepsilon_2} \phi^{10/3}$$

Bruggeman (145) extended the Rayleigh equation $[2.14]$ to more concentrated dispersions by assuming that the equation holds for infinitesimally small increments of concentration of the disperse phase and that the final high concentration of disperse phase is attained by a succession of these processes. This was performed by putting $\varepsilon_1 + \varepsilon$ and $\varepsilon + \varepsilon + \Delta\varepsilon$. The volume fraction term was found by writing that the change in concentration $\Delta\phi$ between stages $i$ and $i + 1$ is given by:

$$\Delta\phi = \frac{V\phi + \Delta V_2}{V + \Delta V_2} - \phi = \frac{\Delta V_2}{V + \Delta V_2}(1 - \phi)$$

where $V$ is the total volume.
\( \Delta V_2 \) is the infinitesimal amount of added disperse phase

and \( \phi^* \) is the concentration at stage \( i \).

On assuming Rayleigh's equation \([2.14]\) holds for infinitesimal incrementation, we can write \( \phi = \frac{\Delta V_2}{V + \Delta V_2} \) giving \( \phi = \frac{\Delta \phi^*}{1 - \phi^*} \).

Replacing \( \varepsilon_1 \) by \( \varepsilon \), \( \varepsilon \) by \( \varepsilon + \Delta \varepsilon \) and \( \phi \) by \( \frac{\Delta \phi^*}{1 - \phi^*} \) gives

\[
\frac{2\varepsilon + \varepsilon_2}{3\varepsilon(\varepsilon - \varepsilon_2)} \Delta \varepsilon = \frac{\Delta \phi^*}{1 - \phi^*}
\]

Integrating \( \varepsilon \) between the limits \( \varepsilon_1 \) and \( \varepsilon \) and \( \phi^* \) between 0 and \( \phi \) gives

\[
\frac{\varepsilon - \varepsilon_2}{\varepsilon_1 - \varepsilon_2} \left( \frac{\varepsilon_1}{\varepsilon} \right)^{\frac{1}{3}} = 1 - \phi \tag{2.16}
\]

which is the Bruggeman equation.

A different approach was taken by Looyenga (146) who assumed that on mixing two components \( \varepsilon_1 \) and \( \varepsilon_2 \), the infinitesimal changes in the Rayleigh equation are of the type \( \varepsilon_1 + \varepsilon - \Delta \varepsilon \) and \( \varepsilon_2 + \varepsilon + \Delta \varepsilon \).

Applying a binomial expansion leads to

\[
\phi^* = \frac{1}{2} + \frac{\Delta \varepsilon}{2(3\varepsilon - 2\Delta \varepsilon)}
\]

The volume fractions \( \phi(\varepsilon) \) at \( \varepsilon, \varepsilon - \Delta \varepsilon \) and \( \varepsilon + \Delta \varepsilon \) were expanded in a Taylor's series form to the second derivative, by considering the mixture as composed of a volume fraction \( (1 - \phi^*) \) with a permittivity \( (\varepsilon - \Delta \varepsilon) \) and fraction \( \phi^* \) with permittivity \( (\varepsilon + \Delta \varepsilon) \) where

\[
\phi(\varepsilon) = (1 - \phi^*).\phi(\varepsilon - \Delta \varepsilon) + \phi^*.\phi(\varepsilon + \Delta \varepsilon)
\]
Using the Taylor's series form for \( \varphi(\varepsilon - \Delta \varepsilon) \) and \( \varphi(\varepsilon - \Delta \varepsilon) \) gives

\[
\varphi^* = \frac{1}{2} - \frac{1}{4} \Delta \varepsilon \frac{d^2 \varphi}{d\varepsilon^2} \tag{2.16a}
\]

Combining the two equations for \( \varphi^* \) leads to the differential equation

\[
3\varepsilon \frac{d^2 \varphi}{d\varepsilon^2} + 2 \frac{d\varphi}{d\varepsilon} = 0
\]

and applying boundary conditions: \( \varepsilon = \varepsilon_1 \) when \( \varphi = 0 \) and \( \varepsilon = \varepsilon_2 \) when \( \varphi = 1 \) gives

\[
\varepsilon = \left[ \left( \varepsilon_2 \frac{1}{3} - \varepsilon_1 \frac{1}{3} \right) \varphi + \varepsilon_1 \frac{1}{3} \right]^3 \tag{2.17}
\]

which is the Looyenga equation. (It should be noted that this was independently derived by Landau and Lifshitz (147)).

An equation of rather similar form was derived by Kraszewski et al (148) for a multi-layer suspension by assuming that a layer of the suspension could be considered as a sum of an infinite number of alternate layers of permittivity \( \varepsilon_1 \) and \( \varepsilon_2 \). By assuming that the propagation constant \( \gamma_m \) of a plane electromagnetic wave through the suspension is given by \( \gamma_m = \gamma_1 t_1 + \gamma_2 t_2 \) where \( t_1 \) and \( t_2 \) represent the thickness of the component layers, they obtained the equation

\[
\varepsilon = \left[ \left( \varepsilon_2 \frac{1}{3} - \varepsilon_1 \frac{1}{3} \right) \varphi + \varepsilon_1 \frac{1}{3} \right]^2 \tag{2.18}
\]

A completely different approach was used by Böttcher (149) who considered the disperse system to be a close aggregate of two kinds of spherical globules. He assumed that the electric field \( E_2 \) inside a sphere of the component of
permittivity \( \varepsilon_2 \) exerted by its inhomogeneous surroundings is equivalent to that of the sphere placed in a homogeneous dielectric of permittivity \( \varepsilon \).

According to electrostatic theory (149), \( E_2 \) is given by
\[
E_2 = \frac{3\varepsilon}{2\varepsilon + \varepsilon_2} E
\]
where \( E \) is the electric field at an infinite distance from the sphere. Similarly for the spheres of permittivity \( \varepsilon_1 \), \( E_1 = \frac{3\varepsilon}{2\varepsilon + \varepsilon_1} E \) and the total polarisation per unit volume of the mixture is given by
\[
P = \varepsilon_0(\varepsilon - 1)E = (1 - \phi)\varepsilon_0(\varepsilon_1 - 1)E_1 + \phi\varepsilon_0(\varepsilon_2 - 1)E_2
\]
giving
\[
\frac{\varepsilon - \varepsilon_1}{3\varepsilon} = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon} \phi \tag{2.19}
\]
which is Bottcher's equation.

The range of \( \phi \) values for which the equations for higher concentrations of dispersed phase should be applicable is not fully established but comparison between experimental values for emulsions with values given by the equations of Hanai, one of which is identical with the Bruggeman equation, discussed in the following section, (120, 121, 150, 151) reveals that the Bruggeman equations can be applicable for volume fractions of dispersed phase \( \phi \) up to approximately 0.8. Mandel (152) suggested that \[2.19\] should be applicable for \( \phi \) up to 0.2.

2.2.2 Dielectric relaxation of spherical dispersions:

Interfacial polarisation

When either or both of the components of a binary mixture has a significant conductivity component, dielectric
dispersion behaviour may be observed. This dispersion is known as the Maxwell-Wagner effect. Maxwell (153) considered a two layer system of permittivities \( \varepsilon_1 \) and \( \varepsilon_2 \), with conductivities \( \sigma_1 \) and \( \sigma_2 \) and derived equations for the high frequency limiting value of the permittivity \( \varepsilon_\infty \), the low frequency limiting value \( \varepsilon_s \), the relaxation time \( \tau \) and the conductivity \( \sigma \).

Wagner (154) presented a dielectric theory for a disperse system of a large number of spherical particles sparsely distributed in a continuous medium. By considering the complex potential due to a dispersion of spheres of permittivity \( \varepsilon_2 \) in a continuous medium of permittivity \( \varepsilon_1 \), the following relation was obtained:

\[
\frac{\varepsilon* - \varepsilon_1*}{\varepsilon* + 2\varepsilon_1*} = \frac{\varepsilon_2* - \varepsilon_1*}{\varepsilon_2* + 2\varepsilon_1*} \theta \quad [2.20]
\]

where \( \varepsilon* \) is the permittivity of the mixture. This is the same as the Rayleigh equation \([2.14]\) except that the permittivities are expressed in complex form.

Solution of \([2.20]\) gives a Debye-type dispersion of relaxation time \( \tau \) given by

\[
\tau = \varepsilon_0 \frac{2\varepsilon_1 + \varepsilon_2 - \theta(\varepsilon_2 - \varepsilon_1)}{2\sigma_1 + \sigma_2 - \theta(\sigma_2 - \sigma_1)} \quad [2.21]
\]

where \( \sigma_1, \sigma_2 \) are the conductivities of components '1' and '2'.

The high and low frequency limiting values of the permittivity \( \varepsilon_\infty \) and \( \varepsilon_s \) are:
\[
\varepsilon_{\infty} = \frac{2\varepsilon_1 + \varepsilon_2 + 2\phi (\varepsilon_2 - \varepsilon_1)}{2\varepsilon_1 + \varepsilon_2 - \phi (\varepsilon_2 - \varepsilon_1)} \quad [2.22]
\]

and

\[
\varepsilon_s = \frac{2\varepsilon_1 + \varepsilon_2 + 2\phi (\varepsilon_2 - \varepsilon_1)}{2\varepsilon_1 + \varepsilon_2 - \phi (\varepsilon_2 - \varepsilon_1)} + \frac{3\phi}{(2\varepsilon_1 + \varepsilon_2 - \phi (\varepsilon_2 - \varepsilon_1))(\varepsilon_1 + \varepsilon_2)} \quad [2.23]
\]

It can be seen that equation \[2.22\] is the same as the Rayleigh equation \[2.14\] and thus the above equations should be similarly applicable to \(\phi < 0.2\).

Hanai (120) extended the Wagner theory to higher concentrations of disperse phase using a method similar to that of Bruggeman by proposing that during the infinitesimal increases in concentration \(\varepsilon_1^* + \varepsilon^*\) and \(\varepsilon^* + \varepsilon^* + \Delta \varepsilon^*\) with \(\phi = \frac{\Delta \varepsilon^*}{1 - \phi}\) giving the equation

\[
\frac{2\varepsilon^* + \varepsilon_2^*}{3\varepsilon^*(\varepsilon^* - \varepsilon_2^*)} \Delta \varepsilon^* = \frac{-\Delta \varepsilon^*}{1 - \phi}
\]

He showed that this expression integrated to:

\[
\varepsilon^* - \varepsilon_2^* = \left(\varepsilon - \varepsilon_2\right)^{1/3} \varepsilon \left(\varepsilon^* \varepsilon^*\right) = 1 - \phi \quad [2.24]
\]

which is the Bruggeman equation for spheres in complex form.

The complex quantities were expressed as

\[
\varepsilon^* - \varepsilon_2^* = \left[\left(\varepsilon - \varepsilon_2\right)^2 + (\gamma - \gamma_2)^2\right]^{1/2} \exp \left[-j \arctan \left(\frac{\gamma - \gamma_2}{\varepsilon - \varepsilon_2}\right)\right]
\]

where \(\gamma\) is the dielectric loss,

\[
\varepsilon_1^* - \varepsilon_2^* = \left[\left(\varepsilon_1 - \varepsilon_2\right)^2 + (\gamma_1 - \gamma_2)^2\right]^{1/2} \exp \left[-j \arctan \left(\frac{\gamma_1 - \gamma_2}{\varepsilon_1 - \varepsilon_2}\right)\right]
\]
\[ \varepsilon_1^* = \left( \varepsilon_1^2 + \gamma_1^2 \right)^{\frac{3}{2}} \exp \left[ -j \arctan \left( \frac{\gamma_1}{\varepsilon_1} \right) \right] \]

and

\[ \varepsilon^* = \left( \varepsilon^2 + \gamma^2 \right)^{\frac{3}{2}} \exp \left[ -j \arctan \left( \frac{\gamma}{\varepsilon} \right) \right] \]

Substitution into equation [2.24] and separation of real and imaginary terms together with use of the relation

\[ \tan (A - B) = \frac{\tan A - \tan B}{1 - \tan A \tan B} \]

gave:

\[ \frac{\left[ (\varepsilon - \varepsilon_2)^2 + (\gamma - \gamma_2)^2 \right]}{\left[ (\varepsilon_1 - \varepsilon_2)^2 + (\gamma_1 - \gamma_2)^2 \right]} \left( \varepsilon_1^2 + \gamma_1^2 \right)^{\frac{1}{3}} = (1 - \vartheta)^2 \quad [2.24a] \]

and

\[ \arctan \left( \frac{\varepsilon_1 - \varepsilon_2}{\gamma_1 + \gamma_2} \right) = 3 \arctan \left[ \frac{\varepsilon_1 - \varepsilon_2)(\gamma_1 - \gamma_2) - (\varepsilon_1 - \varepsilon_2)(\gamma_1 - \gamma_2)}{(\varepsilon_1 - \varepsilon_2)(\varepsilon_1 - \varepsilon_2) + (\gamma_1 - \gamma_2)(\gamma_1 - \gamma_2)} \right] \quad [2.24b] \]

Hanai stated without justification that [2.24b], which is of the form \( \arctan A = 3 \arctan B \), could be written in the simplified form:

\[ A = \frac{B(3 - B^2)}{1 - 3B^2} \quad [2.24c] \]

Investigation by this author has shown that, in order to obtain [2.24c], the \( \arctan X \) functions have been expressed in the series expansion form using the first two terms only, ie

\[ \arctan X = X - \frac{X^3}{3} \]

Neglect of the terms for higher power of \( X \) is open to criticism since the series expansion is only rapidly convergent for \( X < 0.5 \), whereas in [2.24b] values of \( X \) up to \( 2\pi \) are possible.
Applying the series expansion to $A$ and $B$ in [2.24c] reveals a further assumption made by Hanai:

We have $A - \frac{A^3}{3} = 3B - B^3$

ie $\quad A\left(1 - \frac{A^2}{3}\right) = B(3 - B^2)$

or $\quad A = \frac{B(3 - B^2)}{1 - A^2/3}$ \[2.24d\]

In order to obtain [2.24c] we must put:

$\frac{A^2}{3} = 3B^2$

ie $\quad A = 3B$

which is only valid for small values of $A$ and $B$. Thus the upper limit for $A$ and $B$ for the series expressions to be rapidly convergent will be somewhat lower than the 0.5 figure already quoted.

Using a solution of [2.24b] based on [2.24c], Hanai obtained the following cumbersome expression for the "general solution" of [2.24]:

$\left(\epsilon \gamma_1 - \epsilon_1 \gamma\right) \left(\epsilon - \epsilon_2)(\epsilon_1 - \epsilon_2) + (\gamma - \gamma_2)(\gamma_1 - \gamma_2)\right) \left[\left(\epsilon - \epsilon_2)(\epsilon_1 - \epsilon_2) + \right.ight.$

$\left.\left(\gamma - \gamma_2)(\gamma_1 - \gamma_2)\right)^2 - 3\left[\left(\epsilon - \epsilon_2)(\gamma_1 - \gamma_2) - (\gamma - \gamma_2)(\epsilon_1 - \epsilon_2)\right)^2\right]\right] =$

$\left(\epsilon \epsilon_1 + \gamma \gamma_1\right) \left[\left(\epsilon - \epsilon_2)(\gamma_1 - \gamma_2) - (\gamma - \gamma_2)(\epsilon_1 - \epsilon_2)\right)\right] \left[\left(\epsilon - \epsilon_2)(\epsilon_1 - \epsilon_2) + \right.$

$\left.\left(\gamma - \gamma_2)(\gamma_1 - \gamma_2)\right)^2 - \left[\left(\epsilon - \epsilon_2)(\gamma_1 - \gamma_2) - (\gamma - \gamma_2)(\epsilon_1 - \epsilon_2)\right)^2\right]\right] \right] \quad \left[2.24e\right]$
Noting that the $\gamma$ terms represent the dielectric loss 
\[ \left( \frac{\sigma}{\omega \epsilon_0} \right) \], at high frequencies $\epsilon_1 \gg \gamma_1$, $\epsilon_2 \gg \gamma_2$ and $\epsilon \gg \gamma$ ($\epsilon = \epsilon_\infty$), [2.24a] will then reduce to
\[ \frac{\epsilon_\infty - \epsilon_2}{\epsilon_1 - \epsilon_2} \left( \frac{\epsilon_1}{\epsilon} \right)^{1/3} = 1 - \phi \quad [2.25] \]

which is the Bruggeman equation and [2.24e] reduces to
\[ \sigma_\infty \left[ \frac{3}{\epsilon_\infty - \epsilon_2} - \frac{1}{\epsilon_\infty} \right] = 3 \left[ \frac{\sigma_1 - \sigma_2}{\epsilon_1 - \epsilon_2} + \frac{\sigma_2}{\epsilon_\infty - \epsilon_2} \right] - \frac{\sigma_1}{\epsilon_1} \quad [2.26] \]

At low frequencies $\gamma_1 \gg \epsilon_1$, $\gamma_2 \gg \epsilon_2$ and $\gamma \gg \epsilon$ ($\epsilon = \epsilon_\infty$) giving
\[ \epsilon_\infty \left[ \frac{3}{\sigma_\infty - \sigma_2} - \frac{1}{\sigma_\infty} \right] = 3 \left[ \frac{\epsilon_1 - \epsilon_2}{\sigma_1 - \sigma_2} + \frac{\sigma_2}{\sigma_\infty - \sigma_2} \right] - \frac{\epsilon_1}{\sigma_1} \quad [2.27] \]

and
\[ \frac{\sigma_\infty - \sigma_2}{\sigma_1 - \sigma_2} \left( \frac{\sigma_1}{\sigma_\infty} \right)^{1/3} = 1 - \phi \quad [2.28] \]

It should be added that in both the high and low frequency limiting cases considered above, the denominator terms in the arc tan $X$ expressions will be much larger than the numerator terms, and thus the expansion used to obtain [2.24c] will be valid.

Hanai considered two special cases.  
(a) $\sigma_1 \gg \sigma_2$ which is termed an oil in water O/W dispersion since water would be expected to exhibit a substantially higher conductivity than an oily component.

In this case [2.25] is unchanged but [2.26] to [2.28] reduce to:
\[
\frac{\sigma_\infty}{\sigma_1} = \frac{\varepsilon_\infty(\varepsilon_\infty - \varepsilon_1)(2\varepsilon_1 + \varepsilon_2)}{\varepsilon_1(\varepsilon_1 - \varepsilon_2)(2\varepsilon_\infty + \varepsilon_2)} \quad [2.28a]
\]

\[
\varepsilon_S = \sigma_S \frac{3\varepsilon_2\sigma_1 + (2\varepsilon_1 - 3\varepsilon_2)\sigma_S}{\sigma_1(2\sigma_S + \sigma_2)} \quad [2.28b]
\]

and

\[
\frac{\sigma_S - \sigma_2}{\sigma_1} \left( \frac{\sigma_1}{\sigma_S} \right)^{1/3} = 1 - \varphi \quad [2.28c]
\]

In the case of \( \sigma_S \gg \sigma_2 \), the equations further reduce to

\[
\varepsilon_S = \frac{3}{2} \varepsilon_2 + \left( \varepsilon_1 - \frac{3}{2} \varepsilon_2 \right) \left( 1 - \varphi \right)^{3/2} \quad [2.29]
\]

and

\[
\sigma_S = \sigma_1 \left( 1 - \varphi \right)^{3/2} \quad [2.30]
\]

(b) \( \sigma_2 \gg \sigma_1 \) which is termed a water in oil (W/O) dispersion.

Equation [2.25] is again unchanged but [2.26] to [2.28] reduce to:

\[
\frac{\sigma_\infty}{\sigma_2} = \frac{3\varepsilon_\infty(\varepsilon_\infty - \varepsilon_1)}{(\varepsilon_2 + 2\varepsilon_\infty)(\varepsilon_2 - \varepsilon_1)} \quad [2.30a]
\]

\[
\varepsilon_S = \varepsilon_1 \frac{\sigma_S(\sigma_2 - \sigma_S)}{\sigma_1(\sigma_2 + 2\sigma_S)} \quad [2.30b]
\]

and

\[
\frac{\sigma_2 - \sigma_S}{\sigma_2} \left( \frac{\sigma_1}{\sigma_S} \right)^{1/3} = 1 - \varphi \quad [2.30c]
\]

when \( \sigma_2 \gg \sigma_S \) the equations further reduce to

\[
\varepsilon_S = \frac{\varepsilon_1}{(1 - \varphi)^3} \quad [2.31]
\]

and

\[
\sigma_S = \frac{\sigma_1}{(1 - \varphi)^3} \quad [2.32]
\]
Hanai pointed out that for an O/W dispersion $\varepsilon_2 << \varepsilon_1$ reducing the Wagner equations to $\varepsilon_\infty = \varepsilon_1 \frac{2(1 - \varphi)}{2 + \varphi}$ which is approximately equal to $\varepsilon_S$ and the Hanai equations similarly give $\varepsilon_\infty = \varepsilon_S$. Thus for O/W emulsions, the dielectric increment ($\varepsilon_S - \varepsilon_\infty$) predicted by both the Wagner and the Hanai theories will be very small. In contrast, Hanai showed that W/O emulsions should exhibit significant dispersion. An expression from which a relaxation time may be determined has not yet been derived but a numerical estimation by Hanai et al (155) has revealed that the Hanai model gives a Cole-Cole arc type dispersion, with a relaxation time slightly longer than that predicted by the Wagner equations for $\tau$.

As already noted, the Hanai equations have been shown to be applicable for $\varphi$ values of up to 0.8 (120).

2.2.3 Dielectric theory of spheroidal dispersions

Since the average field inside a dispersed globule will depend on its shape, the permittivity of the mixture will be similarly dependent. Sillars (156) extended the Wagner equations to spheroidal particles using equations applicable to the case of $\varphi << 1$. For the special case of $\sigma_1 << \sigma_2$:

$$
\varepsilon_\infty = \varepsilon_1 \left[ 1 + 3\varphi \frac{(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_1 + \varepsilon_2} \right]
$$

[2.33]

For spheroidal particles, Sillars derived the expression
\[ \varepsilon_\infty = \varepsilon_1 \left[ 1 + \frac{\Theta n(\varepsilon_2 - \varepsilon_1)}{(n - 1)\varepsilon_1 + \varepsilon_2} \right] \] \[2.34\]

where \( n = \left[ \frac{1}{e^n} - \left( \frac{(1 - e^2)\frac{1}{2} \arcsin e}{e^2} \right) \right]^{-1} \)

and \( e \) is the eccentricity.

Van Beek (140) reported that the equations of Sillars were applicable for \( \theta < 0.1 \) but that the equations were "easily extended" to the more general case and quoted the following equations which he considered should be applicable for values of \( \theta \) up to 0.2.

\[ \tau = \varepsilon_0 \frac{\varepsilon_1 + A_a (1 - \theta)(\varepsilon_z - \varepsilon_1)}{\sigma_1 + A_a (1 - \theta)(\sigma_z - \sigma_1)} \] \[2.35\]

\[ \varepsilon_\infty = \varepsilon_1 \frac{\varepsilon_1 + A_a (1 - \theta)(\varepsilon_z - \varepsilon_1)}{\varepsilon_1 + A_a (1 - \theta)(\varepsilon_z - \varepsilon_1)} \] \[2.36\]

and

\[ \varepsilon_S = \varepsilon_1 \frac{\sigma_1 + A_a (1 - \theta)(\sigma_z - \sigma_1)}{\sigma_1 + A_a (1 - \theta)(\sigma_z - \sigma_1)} \]

\[ + \Theta \sigma_1 \frac{\sigma_1 + A_a (\sigma_z - \sigma_1)}{\sigma_1 + A_a (\sigma_z - \sigma_1)} (\varepsilon_z - \varepsilon_1) - \sigma_1 + A_a (\varepsilon_z - \varepsilon_1)^2 (\sigma_z - \sigma_1) \]

\[ \sigma_1 + A_a (1 - \theta)(\sigma_z - \sigma_1) \]

\[ \sqrt{\sigma_1 + A_a (1 - \theta)(\sigma_z - \sigma_1)} \]

\[ \text{along the } a \text{ axis} \] \[2.37\]

where \( A_a \) is termed the depolarising factor which is given by the elliptic integral:

\[ A_a = \frac{abc}{2} \int_0^\infty \frac{ds}{(s + a^2)[(s + a^2)(s + b^2)(s + c^2)]^{\frac{3}{2}}} \] \[2.38\]

where \( a, b \) and \( c \) are the semi-axes of the ellipsoid (157).

Van Beek stated, without giving derivations, the following expressions for spheroids of axial ratio \( b/a \):
when $a > b$ (prolate spheroids)

$$A_a = \frac{-1}{(a/b)^2 - 1} + \frac{a/b}{(a/b)^2 - 1} \cdot \ln \left\{ \frac{a/b}{(a/b)^2 - 1} \right\}^{3/2}$$

when $a < b$ (oblate spheroids)

$$A_a = \frac{1}{1 - (a/b)^2} - \frac{a/b}{1 - (a/b)^2} \cdot \arccos \left( \frac{a}{b} \right)$$

when $a = b$ (spheres)

$$A_a = \frac{1}{3}$$

The author added that for practical calculations, the following approximations are often useful:

when $a > b$

$$A_a = \left[ \ln \left( \frac{2a}{b} \right) - 1 \right] \left( \frac{b}{a} \right)^2$$

when $a < b$

$$A_a + 1$$

Van Beek also reported that for small $\Phi$ and $\sigma_1 \ll A_a \sigma_2$

equations $[2.35]$ $[2.36]$ and $[2.37]$ reduce to

$$\tau = \frac{\varepsilon_0 \left( \varepsilon_1 + A_a (\varepsilon_2 - \varepsilon_1) \right)}{A_a \sigma_2}$$

$$\varepsilon_{\infty} = \varepsilon_1 \left[ 1 + \frac{\Phi (\varepsilon_2 - \varepsilon_1)}{\varepsilon_1 + A_a (\varepsilon_2 - \varepsilon_1)} \right]$$

and $\varepsilon_S = \varepsilon_1 \left[ 1 + \frac{\Phi}{A_a} \right]$
effect of ellipsoidal micelles on the permittivity of a mixture by writing the Rayleigh equation in the form:

\[ \varepsilon = \varepsilon_1 \frac{2\varepsilon_1 + \varepsilon_2 + 2\phi(\varepsilon_2 - \varepsilon_1)Q(\varepsilon_2,\varepsilon_1)}{2\varepsilon_1 + \varepsilon_2 - \phi(\varepsilon_2 - \varepsilon_1)Q(\varepsilon_2,\varepsilon_1)} \quad [2.46] \]

where the shape factor \( Q(\varepsilon_2,\varepsilon_1) \) is defined by

\[ Q(\varepsilon_2,\varepsilon_1) = \frac{1}{3} \sum_{s} \frac{1}{1 + \frac{1}{3} \zeta \frac{1}{\varepsilon_2 - \varepsilon_1} / \varepsilon_2 + \varepsilon_1} \quad [2.47] \]

with the \( \zeta \) components given by

\[ \zeta_1 = -\frac{2}{15} \left( 1 - \frac{b^2}{a^2} \right), \quad \zeta_2 = \zeta_3 = -\frac{\zeta_1}{2} \quad [2.48] \]

Since these equations are based on the Rayleigh equation \([2.14]\), they should be similarly applicable to \( \phi < 0.2 \).

This theory was not applied to experimental data nor were the types of micelles identified.

A generalised form of the Böttcher equation was given by Polder and Van Santen (159) who obtained an expression of similar form to the equation of Sillars but by using the approximation that the medium surrounding the dispersed particle was one of permittivity \( \varepsilon \), the following expression was obtained:

\[ \varepsilon = \varepsilon_1 + \frac{\phi(\varepsilon_2 - \varepsilon_1)\varepsilon}{\varepsilon + A_a(\varepsilon_2 - \varepsilon)} \quad [2.49] \]

which reduces to the Böttcher equation when the substitution \( A_a = \frac{1}{3} \) for spheres is applied. The equation is often written in the form applicable to a random distribution of orientations namely:
For spheres $A_a = A_b = A_c = \frac{1}{3}$ giving the Böttcher equation as required.

The authors considered \([2.49]\) to be applicable to "low" values of $\phi$ and Mandel (152) suggested it should be applicable to systems where $\phi$ does not exceed "10 to 20\%".

de Loor (160) proposed a more general expression for \([2.50]\)

$$\varepsilon = \varepsilon_1 + \frac{\phi}{3} \sum_{a,b,c} (\varepsilon_2 - \varepsilon_1) \frac{\varepsilon_1}{\varepsilon_1 + A_j (\varepsilon_2 - \varepsilon_1)}$$

where $\varepsilon_1$ is the permittivity of the immediate surroundings of the dispersed particle. The author added the statement that "thorough investigation has shown that $\varepsilon_1$ always has values between $\varepsilon$ and $\varepsilon_1$" (161).

In the case of $\varepsilon_1 = \varepsilon$, the Polder and van Santen equation is obtained which reduces to the Böttcher equation when $A_j (j = a, b, c) = \frac{1}{3}$, as already discussed. On the other hand, when $\varepsilon_1 = \varepsilon_1$, the Sillar's equation is obtained, since as discussed later $n = \frac{1}{A_a}$. For spheres, the equation reduces to

$$\varepsilon = \varepsilon_1 + \frac{3\phi \varepsilon_1 (\varepsilon_2 - \varepsilon_1)}{2\varepsilon_1 + \varepsilon_2}$$

which is the Wagner equation for $\phi \ll 1 \ [2.33]$. 

Kaatze et al (109) proposed the mixture formula:
\[ \varepsilon = \varepsilon_1 + \frac{3\varphi \varepsilon_1 (\varepsilon_2 - \varepsilon_1)}{2\varepsilon_1 + \varepsilon_2 - \varphi (\varepsilon_2 - \varepsilon_1)} \quad [2.53] \]

These authors claimed that [2.53] was a "refined version of the formula of Polder and van Santen". However, simple re-arrangement of their equation gives
\[ \varepsilon = \varepsilon_1 \frac{2\varepsilon_1 + \varepsilon_2 - 2\varphi (\varepsilon_1 - \varepsilon_2)}{2\varepsilon_1 + \varepsilon_2 + \varphi (\varepsilon_1 - \varepsilon_2)} \quad [2.54] \]

which is identical with the Rayleigh equation [2.14] and should be thus only applicable for \( \varphi < 0.2 \).

These authors also introduced a modification to [2.54] in which \( \varphi \) in the denominator was replaced by a factor \( [1 - \delta (1 - \varphi)] \) where \( \delta \) is an empirically adjustable parameter. The physical significance of the \( \delta \)-value was not discussed.

### 2.2.4 Dielectric theory of spherical dispersions surrounded by shells

Due primarily to relevance to biological cell specimens, the dielectric properties of a dispersed particle surrounded by a shell of different dielectric properties to those of either the particle or the continuous medium, have received considerable attention. Since ternary mixtures of surfactants with water and a hydrocarbon can be regarded as "particle with shell" type structures, the dielectric theory of such systems could well be relevant. The earliest attempt to give a mathematical analysis of a
dispersion of spheres surrounded with shells was by Maxwell (153). For a globule of radius $R$ with a permittivity $\varepsilon_2$ surrounded by a shell of thickness $d$ with a permittivity $\varepsilon_{sh}$ in a continuous medium of permittivity $\varepsilon_1$, Maxwell showed that the permittivity $\varepsilon_I$ of the homogeneous sphere which is equivalent to the shell-covered sphere is given by

$$
\varepsilon_I = \frac{2\varepsilon_{sh} + \varepsilon_2 - 2(\varepsilon_{sh} - \varepsilon_2)v}{2\varepsilon_{sh} + \varepsilon_2 + (\varepsilon_{sh} - \varepsilon_2)v}
$$

where $v = \left(\frac{R}{R + d}\right)^3$.

(It can be seen that [2.55] is identical with the Rayleigh equation [2.14] for a volume fraction $v$ of dispersed phase of permittivity $\varepsilon_2$ in a continuous phase $\varepsilon_{sh}$.)

Maxwell then showed that the permittivity of the mixture, for a dispersion of permittivity $\varepsilon_I$ in a continuous phase $\varepsilon_1$ is given by:

$$
\varepsilon = \varepsilon_1 \frac{2\varepsilon_1 + \varepsilon_I - 2(\varepsilon_1 - \varepsilon_I)p}{2\varepsilon_1 + \varepsilon_I + (\varepsilon_1 - \varepsilon_I)p}
$$

where $p$ is the volume fraction of the dispersed globules with shells.

Combining equations [2.55] and [2.56] enables $\varepsilon$ to be calculated.

Pauly and Schwan (162) extended these equations to include conductivity effects by expressing all the permittivity components in their complex form. Dielectric dispersion
was predicted which was characterised by two relaxation times.

O'Konski (108) considered the case of $\sigma_{sh} >> \sigma_1$ and showed that, since freely movable ionic charges in the shell can be displaced by an applied field, a surface conductivity occurs which can give rise to dielectric dispersion.

The O'Konski approach was further developed by Schwarz (113) in order to account for very large permittivities and very low dispersion frequencies observed in biological cells and colloidal suspensions which could not be accounted for by O'Konski's theory. Schwarz considered the effect of an external field on the counterion distribution in the interface between the particle and its surrounding continuous medium and showed that the asymmetry in the distribution caused by the field causes dielectric dispersion with a relaxation time related to the particle radius and the surface diffusion coefficient of the counterions.

Although the permittivity values predicted by equations [2.55] and [2.56] may well be applicable to ternary mixtures of non-ionic surfactants with water and a hydrocarbon, the absence of counterion effects can be expected to preclude the dielectric dispersion behaviour discussed by O'Konski (108) and Schwarz (113).
2.2.5 **Comparison of heterogeneous mixture equation values with experimental data**

Since there are a large number of mixture equations available, it is considered important that comparison with experimental data be included in order to identify the equations most likely to be applicable to the surfactant studies in this work.

Extensive comparisons have been given in the reviews by van Beek (140) Hanai (120) and Kraszewski (163). Their results are summarised briefly in this section.

The review by van Beek reveals that in a number of investigations covering a range of heterogeneous systems, for a non-conducting dispersed phase, the equations of Bruggeman [2.16], Looyenga [2.17] and Böttcher [2.19] give closest agreement with experimental values for $\phi$ up to typically 0.5.

The survey by Hanai reveals that in emulsions, the Hanai-Bruggeman equations for both O/W and W/O dispersions generally give closest agreement with experimental values for dispersions with $\phi$ up to about 0.8. Marked deviations were revealed when the full Rayleigh equation [2.13] and the Böttcher equation [2.19] were used at volume fractions of dispersed phase higher than 0.2. Similarly, where dielectric dispersion has been observed, it has been shown to be more accurately described by the Hanai equations than the Wagner equations. One notable exception is the data of
Dryden and Meakins (164) for water droplets in wool wax with \( \theta \) up to 0.381 where the Wagner equations give slightly better agreement. Hanai suggested that the deviation between the experimental values and values calculated from the Hanai equations could be due to an aggregation effect, but justification of this proposal was not given.

Good agreement between experimental values for emulsions and the Hanai equations has been reported for W/O dispersions by Chapman (165), Clausse et al (124, 125) and Le Petit et al (166) and for O/W dispersions by Clausse (127). Similarly Clausse et al (131) reported good agreement between experimental values and the Hanai equations for O/W microemulsions, as discussed in Chapter 1 of this work, and it is thus concluded that for concentrated dispersions, the equations of Hanai (which include the Bruggeman equation) and Looyenga are likely to be most suitable.

Comparison of experimental data with theoretical equations for dispersions surrounded by shells has already been given in Chapter 1.

For non-spherical dispersions in other types of system, comparison between experimental and theoretical values is more sparse. The results of Reynolds (167) and Pradham and Gupta (168) for such dispersions have been considered by van Beek (140) and Kraszewski (163).
Although Reynolds was able to obtain good agreement between theory and experiment for glass lamellae and rods in carbon tetrachloride for $\phi$ up to the highest reported value of 0.4 using $\varepsilon_1 = \varepsilon_1$ for lamellae and $\varepsilon_1 = \varepsilon$ for rods in the de Loor equation [2.51], and also obtained close agreement for glass lamellae in nitrobenzene using $\varepsilon_1 = \varepsilon$ for $\phi$ up to 0.2, the calculated values by Kraszewski (163) reveal that even closer agreement is obtained using both the Looyenga and Kraszewski equations with the latter being marginally better.

The data of Pradham and Gupta (168) for MgO lamellae dispersed in rosin for $\phi$ up to 0.5 revealed close agreement between theory and experiment using the de Loor equation [2.51] with $\varepsilon_1 = \varepsilon$ but the agreement was only marginally better than that given by the Kraszewski equation. Further, for cylindrical air-holes in plexiglass for $\phi$ up to 0.55, Kraszewski has pointed out that both the Looyenga and Kraszewski equations give better agreement with experiment than equation [2.51] using either $\varepsilon_1 = \varepsilon_1$ or $\varepsilon_1 = \varepsilon$.

It is concluded that the equation of de Loor which was derived specifically for non-spherical dispersions is not demonstrably better than the Looyenga or the Kraszewski equations, even though these latter two equations are restricted to spherical and multi-layer suspensions respectively. The results support the view that equations for concentrated dispersions of non-spherical particles
are required with equations based on those of Hanai and Looyenga being considered the most suitable.

2.2.6 Derivation of new equations for concentrated dispersions of spheroidal particles

In this work, the studies of micellar mixtures containing non-ionic surfactants have involved concentrated O/W and W/O dispersions and equations enabling a distinction between O/W and W/O dispersions to be made would be of value. Further, following the suggestion of Tanford et al. (1974) that micellar solutions of some of the polyethylene glycol alkyl ether surfactants studied in this work are oblate ellipsoidal rather than spherical in shape, it was clear that mixture equations for concentrated dispersions of a spheroidal nature were required.

The equations of Bruggeman [2.17], Looyenga [2.18] and Hanai [2.27] to [2.32] which were derived for concentrated spherical dispersions were the obvious ones from which attempts to generalise to spheroidal dispersions should be directed. In particular, the equations of Hanai, which include the Bruggeman equation, were of particular interest since they enable a distinction between O/W and W/O dispersions to be made and have, as already discussed, been shown to give good agreement with experimental data for emulsions.
It was therefore decided to apply the Bruggeman integral method to the generalised Wagner equation for spheroidal dispersions quoted by van Beek (equation [2.36]) in order to derive a generalised form of the Bruggeman equation. Using the method of Sillars (156) as a basis, it has been shown how [2.36] can be considered as an extension of the Sillars equation to higher concentrations of dispersed phase.

Following the approach of Hanai (120) a solution of the generalised Bruggeman equation in complex form has been derived, giving generalised forms of the Hanai equations for both O/W and W/O spheroidal dispersions.

Since the equation derived by Looyenga has proved to be of value in dielectric studies of concentrated dispersions (140, 163), a generalised form of the Looyenga equation has been derived, based on the Bruggeman equation instead of the Böttcher equation as used in the original derivation by Looyenga. It should be noted that, although Looyenga claimed that the equation he derived is not restricted to spherical dispersions, this statement must be disputed since both the Bruggeman and the Böttcher equations were derived on the basis of spherical dispersions and thus any extension of them will still be only applicable to such dispersions.

It is worthy of note that since the shape factors $A_a$ used in the derivations in this work can be determined for both
prolate and oblate ellipsoids, the derived equations will be applicable to both types of ellipsoidal shape.

The approach adopted has therefore been as follows:

(i) use of the method of Sillars to obtain the generalised Wagner equation quoted by van Beek,

(ii) application of the Bruggeman integral method to the equation quoted by van Beek to derive a generalised Bruggeman equation,

(iii) application of the method of Hanai to the generalised Bruggeman equation in complex form to derive generalised Hanai equations for both O/W and W/O dispersions and

(iv) application of the method of Looyenga to the generalised Bruggeman equation to derive a generalised Looyenga equation.

### 2.2.6.1. Extension of Sillars equation to obtain equation quoted by van Beek

Sillars (156) used the equation given by Wagner applicable to $\phi \ll 1$.

$$\varepsilon^* = \varepsilon_1 \left[ 1 + 3\phi \frac{\varepsilon_2^* - \varepsilon_1^*}{2\varepsilon_1^* + \varepsilon_2^*} \right] \quad [2.56a]$$

which gives

$$\varepsilon_\infty = \varepsilon_1 \left[ 1 + \frac{3\phi(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_1 + \varepsilon_2} \right]$$

(see $[2.33]$)
\[
\varepsilon_i = \varepsilon_1 \left[ \frac{2\varepsilon_1 + \varepsilon_2 + 3\Phi(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_1 + \varepsilon_2} \right] \tag{2.57}
\]

For spheroids of axial ratio b/a, Sillars derived the equation

\[
\varepsilon_\infty = \varepsilon_1 \left[ 1 + \frac{\Phi n(\varepsilon_2 - \varepsilon_1)}{\varepsilon_1(n-1) + \varepsilon_2} \right]
= \varepsilon_1 \left[ \frac{\varepsilon_1(n-1) + \varepsilon_2 + \Phi n(\varepsilon_2 - \varepsilon_1)}{\varepsilon_1(n-1) + \varepsilon_2} \right] \tag{2.58}
\]

where \(n = \left[ \frac{1}{\varepsilon^2} - \frac{(1 - \varepsilon^2)^{3/2} \arcsin \varepsilon}{\varepsilon^3} \right]^{-1} \tag{2.59}\)

[2.58] reduces to [2.57] when \(n = 3\).

\(e\) was termed the eccentricity which for oblate spheroids \((b > a)\) is given by

\[
e = \left[ 1 - \left( \frac{a}{b} \right)^2 \right]^{1/2} \tag{2.59a}
\]

Now let \(\arcsin e = \theta\)

\[i.e \sin \theta = e\]

\[1 - \sin^2 \theta = e^2 = \cos^2 \theta\]

\[i.e \cos \theta = (1 - e^2)^{1/2}\]

\[= \left[ 1 - \left( 1 - \left( \frac{a}{b} \right)^2 \right) \right]^{1/2} = \frac{a}{b}\]

hence \(\theta = \arccos \left( \frac{a}{b} \right)\)

thus for oblate spheroids [2.59] can be re-written as

\[
\frac{1}{n} = \frac{1}{1 - (a/b)^2 - \left( \frac{a}{b} \right) \arccos \left( \frac{a}{b} \right)} \left[ 1 - (a/b)^2 \right]^{3/2} \tag{2.60}
\]

which is equation [2.40] given by van Beek when \(\frac{1}{n} = A_a\).
For prolate spheroids, Sillars obtained the relation
\[
\frac{1}{n} = \left( \frac{1}{e^2} - 1 \right) \left[ \frac{1}{2e} \ln \left( \frac{1 + e}{1 - e} \right) - 1 \right] \quad [2.60a]
\]

where \( e = \left[ 1 - (b/a)^2 \right]^{\frac{1}{2}} \) \( (a > b) \).

Re-arranging \([2.60a]\) gives
\[
\frac{1}{n} = \frac{1}{e^2} \left[ \frac{1}{2e} \ln \left( \frac{(1 + e)^2}{1 - e^2} \right) - 1 \right]
\]

\[
= \frac{(b/a)^2}{e^2} \left[ \frac{1}{e} \ln \left( 1 + e \frac{a}{b} \right) - 1 \right]
\]

\[
= \frac{(b/a)^2}{1 - (b/a)^2} \ln \left( \frac{a}{b} + \left[ 1 - (b/a)^2 \right]^{\frac{1}{2}} \frac{a}{b} \right) - \frac{(b/a)^2}{1 - (b/a)^2}
\]

\[
= \frac{\left( \frac{a}{b} \right)^2}{(a/b)^2 - 1} + \frac{\left( \frac{a}{b} \right)^2}{\left( (a/b)^2 - 1 \right)^{\frac{3}{2}}} \ln \left\{ \frac{a}{b} + \left[ (a/b)^2 - 1 \right]^{\frac{1}{2}} \right\}
\]

which is equation \([2.39]\) quoted by van Beek where \( n = \frac{1}{A_a} \).

Now the complete equation for \( \epsilon_\infty \) given by Wagner is:
\[
\epsilon_\infty = \epsilon_1 \left( \frac{2 \epsilon_1 + \epsilon_2 + 2 \phi (\epsilon_2 - \epsilon_1)}{2 \epsilon_1 + \epsilon_2 - \phi (\epsilon_2 - \epsilon_1)} \right) \quad \text{(see [2.22])}
\]

Following the procedure of Sillars but here retaining the volume fraction term in the denominator to enable application to higher volume fraction of dispersed phase and, in addition, noting that the volume fraction term in the numerator contains the factor two instead of three, we can write:
\[ \varepsilon_\infty = \varepsilon_1 \frac{(n - 1)\varepsilon_1 + \varepsilon_2 + (n - 1)\varphi(\varepsilon_2 - \varepsilon_1)}{(n - 1)\varepsilon_1 + \varepsilon_2 - \varphi(\varepsilon_2 - \varepsilon_1)} \quad [2.61] \]

In the case of \( n = 3 \) [2.61] reduces to [2.22] as required.

Writing \( n = \frac{1}{A_a} \) gives

\[
\varepsilon_\infty = \varepsilon_1 \frac{\left( 1 - \frac{1}{A_a} \right)\varepsilon_1 + \varepsilon_2 + \left( 1 - \frac{1}{A_a} \right)\varphi(\varepsilon_2 - \varepsilon_1)}{\left( 1 - \frac{1}{A_a} \right)\varepsilon_1 + \varepsilon_2 - \frac{1}{A_a}\varphi(\varepsilon_2 - \varepsilon_1)}
\]

\[ = \varepsilon_1 \frac{(1 - A_a)\varepsilon_1 + A_a\varepsilon_2 + (1 - A_a)\varphi(\varepsilon_2 - \varepsilon_1)}{(1 - A_a)\varepsilon_1 + A_a\varepsilon_2 - A_a\varphi(\varepsilon_2 - \varepsilon_1)} \]

\[ = \varepsilon_1 \frac{A_a(\varepsilon_2 - \varepsilon_1) + \varepsilon_1 + (1 - A_a)\varphi(\varepsilon_2 - \varepsilon_1)}{A_a(\varepsilon_2 - \varepsilon_1) + \varepsilon_1 - A_a\varphi(\varepsilon_2 - \varepsilon_1)} \]

\[ = \varepsilon_1 \frac{\varepsilon_1 + \{ A_a(1 - \varphi) + \varphi \}(\varepsilon_2 - \varepsilon_1)}{\varepsilon_1 + A_a(1 - \varphi)(\varepsilon_2 - \varepsilon_1)} \quad [2.62] \]

which is equation [2.36] quoted by van Beek. Substitution of \( A_a = \frac{1}{3} \) into the equation gives the Wagner equation for \( \varepsilon_\infty [2.22] \) as required.

### 2.2.6.2 Derivation of generalised Bruggeman equation

We have, from above,

\[ \varepsilon_\infty = \varepsilon = \varepsilon_1 \frac{\varepsilon_1 + \{ A_a(1 - \varphi) + \varphi \}(\varepsilon_2 - \varepsilon_1)}{\varepsilon_1 + A_a(1 - \varphi)(\varepsilon_2 - \varepsilon_1)} \]

or \( \varepsilon\varepsilon_1 + A_a\varepsilon(1 - \varphi)(\varepsilon_2 - \varepsilon_1) = \varepsilon_1^2 + \varepsilon_1\{ A_a(1 - \varphi) + \varphi \}(\varepsilon_2 - \varepsilon_1) \)

\[ \varepsilon_\varepsilon_1 - \varepsilon_1^2 = A_a(1 - \varphi)(\varepsilon_2 - \varepsilon_1)(\varepsilon_1 - \varepsilon) + \varepsilon_1\varphi(\varepsilon_2 - \varepsilon_1) \]
\[ \epsilon_1 (\epsilon - \epsilon_1) = (\epsilon_2 - \epsilon_1) (A_a \epsilon_1 - A_a \epsilon - A_a \varphi_1 + A_a \varphi + \epsilon_1 \varphi) \]

\[ = (\epsilon_2 - \epsilon_1) [A_a (\epsilon_1 - \epsilon) + \varphi (\epsilon_1 + A_a \epsilon - A_a \epsilon_1)] \]

\[ = (\epsilon_2 - \epsilon_1) [\frac{A_a (\epsilon_1 - \epsilon) + \varphi \{ \epsilon_1 + A_a (\epsilon - \epsilon_1) \}}{1 - \varphi}] \]

Using the Bruggeman method as discussed earlier \( \epsilon_1 + \epsilon \) and \( \epsilon + \epsilon + \Delta \epsilon \), also \( \varphi + \frac{\Delta \varphi}{1 - \varphi} \), then

\[ \epsilon \Delta \epsilon = (\epsilon_2 - \epsilon) \left[ -A_a \Delta \epsilon + \frac{\Delta \varphi}{1 - \varphi} \right] (\epsilon + A_a \Delta \epsilon) \]

\[ = (\epsilon_2 - \epsilon) \left[ -A_a \Delta \epsilon + \frac{\Delta \varphi}{1 - \varphi} \right] (\epsilon_2 - \epsilon) \quad \text{(neglecting \( \Delta \varphi \Delta \epsilon \))} \]

\[ \Delta \epsilon (\epsilon + \epsilon A_a - \epsilon_2 A_a) = \frac{-\Delta \varphi}{1 - \varphi} \epsilon (\epsilon_2 - \epsilon) \]

\[ \Delta \epsilon \left[ \frac{\epsilon (-1 + A_a) - \epsilon_2 A_a}{\epsilon (\epsilon_2 - \epsilon)} \right] = \frac{-\Delta \varphi}{1 - \varphi} \quad \text{[2.63]} \]

Express LHS in form \( \frac{ax - b}{x(c - x)} = M + \frac{N}{c - x} \)

or \( M(c - x) + Nx = ax - b \)

Equating coefficients: \( Mc = -b \) ie \( M = -b/c \)

and \( -M + N = a \) ie \( N = a + M = a - \frac{b}{c} \)

thus in equation for \( \epsilon \): \( M = -\epsilon_2 A_a / \epsilon_2 = -A_a \)

\( N = (-1 + A_a) - A_a = -1 \)

Rewriting equation [2.63] and inserting limits that \( \epsilon \) is integrated between \( \epsilon_1 \) and \( \epsilon \), \( \varphi \) between 0 and \( \varphi \)
\[
- \left( \frac{d\varepsilon}{\varepsilon} \right)_{\varepsilon_1} = \left( \frac{d\varepsilon}{\varepsilon_2 - \varepsilon} \right)_{\varepsilon_1} = - \left( \frac{d\varphi}{1 - \varphi^2} \right)
\]

\[
- \frac{A_a}{\varepsilon_2 - \varepsilon_1} \ln \left( \frac{\varepsilon_1}{\varepsilon_2} \right) + \ln \left( \frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 - \varepsilon_1} \right) = \ln (1 - \varphi)
\]

or \[
A_a \ln \left( \frac{\varepsilon_1}{\varepsilon} \right) + \ln \left( \frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 - \varepsilon_1} \right) = \ln (1 - \varphi)
\]

\[
\therefore \quad \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 - \varepsilon_1} \left( \frac{\varepsilon_1}{\varepsilon} \right)^A_a = 1 - \varphi
\]

For spheres \( A_a = \frac{1}{3} \), giving the Bruggeman equation, thus equation [2.64] can be regarded as the Bruggeman equation extended to spheroidal dispersions and can be used for \( 0 \leq A_a \leq 1 \).

2.2.6.3 Derivation of generalised Hanai equations

Using the approach of Hanai (120), the generalised Bruggeman equation [2.64] can be similarly expressed in complex form, and solution is obtained simply by replacing the \( \frac{1}{3} \) in [2.24a] by \( A_a \) and the 3 in [2.24b] by \( \frac{1}{A_a} \).

In the high frequency limiting case \( \varepsilon_1 >> \gamma_1, \varepsilon_2 >> \gamma_2 \)

and \( \varepsilon >> \gamma \left( \gamma = \frac{\sigma}{j\omega \varepsilon_0} \right) \) giving

\[
\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 - \varepsilon_2} \left( \frac{\varepsilon_1}{\varepsilon_\infty} \right)^A_a = 1 - \varphi
\]

[2.65]
and
\[
\phi = \frac{1}{A_a (\varepsilon - \varepsilon_2)} - \frac{1}{\varepsilon_2} = (A_a^{-1}) \left[ \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 - \varepsilon_2} + \frac{\varepsilon_2}{\varepsilon_1 - \varepsilon_2} \right] - \frac{\sigma_1}{\varepsilon_1} \quad [2.66]
\]

In the low frequency limiting case \( \gamma_1 \gg \varepsilon_1, \gamma_2 \gg \varepsilon_2 \) and \( \gamma \gg \varepsilon \) giving
\[
\varepsilon \left[ \frac{1}{A_a (\varepsilon - \varepsilon_2)} - \frac{1}{\varepsilon_2} \right] = \frac{1}{A_a} \left[ \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 - \varepsilon_2} + \frac{\varepsilon_2}{\varepsilon_1 - \varepsilon_2} \right] - \frac{\varepsilon_1}{\varepsilon_1} \quad [2.67]
\]

and
\[
\frac{\sigma - \sigma_2}{\sigma - \sigma_1} \left( \frac{\sigma_1}{\varepsilon_2} \right) A_a = 1 - \phi \quad [2.68]
\]

### 2.6.3.1 O/W Dispersion

Writing \( \sigma_1 \gg \sigma_2 \) and \( \sigma \gg \sigma_2 \), [2.65] is unchanged, [2.66] reduces to:
\[
\phi = (A_a^{-1}) \left[ \frac{1}{\varepsilon_1 - \varepsilon_2} - \frac{1}{\varepsilon_2} \right] = (A_a^{-1}) \left[ \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 - \varepsilon_2} - \frac{\varepsilon_1}{\varepsilon_1} \right]
\]

\[
= (A_a^{-1}) \left[ \frac{1}{\varepsilon_1 - \varepsilon_2} - \frac{1}{\varepsilon_1} \right] \quad [2.69]
\]

[2.67] reduces to
\[
\varepsilon \left[ \frac{1}{A_a \varepsilon - \varepsilon_2} - \frac{1}{\varepsilon_2} \right] = \frac{1}{A_a} \left[ \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 - \varepsilon_2} + \frac{\varepsilon_2}{\varepsilon_1 - \varepsilon_2} \right] - \frac{\varepsilon_1}{\varepsilon_1}
\]

\[
\varepsilon S \left[ \frac{1 - A_a}{A_a \sigma - \sigma_2} \right] = \frac{1}{A_a} \left[ \frac{\varepsilon_1 - \varepsilon_2 + \varepsilon_2 \sigma_1 - A_a \varepsilon_1}{\sigma_1 \sigma_2} \right]
\]
\[ \varepsilon_s \sigma_s (1 - A_a) = \frac{\sigma_s}{\sigma_1} \left[ \varepsilon_1 (1 - A_a) - \varepsilon_2 \sigma_s + \varepsilon_2 \sigma_1 \right] \quad [2.70] \]

Also \[2.68\] reduces to

\[ \frac{\sigma_s}{\sigma_1} \left( \frac{\sigma_1}{\sigma_s} \right)^A = 1 - \phi \]

ie

\[ \frac{A - 1}{\sigma_1} = \left( \frac{\sigma_1}{\sigma_s} \right)^A = 1 - \phi \]

\[ \sigma_1 = \sigma_s (1 - \phi) \]

or

\[ \sigma_s = \sigma_1 (1 - \phi) \frac{1}{1 - A_a} \quad [2.71] \]

Substitution into \[2.70\] gives

\[ \varepsilon_s (1 - A_a) \sigma_s = (1 - \phi) \frac{1}{1 - A_a} \left[ \varepsilon_1 (1 - A_a) - \varepsilon_2 \sigma_s + \frac{\varepsilon_2 \sigma_s}{1 - A_a} \right] \]

ie

\[ \varepsilon_s = \frac{1}{1 - A_a} \left[ \varepsilon_1 (1 - A_a) - \varepsilon_2 (1 - \phi) \right] \frac{1}{1 - A_a} + \varepsilon_2 \quad [2.72] \]

For spheres \( A_a = \frac{1}{3} \) giving the Hanai equations for an O/W dispersion, thus \[2.65\], \[2.69\], \[2.71\] and \[2.72\] can be regarded as the Hanai equations extended to spheroidal dispersions and can be used for \( 0 < A_a < 1 \).
2.2.6.3.2 W/O Dispersion

Writing $\sigma_2 >> \sigma_1$ and $\sigma_2 >> \sigma_S$ [2.65] is unchanged.

[2.66] reduces to

\[
\sigma_\infty \left[ \frac{1}{\epsilon_\infty - \epsilon_2} - \frac{1}{\epsilon_\infty} \right] = (A)a \left[ \frac{-\sigma_2}{\epsilon_1 - \epsilon_2} + \frac{\sigma_2}{\epsilon_\infty - \epsilon_2} \right]
\]

\[
= (A)a^2 \sigma_2 \left[ \frac{1}{\epsilon_\infty - \epsilon_2} - \frac{1}{\epsilon_1 - \epsilon_2} \right] \tag{2.73}
\]

[2.67] reduces to:

\[
\frac{\epsilon_S}{\sigma_S} = -\frac{\epsilon_1}{\sigma_1}
\]

ie

\[
\epsilon_S = \epsilon_1 \frac{\sigma_S}{\sigma_1} \tag{2.74}
\]

Also [2.68] reduces to

\[
\left( \frac{\sigma_1}{\sigma_S} \right)^A_A = 1 - \phi
\]

or

\[
\sigma_S = \frac{\sigma_1}{1 - \phi} A^A_a \tag{2.75}
\]

Substitution of [2.74] into [2.75] gives

\[
\epsilon_S = \frac{\epsilon_1}{1 - \phi} A^A_a \tag{2.76}
\]

For spheres $A_a = \frac{1}{3}$ giving the Hanai equations for a W/O dispersion, thus [2.65], [2.73], [2.75] and [2.76]
can be regarded as the Hanai equations extended to spheroidal dispersions and can be used for \( 0 < A_a < 1 \).

2.2.6.4 Derivation of generalised Looyenga equation

Using the generalised Bruggeman equation [2.64] and assuming the infinitesimal changes \( \varepsilon_1 \rightarrow \varepsilon - \Delta \varepsilon \) and \( \varepsilon_2 \rightarrow \varepsilon + \Delta \varepsilon \) and replacing \( \phi \) by the variable volume fraction \( \phi^* \) as in the derivation of the Looyenga equation [2.17] gives:

\[
\left( \frac{\varepsilon + \Delta \varepsilon}{\varepsilon + \Delta \varepsilon} \right) - \frac{\Delta \varepsilon}{\varepsilon - \Delta \varepsilon} \left( \frac{\varepsilon - \Delta \varepsilon}{\varepsilon} \right)^{A_a} = 1 - \phi^*
\]

or

\[
\frac{\Delta \varepsilon}{2 \Delta \varepsilon} \left( \frac{\varepsilon - \Delta \varepsilon}{\varepsilon} \right)^{A_a} = 1 - \phi^*
\]

\[
\frac{1}{2} \left( 1 - \frac{\Delta \varepsilon}{\varepsilon} \right)^{A_a} = 1 - \phi^*
\]

Applying binomial expansion and neglecting \((\Delta \varepsilon)^2\) terms

\[
\frac{1}{2} - \frac{A_a}{2} \frac{\Delta \varepsilon}{\varepsilon} = 1 - \phi^*
\]

ie

\[
\phi^* = 1 - \left( \frac{1}{2} - \frac{A_a}{2} \frac{\Delta \varepsilon}{\varepsilon} \right)
\]

\[
= \frac{1}{2} + \frac{A_a}{2} \frac{\Delta \varepsilon}{\varepsilon} \tag{2.77}
\]

Combining [2.77] with [2.16a] gives

\[
\frac{1}{2} + \frac{A_a}{2} \frac{\Delta \varepsilon}{\varepsilon} = \frac{1}{2} - \frac{1}{4} \Delta \varepsilon \frac{d^2 \phi}{d \varepsilon^2}
\]
\[
\left(\frac{1}{2Aa}\right) \frac{d^2 \varphi}{d \xi^2} + \frac{d \varphi}{d \xi} = 0
\]

This equation is of the form \( kx \frac{d^2 y}{dx^2} + \frac{dy}{dx} = 0 \) and has a solution
\[
y = \frac{Cx^{1 - 1/k}}{1 - 1/k} + D
\]
where \( C \) and \( D \) are constants.

Hence we can write
\[
\varphi = \frac{C \varepsilon^{1 - 1/k}}{1 - 1/k} + D \quad \text{where} \quad k = \frac{1}{2Aa}
\]

\[\therefore \varphi = \frac{C \varepsilon^{1 - 2Aa}}{1 - 2Aa} + D\]

Applying boundary conditions when \( \varphi = 0, \varepsilon = \varepsilon_1 \) and when \( \varphi = 1, \varepsilon = \varepsilon_2 \) gives:
\[
0 = \frac{C \varepsilon_1^{1 - 2Aa}}{1 - 2Aa} + D \quad \text{ie} \quad \varepsilon_1^{1 - 2Aa} = -\frac{D}{C}(1 - 2Aa)
\]

and
\[
1 = \frac{C \varepsilon_2^{1 - 2Aa}}{1 - 2Aa} + D \quad \text{ie} \quad \varepsilon_2^{1 - 2Aa} = \frac{(1 - D)}{C}(1 - 2Aa)
\]

\[\therefore \frac{\varepsilon_1^{1 - 2Aa}}{\varepsilon_2^{1 - 2Aa}} = \frac{-D}{1 - D} \quad \text{or} \quad D = \frac{\varepsilon_1^{1 - 2Aa}}{\varepsilon_1^{1 - 2Aa} - \varepsilon_2^{1 - 2Aa}}
\]

thus
\[
C = \frac{-D(1 - 2Aa)}{\varepsilon_1^{1 - 2Aa} - \varepsilon_1^{1 - 2Aa} - \varepsilon_2^{1 - 2Aa}}
\]
\[ \therefore \phi = \frac{-\varepsilon}{1 + 2Aa} + \frac{\varepsilon}{1 - 2Aa - \varepsilon_2 (1 - 2Aa)} \]

or

\[ \varepsilon = \left[ \frac{1 - 2Aa}{\varepsilon_2 (1 - 2Aa) - \varepsilon_1 (1 - 2Aa)} \right]^{1 - 2Aa} \]

[2.78]

For spheres \( A_a = \frac{1}{3} \) giving the Looyenga equation.

In addition, when \( A_a = \frac{1}{4} \) [2.78] reduces to the Kraszewski equation [2.18]. For this extension, the range of \( A_a \) is restricted to \( 0 < A_a < 0.5 \).

2.2.6.5 Summary of new equations

2.6.5.1 Permittivity

The following new equations for the permittivity of a mixture have been derived:

(i) \[ \frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 - \varepsilon_1} = 1 - \phi \]  

[2.64]

\( 0 < A_a < 1 \)

which is the Bruggeman equation extended to spheroidal dispersions of both prolate and oblate shape.

(ii) \[ \varepsilon_s = \frac{1}{1 - A_a} \left[ (\varepsilon_1 (1 - A_a) - \varepsilon_2 (1 - \phi))^{1/1-A_a} + \varepsilon_2 \right] \]

[2.72]
which is the Hanai equation for the low frequency limiting value of $\varepsilon$ extended to O/W spheroidal dispersions of both prolate and oblate shape.

The high frequency limiting value of $\varepsilon$ \([2.65]\) is given by (i) above writing $\varepsilon = \varepsilon_\infty$.

\[
(iii) \quad \varepsilon_s = \frac{\varepsilon_1}{(1 - \phi)^{1/A_a}} \quad [2.76]
\]

\[0 < A_a < 1\]

which is the Hanai equation for the low frequency limiting value of $\varepsilon$ extended to a W/O spheroidal dispersion of both prolate and oblate shape.

The high frequency limiting value is again given by (i) \([2.64]\) writing $\varepsilon = \varepsilon_\infty$.

\[(iv) \quad \varepsilon = \left[ \varepsilon_1 \left( 1 - 2A_a \right) + \phi \left( \varepsilon_2 \left( 1 - 2A_a \right) - \varepsilon_1 \left( 1 - 2A_a \right) \right) \right]^{-1} \quad [2.78]
\]

\[0 < A_a < 0.5\]

which is the Looyenga equation extended to spheroidal dispersions of both prolate and oblate shape.

2.6.5.2 Conductivity

The following new equations for the high and low frequency limiting values of the conductivity of a
mixture, $\sigma_\infty$ and $\sigma_S$, have been derived:

\begin{equation}
\sigma_\infty \left[ \frac{1}{A_a (\varepsilon_\infty - \varepsilon_2)} - \frac{1}{\varepsilon_\infty} \right] = (A_a)^{\frac{1}{2}} \left[ \frac{1}{\varepsilon_1 - \varepsilon_2} - \frac{1}{\varepsilon_1} \right] \tag{2.69}
\end{equation}

\(0 \leq A_a < 1\)

(ii)

\begin{equation}
\sigma_S = \sigma_1 (1 - \theta) \frac{1}{1 - A_a} \tag{2.71}
\end{equation}

\(0 \leq A_a < 1\)

(i) and (ii) are the Hanai equations extended to an O/W spheroidal dispersion of both prolate and oblate shape.

(iii)

\begin{equation}
\sigma_\infty \left[ \frac{1}{A_a (\varepsilon_\infty - \varepsilon_2)} - \frac{1}{\varepsilon_\infty} \right] = (A_a)^{\frac{1}{2}} \left[ \frac{1}{\varepsilon_1 - \varepsilon_2} - \frac{1}{\varepsilon_1} \right] \tag{2.73}
\end{equation}

\(0 < A_a < 1\)

(iv)

\begin{equation}
\sigma_S = \frac{\sigma_1}{(1 - \theta)^{1/A_a}} \tag{2.75}
\end{equation}

\(0 < A_a < 1\)

(iii) and (iv) are the Hanai equations extended to a W/O spheroidal dispersion of both prolate and oblate shape.
CHAPTER 3 EXPERIMENTAL

3.1 Materials and Preparation of Mixtures

3.1.1 Alcohols
The alcohol t-butanol was Analar grade (BDH), the cyclohexanol and the 1-heptanol were both General Purpose Reagent grade (BDH) and the 1-butanol was Puriss grade (Koch Light). All the alcohols were fractionally distilled immediately before use from freshly ignited quick-lime using a Gallenkamp fractional distillation unit with variable take-off head. When the alcohols had to be stored, they were kept in dessicators over phosphorus pentoxide.

3.1.2 Water
Pure water was obtained by refluxing distilled water over alkaline permanganate and then distilling through a 61 cm fractionating column. Later in the experimental programme double-distilled water was obtained directly from a Fisons Fi-Stream unit.

3.1.3 Alcohol-water Mixtures
Alcohol-water mixtures were prepared by weighing the required amounts of liquid using a precision balance which was usually a Mettler H10 or Oertling V20. These balances enabled masses to be determined to a precision of better than ±0.0005 g, and the mole fractions of the mixtures could be formulated to a precision of better than ±0.01.
3.1.4 **Surfactants**

The commercial surfactant Brij 30 (Batch 51) was obtained from Honeywill-Atlas Ltd. The pure surfactants $C_{12}E_4$, $C_{12}E_6$ and $C_{12}E_8$ were obtained from Nikkol Chemicals Ltd; Japan. In order to achieve consistency, the Brij 30 was stored for 24 hours at $30^\circ$C and then filtered through Whatman 41 ashless paper at the same temperature. The filtering requirement arose because this batch of Brij 30 contained a small amount of insoluble solids. Again to achieve consistency, all measurements were performed using the same batch (51). The pure surfactants were used as obtained without further purification.

3.1.5 **Hydrocarbons**

The hydrocarbon heptane was IP normal grade (BDH), the decane was Laboratory Reagent grade (BDH) and the hexadecane was Puriss grade (Koch Light). The hydrocarbons were used as obtained without further purification.

3.1.6 **Binary and ternary mixtures of surfactants**

The binary and ternary mixtures of surfactant with water, surfactant with hydrocarbon and surfactant with water and a hydrocarbon were prepared by the precision balance method already described, where for the binary aqueous mixtures of $C_{12}E_n$ ($n = 4, 6$ and $8$), a successive dilution method was adopted because of the high cost of the surfactants. The method involved addition of the required amount of water by a pipette so that the mixtures could be
studied over the whole composition range at 10% by mass intervals. In order to ensure consistency and reproducibility of results, additional mixtures at both 90% and 80% by mass of water were formulated by the method of addition of surfactant to water. For these two mixtures, the values of $\varepsilon^*$ obtained by the two formulation methods agreed within $\pm 0.2\%$.

3.2 Development of time domain technique and its use

3.2.1 Introduction

At the time that this research programme was commenced, time domain spectroscopy was in an early stage of development for use in liquids. Accordingly, the development of a specific method applicable to the materials of interest here has formed an essential part of the work and is presented as such.

Time domain reflectometry (TDR) has been used for some years in cable testing and makes use of the very fast switching properties of tunnel diodes and wide band facilities of sampling oscilloscopes together with the good VSWR properties of precision coaxial air lines such as the Amphenol APC7 and General Radio GR 900.

The application of TDR techniques to dielectric measurements was originally suggested by Fellner-Feldegg (169). The method involves the generation of a fast rise-time (and thus wideband) pulse and study of the change in pulse
shape after reflection from the surface of a dielectric medium inside a coaxial air-line. A representative time dependence of the reflection coefficient for reflection from a dielectric is given in Figure 7.

\[ \rho_{\infty} = \text{high frequency limiting value of reflection coefficient} \]
\[ \rho_S = \text{low frequency limiting value of reflection coefficient} \]

In the paper of Fellner Feldegg (169) rather poor agreement was obtained between the measured relaxation time of some alcohols compared with literature values. However, Whittingham (170) pointed out that the method of determining relaxation times used by Fellner-Feldegg was not mathematically valid and subsequent work by Suggett et al (171) using the correct forms of the equations gave results which compared favourably with literature values. Loeb et al (172) discussed some of the errors associated with the
time domain reflection technique and, in addition, described an alternative measurement method based on transmission instead of reflection. The transmission method is more involved in that a transfer function is required from two cells of different lengths in order to determine $\varepsilon^*$. The method has the advantage of improved high frequency precision due to the generation of larger phase shifts which results in substantially less error in time referencing, but it suffers from the disadvantage of more limited frequency range than the reflection methods as well as requiring results from two different measuring cells. Van Gemert et al (173) have reported an accuracy in relaxation times of "about 5%" for the single reflection method.

Following the suggestion of Fellner-Feldegg (174), multiple reflections from a thin dielectric sample can be utilised and a number of multiple response methods have been developed. These demand greater experimental expertise but have advantages in biological applications since little liquid is required.

A number of review articles in which the various time domain methods are evaluated have been published with the work of van Gemert (175), Suggett (176), Clark et al (177), Clarkson et al (178) Giese and Tiemann (179) and Grant et al (42) being particularly worthy of mention.

Clarkson et al (178) suggested that in many medium to
high loss systems, the single reflection method is the most favourable since (i) the effects of sample termination do not need to be taken into account and (ii) that extraneous reflections can be minimised by appropriate choice of delay lines linking the components of the system. This method has formed the basis of the time domain part of the experimental programme in this work. Relaxation times can be determined directly from the time domain data or by use of Fourier transformation. Both of these techniques are described in the following sections.

3.2.2 Direct time domain methods

3.2.2.1 Fellner-Feldegg method $\tau_D$

In this method, it is assumed that the time-dependence of the reflection coefficient $\rho$ is such that the time dependent permittivity $\varepsilon$, which is given by $\varepsilon = \left(\frac{1 + |\rho|}{1 - |\rho|}\right)^2$, obeys an exponential relationship. This gives a linear relation between $\ln (\varepsilon_S - \varepsilon)$ against time, $t$, where $\varepsilon_S$ is the low frequency limiting value of the permittivity and the reciprocal of the slope of the $\ln (\varepsilon_S - \varepsilon)$ against $t$ graph is the relaxation time $\tau_D$.

Despite its basic mathematical invalidity in assuming that the complex component in $\rho$ may be neglected, Loeb et al (172) have reported that this $\tau_D$ method can be of value when used together with a single low frequency measurement to estimate relaxation times in liquids where echo reflections appear before the relaxation process is complete.
Such behaviour occurs in slower relaxation processes. Although examples were not given, these authors reported that in Debye-type dispersions, the method gives good agreement with literature values. They further added that this direct method is useful in revealing the presence of overlapping relaxations.

The \( \tau_D \) method has been applied to the time domain data obtained in this work with the values of \( \epsilon_s \) being obtained from Dipolmeter values using the procedure described in 3.2.4.4.

3.2.2.2 Fellner-Feldegg and Barnett method \( \tau_{FF+B} \)

The basic mathematical invalidity in the \( \tau_D \) method has been corrected by Fellner-Feldegg and Barnett but the method is restricted to single relaxation time (Debye-type) dispersions.

The Fellner-Feldegg and Barnett (FF+B) paper (180) presents three sets of curves for values of the time-dependent reflection coefficient, \( \rho \), given by:

\[
\frac{\rho_S - \rho}{\rho_S - \rho_\infty} = 0.2, \frac{1}{e} \text{ and } 0.8 \text{ respectively where } \rho_S \text{ and } \rho_\infty \text{ are the respective low and high frequency limiting values of the reflection coefficient.}
\]

The curves permit the determination of the relaxation time \( \tau_{FF+B} \) from the measured time \( \tau^* \), at the 0.8, \( \frac{1}{e} \) and 0.2 values respectively of the reflection coefficient, by
providing scaling factors whose values depend on (a) which of the reflection coefficient values is selected and (b) the values of $\varepsilon_S$ and $\varepsilon_\infty$. The \[
\frac{\rho_S - \rho}{\rho_S - \rho_\infty} = 0.2
\] curves enable the most precise determination of the required scaling factor and were therefore used whenever possible in this work.

In this work, the values of $\varepsilon_S$ and $\rho_S$ were obtained from Dipolmeter values. Estimated of the $\rho_\infty$ values posed some difficulty due to the reflection coefficient at times close to $t = 0$ being very sensitive to error in the time zero reference. The value of $\rho_\infty$ adopted was the one which was the lowest value given by the time domain data. This was attained after typically two data points from the time zero and corresponded to about 30 ps. This figure is considered reasonable as the system rise-time was quoted as 35 ps. The values of $\tau^*$ at the 0.8, 1/$e$ or 0.2 points of the reflection coefficient curve were obtained directly from the time domain data.

3.2.2.3 Brehm and Stockmayer method $\tau_{B+S}$

The basic mathematical invalidity in the $\tau_D$ method has been corrected by Brehm and Stockmayer (181) and their treatment is more general than that of FF+B as the possibility of Cole-Davidson type dispersion (equation [2.9]) with values of the parameter $\beta$ between 0.3 and 1 is taken into account. However, the curves in this paper
are much less detailed than those in FF+B.

The Brehm and Stockmayer method requires the determination of two times $t_{\frac{1}{3}}$ and $t_{\frac{2}{3}}$ when the reflection coefficient has fallen by $\frac{1}{3}$ and $\frac{2}{3}$ respectively from its initial $\rho_\infty$ value to its final $\rho_S$ value. Two sets of curves are given, one set enables the $\beta$ parameter to be determined from the ratio $t_{\frac{1}{3}}/t_{\frac{2}{3}}$ for values of $\varepsilon_S$ and $\varepsilon_\infty$ in the ratios $\varepsilon_S/\varepsilon_\infty = 4, 3, 2$ and $1$ respectively. The other set of curves enables the relaxation time $\tau_{B+S}$ to be determined, for values of $\varepsilon_S/\varepsilon_\infty$ as given above, from the $t_{\frac{1}{3}}$ data.

In this work, the same procedure as used in the FF+B method was used for the determination of $\varepsilon_S$, $\varepsilon_\infty$, $\rho_S$ and $\rho_\infty$. The $t_{\frac{1}{3}}$ and $t_{\frac{2}{3}}$ values were obtained directly from the time domain data.

3.2.3 Fourier transform method $\tau_F$

3.2.3.1 Theory

Time domain spectroscopy (TDS) applied to dielectric studies has been discussed in some detail by a number of authors; the approach below follows that of Loeb et al (172).

For a coaxial line filled with a dielectric of permittivity $\varepsilon^*(\omega)$ the characteristic impedance $Z$ is given by

$$Z = \frac{Z_0}{[\varepsilon^*(\omega)]^{\frac{2}{3}}} \quad [3.1]$$

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where $\varepsilon^* = \varepsilon' - j\varepsilon'' - \frac{j\sigma}{\omega \varepsilon} = \varepsilon' - j\varepsilon''$ when conductivity is negligible. \[3.2\]
and $Z_0$ is the characteristic impedance of an air-filled line.

The propagation constant $\gamma$ is given by

$$\gamma = \gamma_0 \left[ \left( \varepsilon^*(\omega) \right) \right]^{\frac{1}{2}} \quad \[3.3\]$$

where $\gamma_0 = \frac{j\omega}{c}$ is the propagation constant of an air-filled line.

When the wave encounters a region of characteristic impedance $Z$ where $Z \neq Z_0$, reflection occurs with reflection coefficient, $\rho^*(\omega)$ where

$$\rho^*(\omega) = \frac{Z - Z_0}{Z + Z_0} \quad \[3.4\]$$

and since $Z, Z_0$ are complex, $\rho^*(\omega)$ will also be complex.

In order to convert the time domain data into the equivalent frequency domain information, Fourier transformation is necessary. The Fourier transform expression states that

$$F(\omega) = \int_{-\infty}^{\infty} f(t) \exp(-j\omega t) \, dt \quad \[3.5\]$$

indicating that any time domain response $f(t)$ is equivalent to an infinite number of frequency components.

The frequency domain response of a dielectric sample is determined by calculating the ratio of the Fourier transforms of the time domain responses of the incident and reflected pulses.
For an incident pulse $f_i(t)$ and reflected pulse $f_r(t)$, the frequency response of the system $G(\omega)$ is given by:

$$G(\omega) = \frac{F_r(\omega)}{F_i(\omega)} = \frac{\int_{-\infty}^{\infty} f_r(t) \exp(-j\omega t) \, dt}{\int_{-\infty}^{\infty} f_i(t) \exp(-j\omega t) \, dt} \quad [3.6]$$

Fourier transformation is achieved using the modification to the Shannon sampling theorem (182) due to Samulon (183) by writing:

$$F(\omega) = \frac{\exp(j\omega \Delta t/2)}{2j \sin(\omega \Delta t/2)} \sum_{n=-\infty}^{\infty} [f(n\Delta t) - f(n\Delta t - \Delta t)] \exp(-jn\omega \Delta t) \quad [3.7]$$

provided $F(\omega) = 0$ for $\omega > \pi/\Delta t$

Combining equations [3.1] and [3.4] yields

$$\varepsilon^*(\omega) = \left[\frac{1 - \rho^*(\omega)}{1 + \rho^*(\omega)}\right]^2 \quad [3.8]$$

and writing $\rho^*(\omega) = r \exp(j\phi)$ gives after separating real and imaginary parts:

$$\varepsilon' = \frac{(1 - r^2)^2 - 4(r \sin \phi)^2}{(1 + r^2 + 2r \cos \phi)^2} \quad [3.9]$$

and $\varepsilon'' = \frac{4(1 - r^2) r \sin \phi}{(1 + r^2 + 2r \cos \phi)^2} \quad [3.10]$

### 3.2.3.2 Development of computer program

The experimental procedure for determining $F_r(\omega)$ involves measuring the amplitudes of the reflected pulse $a_1, a_2, a_3, \ldots, a_n$ from the dielectric at time intervals $\Delta t$. 

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The change in amplitude $b_n = a_n - a_{n-1}$ is then determined for $b_1 = a_1$ and substitution into the transform expression gives for a frequency $\omega = \omega_1$:

$$F_r(\omega_1) = \frac{-\exp(j\omega_1 \Delta t/2)}{2j \sin(\omega_1 \Delta t/2)} \left[ b_1 \exp(-j\omega_1 \Delta t) + b_2 \exp(-\exp j2\omega_1 \Delta t) + \ldots + b_n \exp(-jn\omega_1 \Delta t) \right]$$

$$= \frac{-1}{2j \sin(\omega_1 \Delta t/2)} \left[ b_1 \cos\left(\frac{\omega_1 \Delta t}{2}\right) - j b_1 \sin\left(\frac{\omega_1 \Delta t}{2}\right) + b_2 \cos\left(\frac{3\omega_1 \Delta t}{2}\right) - j b_2 \sin\left(\frac{3\omega_1 \Delta t}{2}\right) + \ldots + b_n \cos\{(n - \frac{1}{2})\omega_1 \Delta t\} - j b_n \sin\{(n - \frac{1}{2})\omega_1 \Delta t\} \right]$$

$$= \sum_{n=0}^{\infty} b_n \sin\{(n - \frac{1}{2})\omega_1 \Delta t\} + j \sum_{n=0}^{\infty} b_n \cos\{(n - \frac{1}{2})\omega_1 \Delta t\}$$

$$= B_s + jB_c$$

putting $B_s + jB_c = R \exp j\theta$

then $R = (B_s^2 + B_c^2)^{\frac{1}{2}}$

and $\theta = \arctan (B_c/B_s)$

The transform for the incident pulse is determined by measuring the amplitude of the pulse obtained when a short circuit termination replaces the dielectric. In this case amplitudes $c_1, c_2, \ldots, c_n$ are measured at intervals of $\Delta t$ and

$$d_n = c_n - c_{n-1} \text{ for } d_1 = c_1 \text{ is found.}$$
An expression similar to that for \( F_r(\omega) \) is obtained except that the negative sign is not required. We thus obtain:

\[
F_i(\omega) = -\left[ \sum_{n=0}^{n} d_n \sin\{(n - \frac{1}{2})\omega_1\Delta t\} + j\sum_{n=0}^{n} d_n \cos\{(n - \frac{1}{2})\omega_1\Delta t\} \right] \frac{2\sin\left(\frac{\omega_1\Delta t}{2}\right)}{2}
\]

and putting \( D_S + jD_C = S \exp^{j\alpha} \)

\[
S = -\left( D_S^2 + D_C^2 \right)^{\frac{1}{2}} \quad \text{and} \quad \alpha = \arctan\left(\frac{D_C}{D_S}\right)
\]

Now \( G(\omega) = \frac{F_r(\omega)}{F_i(\omega)} \)

putting \( G(\omega) = T \exp^{j\phi} \)

then \( T = \frac{R}{S} \) and \( \phi = \theta - \alpha \)

Hence by application of equations [3.9] and [3.10] \( \varepsilon^\prime \) and \( \varepsilon^\prime\prime \) can be found.

A computer program for the determination of \( \varepsilon^* \) from \( a_n \) and \( c_n \) values has been written in Fortran IV MUSIC.

The computer program for the transform has been extended in order to give improved performance in data-handling. This has been done to permit

(i) evaluation of the effect of error in the time zero reference points,

(ii) optimisation of the number of data points to minimise both short time and long time truncation errors in
the Fourier transform.

Truncation effects can be studied because the computer program enables the Fourier transform to be obtained for a specified varying number of data points. Also the transform for each number of data points can be found for a number of time zero reference points by repeating the transform for the zero data point shifted by a specified integral number of data points. This latter procedure can be applied to both the dielectric and the short circuit data and enables the time zero reference to be effectively both advanced and retarded by one or more data points as instructed in the program input data.

An addition that has been included is an instruction to the short circuit transform program ensuring that the transform has the correct sign. This is required due to the non-ideal shapes of the time domain waveforms which occasionally reverse the transform sign for the short circuit data at certain frequencies, resulting in $\varepsilon^*$ being unobtainable at those frequencies. The program instruction removes this possibility. A copy of the computer program is given in the Appendix.

3.2.4 TDR measurement system

3.2.4.1 Basic system

The measurement system incorporated a Hewlett Packard HP 180A mainframe oscilloscope, HP 1815A TDR/sampler, HP 1817A sampling-gate and HP 1106A tunnel diode mount.
The coaxial air lines incorporated Amphenol APC 7 type connectors and two brands were used, namely HP 11567A 20 cm lines and Amphenol APC7 30 cm lines. Since the Amphenol lines were the only ones which could be dismantled, these were used as the measurement cell. The time domain data was recorded on an HP 7035B X-Y recorder which was replaced in later measurements by a Farnell PR1 chart recorder. The X-Y recorder was directly connected to the system via the output connections on the rear of the 180A main frame. The "Main Sweep Output" provided the X input and the "Delayed Gate Output" provided the Y input. An appropriately large sized X-Y plot was obtained simply by adjusting the vernier controls on the recorder. In later measurements the HP recorder exhibited poor stability and was replaced by a Farnell PR1 chart recorder. With this instrument it was necessary to 'back off' some of the recorder input in order to obtain a suitable sized trace. This was achieved by placing a stabilised voltage supply (Farnell E30) in conjunction with a Beckman Helipot potentiometer in series with the input. The PR1 chart recorder was found to give comparable performance to the HP 7035B X-Y recorder.

A variety of air line configurations were studied in order to gain information on the relative effects of the various impedance mismatches in the system and thus ultimately obtain the optimum response. A configuration as given in
Figure 8 was found to be the most suitable with the air line components available, and is similar, but not identical, to that described by Loeb et al (172).

The 1815A was used in the Signal Averaging mode as the operating manual quoted an improvement of 2:1 in noise and "jitter" when compared with the Normal mode. This clearly cannot offer the precision obtainable with the Signal Averagers used by many workers in this field, but it is suitable for studies up to a maximum frequency of approximately 3 GHz (171, 172, 175).
The Amphenol APC7 30 cm line measurement cell could be dismantled without difficulty. The translucent nature of the bead which terminated the line used in the earlier part of the experimental programme enabled any air bubbles present in the sample to be seen and thus minimal problems due to air bubbles were encountered. In the latter part of the programme, a later design Amphenol line was used. This had an opaque bead and thus made air bubble elimination more difficult, but because the presence of a significant air bubble content is revealed in the time domain trace, minimisation of such effects was achieved without difficulty.

Most of the measurements were made at temperatures close to 25° C with temperature control being achieved by enclosing the coaxial line measurement cell in a glass jacket which was circulated with water driven by a Grant SU controller which maintained the temperature constant to better than ± 0.2° C. In order to facilitate measurements at lower temperatures, a refrigeration unit was also incorporated and used when required. After allowing sufficient time for the dielectric liquid to attain the required temperature, a minimum of five traces on the X-Y recorder were taken to ensure stability was maintained. Similarly, when the dielectric was replaced with an APC 7 precision short circuit, a minimum of five X-Y plots were again taken.
3.2.4.2 Voltage base line and time zero reference determination
The base line for the voltage transient on the X–Y plot was determined using a method similar to that of Clarkson and Williams (184). The base line chosen was obtained from an average of typically 30 values of the voltage level before the reference step signal. This procedure was used for both a dielectric and short-circuit terminated line. The time zero reference point was obtained using a method described by Loeb et al (172) in which linear extrapolation from the steepest part of the voltage step to intersect with the voltage base line was drawn. This intersection was used as the time zero reference.

3.2.4.3 Errors in time domain data
Giese and Tiemann (179) have shown that the impedance mismatch between the sampler and air line causes erroneous values at lower frequencies. This problem was also discussed by Campbell et al (34) in studies of dilute alcohols in non-polar solvents. These authors used liquid benzene, which is known not to exhibit dielectric dispersion in this time range, to obtain a frequency dependent apparent reflection coefficient for the benzene this was then used to correct the data obtained for the alcohol solutions. The method used for this correction, which effectively incorporates a data smoothing procedure, was not described but the authors reported that the mismatch between the sampler and air line was corrected by
adjusting the measured reflection coefficient for the benzene until the low frequency permittivity of the pure alcohol, as extrapolated from the time domain data, attained its experimentally correct value. It is presumed that the 'correct' value was obtained from literature data.

The approach of Campbell et al is open to criticism because some of the effects of the impedance mismatch in the system are dependent on the magnitude of the reflection coefficient of the dielectric. This aspect has been discussed in detail by Loeb et al (1972) and the outcome is that the approach is only strictly valid for liquids with the same permittivity as that of the reference liquid.

3.2.4.4 Correction Procedure: WTW Dipolmeter

In this work, correction for the sampler and air line mismatch together with voltage drift and time "jitter" was achieved by adjusting the measured steady state reflection coefficient of the liquid until the low frequency permittivity obtained from the time domain data agreed with the value given by a WTW Dipolmeter type DM01 which operated at the constant frequency of 2MHz.

The measurement cell used with the Dipolmeter was the cell type MFL 2 which enabled relative permittivities within a range of 3.6 to 22 to be measured. The MFL 2 cell was calibrated using the following purified liquids at 25°C as standards: chlorobenzene (ε' = 5.602), 1,2 - dichloroethane (ε' = 10.387) and acetone (ε' = 20.820). The
Dipolmeter readings were used to determine the constants a, b and c in a polynomial expression relating $\varepsilon^*$ to the Dipolmeter reading D of the form $\varepsilon^* = a + bD + cD^2$. This method gave higher precision in determining $\varepsilon^*$ than the calibration procedure of Stevens (185) which involved determination of the best straight line for an assumed linear relation between $\varepsilon^*$ and D. An uncertainty of less than 0.01 in $\varepsilon^*$ was achieved here.

Application of this correction procedure involved scaling the dielectric data by a constant factor which was always within the range 0.98 to 1.02. It was found that the results obtained by the method used in this work gave Cole-Cole plots and a relaxation time value for the pure alcohol 1-butanol very similar to those obtained by Campbell et al (34), thus validating this correction procedure.

Correction could not be applied to the cyclohexanol-water mixtures at less than 0.2 mf of water nor to the pure alcohol 1-heptanol. This was because the steady state reflection coefficient was not attained at the completion of the time domain scan due to the long relaxation times of these liquids. Thus scaling was not applied to the time domain data for these liquids.

3.3 Other measurement techniques: RF bridge studies of surfactant mixtures

3.3.1 Calibration of RF bridge
The surfactant mixtures were studied primarily in the RF range. Measurements were performed within the frequency range 30 kHz to 15 MHz using a Hatfield transformer ratio arm bridge type 300 A with an Airmec video oscillator type 399 as source and an Eddystone communication receiver type 830 as detector in the range 300 kHz to 15 MHz. At the lower frequencies, a Telequipment oscilloscope type D53 was used as detector. The oscilloscope was much less sensitive than the receiver as a detector but was able to reveal large amplitude dispersion effects. The Hatfield bridge was found to give a progressively poorer performance during the latter part of the experimental programme and was replaced in subsequent measurements by a Wayne Kerr bridge type B601. This operated in the frequency range 30 kHz to 5 MHz.

On both the Hatfield and Wayne Kerr bridges, the balance conditions for both the conductance and capacitance components were established by use of standard resistors and standard capacitors. It was found necessary to set the balance conditions for both bridges at each measurement frequency used, with this requirement being particularly important with the B601.

The WTW cell type MFL 2 was used as the measurement cell for the RF bridges. The cell was connected to the bridge by a short length of coaxial cable. The cell constants for the RF bridge were established by measuring a number
of liquids on both the RF bridge at 2 MHz and the Dipolmeter. In addition, double distilled water at 20° C was used as a standard since the upper limit of permittivity, \( \varepsilon' \), of the MFL2 cell on the Dipolmeter was 22.

With the cell constants obtained, permittivity values could be determined with the Hatfield bridge, to a precision of \( \pm 0.2 \) for \( \varepsilon' \) values in the range 1.8 to 78.0.

In order to achieve the highest precision in determining \( \varepsilon' \) values with the Wayne Kerr bridge, it was found necessary to use slightly different values for the cable capacitance component depending on the value of the measured capacitance on the bridge. This effect was attributed to the relatively poor (\( \pm 1\% \)) precision quoted for the bridge. By using the cable capacitance values obtained, the precision of the results was increased and enabled permittivity values to be determined to the same precision as that for the Hatfield bridge for the same permittivity range.

3.4 Specimen conditions

3.4.1 Measurement temperatures

For nearly all of the investigations of the surfactant behaviour, measurements were performed only when the mixtures were optically transparent. The required temperatures for the \( \text{C}_{12}\text{E}_4^- \) and Brij 30- water mixtures were obtained from phase diagram data of Bostock (83). These
diagrams are reproduced by kind permission of the author in chapter 5 of this work. The phase diagram for C_{12}E_6-water mixtures was obtained from literature data (186) and that for C_{12}E_8-water mixtures from Unilever Ltd (187). These phase diagrams are also given in chapter 5.

An important feature of some of the surfactant-water and surfactant-water-hydrocarbon compositions was that optical transparency was attained only over a very narrow temperature range, being typically about 1^\circ C. In order to ensure that the mixtures were measured in the transparent state, the cap of the MFL2 cell was briefly removed to inspect the mixture in the cell and secondly, it was also checked that the mixture was transparent when drained from the cell immediately on completion of the measurements.

3.4.2 Surfactant-water and surfactant-hydrocarbon binary mixtures

Binary mixtures of the surfactants C_{12}E_n (n = 4, 6 and 8) and Brij 30 with water were studied over the whole composition range at 10\% by mass intervals. Their temperatures were adjusted as required in order to maintain the transparency condition.

For all of the surfactants and, in addition for mixtures which were transparent over a wide temperature range, the temperature dependence of the permittivity was studied.

Some studies were performed on binary mixtures of Brij 30 with the hydrocarbon heptane. In contrast to the Brij 30
water mixtures, the binary mixtures with heptane were
miscible at all compositions at temperatures above 45° C.
The mixtures were all studied at 56° C at 20% by mass
intervals using the Dipolmeter with the DFL2 cell on the
D1 range. Cell calibration was performed with heptane
($\varepsilon^\prime = 1.92$) and Brij 30 as the reference liquids with
a presumed linear relationship between the Dipolmeter
reading (D1) and permittivity $\varepsilon^\prime$ being considered of
adequate precision. The permittivity of Brij 30 was
obtained from data given by the calibrated MFL2 cell. A
precision of better than ± 0.03 in $\varepsilon^\prime$ values was obtained.

3.4.3 Surfactant, water and hydrocarbon ternary mixtures
The ternary mixture investigations were restricted to the
surfactants C$_{12}$E$_4$ and Brij 30. The compositions studied
were selected in order to cover the major transparent
regions of the ternary phase diagrams of the two surfactants and, in addition, to check dielectrically proposals
of micellar inversion suggested by Bostock (83) on the
basis of phase diagram and conductivity investigations.

In addition, some ternary mixtures of Brij 30 were studied
at temperatures just outside the upper and lower limits
for transparency in order to detect possible structural
changes which occur in the transition from transparent
solution to a two phase or liquid crystalline structure.

3.4.4 Time domain studies of surfactant mixtures
In order to check for the occurrence or otherwise of
dielectric relaxation effects, the surfactant Brij 30 and some of the binary and ternary mixtures of the surfactants \( \text{C}_{12}\text{E}_{4} \) and Brij 30 were studied using the time domain measuring system. For mixtures having a relatively wide temperature range of transparency, performing these measurements proved straightforward but for mixtures where the temperature range was narrow and significantly different from room temperature, serious measurement difficulties were encountered. In particular, it was deemed impossible to obtain reliable data on such systems. The difficulty was attributed to the high thermal conductivity of the air-line system causing the liquid at the ends of the coaxial line measuring cell to be at some temperature intermediate between the cell and room temperature. This view was strengthened by the observation of the liquid being cloudy when drained from the cell even though the cell was at the required temperature. It was considered that for this problem to be overcome, it would be necessary to completely re-design the temperature control system so that the whole air-line system between the sampler gate and the measuring cell, together with the 50 \( \Omega \) line termination, could be held at the required temperature by an appropriate cooling or heating method. Since such a design modification was not feasible, the data on such mixtures is not open to unequivocal interpretation and the results have not been included.
4.1 Calibration of the WTW Dipolmeter

4.1.1 MFL2 Cell

Table 1
Measurement temperature = 25.0°C

<table>
<thead>
<tr>
<th>Calibration Liquid</th>
<th>Permittivity $\varepsilon^\prime$</th>
<th>Dipolmeter scale reading D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>5.602</td>
<td>364.3</td>
</tr>
<tr>
<td>1,2 dichloroethane</td>
<td>10.387</td>
<td>1224.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.820</td>
<td>3031.0</td>
</tr>
</tbody>
</table>

Writing $\varepsilon^\prime = a + bD + cD^2$

the constants are

a = 3.609
b = 5.442 x $10^{-3}$
c = 7.790 x $10^{-8}$

Using these values for a, b and c, the permittivity value for each of the three calibration liquids is obtained correct to the third decimal place with the above values for D. It is therefore considered appropriate to assign a maximum uncertainty of ±0.01 for the permittivity values for the range over which the cell can be used namely $\varepsilon^\prime = 3.60$ to 21.00.
4.1.2 DFL2 Cell

Table 2

<table>
<thead>
<tr>
<th>Calibration Liquid</th>
<th>Temperature (°C)</th>
<th>Permittivity ε'</th>
<th>Dipolmeter scale reading (Dl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>24.8</td>
<td>1.92</td>
<td>380.0</td>
</tr>
<tr>
<td>Brij 30</td>
<td>56.5</td>
<td>5.61</td>
<td>2739.0</td>
</tr>
</tbody>
</table>

Writing $\varepsilon' = a' + b'(D1)$

the constants obtained are

$a' = 1.326$

$b' = 1.564 \times 10^{-3}$

Use of these values gives a maximum uncertainty of ± 0.03 for $\varepsilon'$ values between 1.90 and 6.00.

4.2 Calibration of the RF bridges

4.2.1 Hatfield 300A

Measurement temperature = 24.9° C

Table 3

<table>
<thead>
<tr>
<th>Calibration Liquid</th>
<th>Capacitance on bridge (pF)</th>
<th>Permittivity ε'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>36.9</td>
<td>1.92</td>
</tr>
<tr>
<td>1 butanol</td>
<td>77.1</td>
<td>17.60</td>
</tr>
<tr>
<td>Acetone</td>
<td>85.2</td>
<td>20.82</td>
</tr>
<tr>
<td>Water</td>
<td>231.7</td>
<td>78.3</td>
</tr>
</tbody>
</table>

Applying the relation:

Capacitance on bridge = capacitance of cell + capacitance of cable
with the known $\varepsilon'$ values gives:

Capacitance cell when empty, $C_0 = 2.55$ pF and

Capacitance of cable = 32.0 pF.

With these values for the bridge constants, relative
permittivity $\varepsilon'$ values could be determined with a
maximum uncertainty in $\varepsilon'$ of $\pm$ 0.2 for $\varepsilon'$ between 1.9 and 79.0.

4.2.2 Wayne Kerr B601

Measurement temperature = 25.0° C

Table 4

<table>
<thead>
<tr>
<th>Calibration Liquid</th>
<th>Capacitance on bridge (pF)</th>
<th>Permittivity $\varepsilon'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>24.0</td>
<td>1.92</td>
</tr>
<tr>
<td>1 butanol</td>
<td>64.2</td>
<td>17.60</td>
</tr>
<tr>
<td>Acetone</td>
<td>71.8</td>
<td>20.82</td>
</tr>
<tr>
<td>Water</td>
<td>218.2</td>
<td>78.3</td>
</tr>
</tbody>
</table>

Using the same procedure as for 4.2.1, the capacitance of
cell when empty, $C_0 = 2.55$ pF. In order to correct for a
dial reading error which increased with increased
capacitance values, as discussed in the experimental
section, a value of cable capacitance, $C_c$, which varied
with the capacitance reading on the bridge, $C_B$, was adopted.
Using the values of $C_c$ as a function of $C_B$ given in Table 5
the calibration graph (Figure 9) was drawn.
Table 5

<table>
<thead>
<tr>
<th>Capacitance on bridge $C_B$/pF</th>
<th>Capacitance of cable $C_C$/pF</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>19.3</td>
</tr>
<tr>
<td>60</td>
<td>19.1</td>
</tr>
<tr>
<td>100</td>
<td>18.9</td>
</tr>
<tr>
<td>140</td>
<td>18.7</td>
</tr>
<tr>
<td>220</td>
<td>18.4</td>
</tr>
</tbody>
</table>

With values of $C_c$ obtained from the calibration graph together with the value of 2.55 pF for $C_o$, the maximum uncertainty in $\varepsilon'$ was ± 0.2 for $\varepsilon'$ values between 1.9 and 79.0.

4.3 Dipolmeter values for the static permittivity of alcohol-water mixtures

The values in Tables 6 to 9 were obtained from results with the MFL2 using the constants given in 4.1.1.

Table 6
t-butanol-water mixtures

<table>
<thead>
<tr>
<th>Mole fraction of water</th>
<th>Temperature $/^\circ$C</th>
<th>Static Permittivity $\varepsilon_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>27.3</td>
<td>11.93</td>
</tr>
<tr>
<td>0.052</td>
<td>27.3</td>
<td>11.53</td>
</tr>
<tr>
<td>0.101</td>
<td>27.3</td>
<td>11.44</td>
</tr>
<tr>
<td>0.153</td>
<td>27.3</td>
<td>11.59</td>
</tr>
<tr>
<td>0.197</td>
<td>27.3</td>
<td>11.90</td>
</tr>
<tr>
<td>0.250</td>
<td>27.3</td>
<td>12.38</td>
</tr>
<tr>
<td>0.299</td>
<td>27.3</td>
<td>12.96</td>
</tr>
<tr>
<td>0.350</td>
<td>27.3</td>
<td>13.76</td>
</tr>
<tr>
<td>0.400</td>
<td>27.3</td>
<td>14.72</td>
</tr>
</tbody>
</table>
These values agree within ± 0.02 with the values obtained by Brown and Ives (7).

Table 7
Cyclohexanol-water mixtures

<table>
<thead>
<tr>
<th>Mole fraction of water</th>
<th>Temperature /°C</th>
<th>Static Permittivity εs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>25.0</td>
<td>16.49</td>
</tr>
<tr>
<td>0.098</td>
<td>25.0</td>
<td>15.60</td>
</tr>
<tr>
<td>0.148</td>
<td>24.0</td>
<td>15.39</td>
</tr>
<tr>
<td>0.198</td>
<td>24.2</td>
<td>15.30</td>
</tr>
<tr>
<td>0.251</td>
<td>24.2</td>
<td>15.34</td>
</tr>
<tr>
<td>0.298</td>
<td>24.1</td>
<td>15.53</td>
</tr>
<tr>
<td>0.353</td>
<td>24.1</td>
<td>15.92</td>
</tr>
<tr>
<td>0.399</td>
<td>24.5</td>
<td>16.35</td>
</tr>
</tbody>
</table>

These values are between 0.05 and 0.09 lower than the values obtained by Stevens (185). Small differences are to be expected due to the different calibration procedure used in this work.

Table 8
1-butanol-water mixtures

<table>
<thead>
<tr>
<th>Mole fraction of water</th>
<th>Temperature /°C</th>
<th>Static Permittivity εs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>24.9</td>
<td>17.31</td>
</tr>
<tr>
<td>0.150</td>
<td>24.8</td>
<td>17.56</td>
</tr>
<tr>
<td>0.248</td>
<td>24.8</td>
<td>17.79</td>
</tr>
<tr>
<td>0.351</td>
<td>24.9</td>
<td>18.04</td>
</tr>
</tbody>
</table>

The value for the pure alcohol compares very satisfactorily with the value of 17.3 obtained by both Suggett et al (171).
and van den Berg et al (37). Published values for 1-butanol-water mixtures are not available.

Table 9
1-heptanol-water mixtures

<table>
<thead>
<tr>
<th>Mole fraction of water</th>
<th>Temperature °C</th>
<th>Static Permittivity ε_S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>24.9</td>
<td>11.48</td>
</tr>
<tr>
<td>0.153</td>
<td>24.9</td>
<td>10.52</td>
</tr>
<tr>
<td>0.252</td>
<td>24.8</td>
<td>10.41</td>
</tr>
</tbody>
</table>

These values are 0.05 lower than the values obtained by Stevens (185). This will be again due to the different calibration procedure used.

4.4 Dielectric relaxation of alcohol-water mixtures

4.4.1 Fourier transform values

Optimisation of the number of data points to minimise errors due to anomalous truncation was performed by inspection of the results for a varying number of data cards, N, and then noting the minimum value \( N_{\text{min}} \) for which the Fourier transform interpolated static permittivity \( \varepsilon_S \) attained the Dipolmeter value to within 3%. This 3% figure was adopted to take account of uncertainties arising in amplitude measurements of the reflection from both the dielectric and short-circuit terminated line.

The relaxation time \( \bar{\tau}_F \) was determined from the mean value of \( \tau_F \) corresponding to all values of N where \( N > N_{\text{min}} \). The standard deviation of the \( \tau_F \) values was adopted as a measure of the uncertainty arising from truncation errors.
This procedure was not applied to the cyclohexanol-water mixture results for x < 0.250 as the slower relaxation in these mixtures precluded complete truncation of the transform within the time window of the time domain scan (≈ 2 ns).

The relaxation frequencies $v_c = \left(\frac{1}{2\pi \tau_F}\right)$ together with the interpolated $\varepsilon_s$ values for $N > N_{\text{min}}$ are given in Tables 10 to 13.

Mean values of $v_c$, $\tau_F$ and $\varepsilon_s$ together with the standard deviation values are also given with the tables.

It should be noted that the largest range of $N$-values was used in the higher water content $t$-butanol mixtures due to the relaxation being particularly rapid and therefore most susceptible to error. In addition, the very similar $\tau_F$ values for two of the $t$-butanol mixtures reinforced the requirement to give more attention to these mixtures. In order to be economical in time usage in the Central Processor Unit of the computer, other mixtures were studied over a more limited range of $N > N_{\text{min}}$ values.

### 4.4.2 Determination of relaxation time $\tau_F$

**Table 10**

$t$-butanol-water mixtures

<table>
<thead>
<tr>
<th>$N$</th>
<th>$v_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 11.93)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>330</td>
<td>11.63</td>
<td></td>
</tr>
<tr>
<td>106</td>
<td>306</td>
<td>11.70</td>
<td></td>
</tr>
<tr>
<td>96</td>
<td>350</td>
<td>11.51</td>
<td></td>
</tr>
</tbody>
</table>
\[ \bar{\varepsilon}_S = 11.60 \pm 0.10 \]
\[ \bar{\nu}_c = (329 \pm 22) \text{ MHz} \]
\[ \bar{\tau}_F = (486 \pm 32) \text{ ps} \]

**t butanol with 0.052 mf of water**

<table>
<thead>
<tr>
<th>N</th>
<th>( \nu_c/\text{MHz} )</th>
<th>( \varepsilon_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>408</td>
<td>11.61</td>
</tr>
<tr>
<td>106</td>
<td>408</td>
<td>11.53</td>
</tr>
<tr>
<td>101</td>
<td>412</td>
<td>11.56</td>
</tr>
<tr>
<td>96</td>
<td>410</td>
<td>11.73</td>
</tr>
<tr>
<td>91</td>
<td>418</td>
<td>11.63</td>
</tr>
<tr>
<td>86</td>
<td>437</td>
<td>11.67</td>
</tr>
<tr>
<td>81</td>
<td>394</td>
<td>11.70</td>
</tr>
</tbody>
</table>

\[ \bar{\varepsilon}_S = 11.63 \pm 0.07 \]
\[ \bar{\nu}_c = (412 \pm 12) \text{ MHz} \]
\[ \bar{\tau}_F = (386 \pm 12) \text{ ps} \]

**t butanol with 0.101 mf of water**

<table>
<thead>
<tr>
<th>N</th>
<th>( \nu_c/\text{MHz} )</th>
<th>( \varepsilon_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>81</td>
<td>500</td>
<td>11.74</td>
</tr>
<tr>
<td>76</td>
<td>616</td>
<td>11.78</td>
</tr>
<tr>
<td>71</td>
<td>530</td>
<td>11.56</td>
</tr>
<tr>
<td>66</td>
<td>548</td>
<td>11.45</td>
</tr>
<tr>
<td>61</td>
<td>548</td>
<td>11.42</td>
</tr>
<tr>
<td>56</td>
<td>575</td>
<td>11.29</td>
</tr>
<tr>
<td>51</td>
<td>565</td>
<td>11.36</td>
</tr>
</tbody>
</table>

(Dipolmeter value = 11.53)

(Dipolmeter value = 11.44)
\[ \bar{\varepsilon}_S = 11.51 \pm 0.19 \]
\[ \bar{\nu}_c = (555 \pm 36) \text{ MHz} \]
\[ \bar{\tau}_F = (288 \pm 19) \text{ ps} \]

t butanol with 0.153 mf water

<table>
<thead>
<tr>
<th>N</th>
<th>( \nu_c/\text{MHz} )</th>
<th>( \varepsilon_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>71</td>
<td>770</td>
<td>11.70</td>
</tr>
<tr>
<td>66</td>
<td>683</td>
<td>11.46</td>
</tr>
<tr>
<td>61</td>
<td>690</td>
<td>11.63</td>
</tr>
<tr>
<td>56</td>
<td>705</td>
<td>11.49</td>
</tr>
<tr>
<td>51</td>
<td>692</td>
<td>11.57</td>
</tr>
<tr>
<td>46</td>
<td>710</td>
<td>11.51</td>
</tr>
</tbody>
</table>

\[ \bar{\varepsilon}_S = 11.56 \pm 0.09 \]
\[ \bar{\nu}_c = (708 \pm 32) \text{ MHz} \]
\[ \bar{\tau}_F = (225 \pm 10) \text{ ps} \]

t butanol with 0.197 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>( \nu_c/\text{MHz} )</th>
<th>( \varepsilon_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>780</td>
<td>11.90</td>
</tr>
<tr>
<td>56</td>
<td>752</td>
<td>11.76</td>
</tr>
<tr>
<td>51</td>
<td>750</td>
<td>11.90</td>
</tr>
<tr>
<td>46</td>
<td>790</td>
<td>11.83</td>
</tr>
<tr>
<td>41</td>
<td>790</td>
<td>11.80</td>
</tr>
<tr>
<td>36</td>
<td>740</td>
<td>12.00</td>
</tr>
</tbody>
</table>

\[ \bar{\varepsilon}_S = 11.92 \pm 0.13 \]
\[ \bar{\nu}_c = (805 \pm 73) \text{ MHz} \]
\[ \bar{\tau}_F = (208 \pm 6) \text{ ps} \]
$t$ butanol with 0.250 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$v_c$/MHz</th>
<th>$\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>81</td>
<td>916</td>
<td>12.40</td>
</tr>
<tr>
<td>76</td>
<td>930</td>
<td>12.43</td>
</tr>
<tr>
<td>71</td>
<td>972</td>
<td>12.50</td>
</tr>
<tr>
<td>66</td>
<td>890</td>
<td>12.30</td>
</tr>
<tr>
<td>61</td>
<td>812</td>
<td>12.18</td>
</tr>
<tr>
<td>56</td>
<td>848</td>
<td>12.25</td>
</tr>
<tr>
<td>51</td>
<td>852</td>
<td>12.26</td>
</tr>
<tr>
<td>46</td>
<td>850</td>
<td>12.26</td>
</tr>
<tr>
<td>41</td>
<td>880</td>
<td>12.16</td>
</tr>
<tr>
<td>36</td>
<td>822</td>
<td>12.36</td>
</tr>
<tr>
<td>31</td>
<td>863</td>
<td>12.22</td>
</tr>
</tbody>
</table>

$\overline{\varepsilon_s} = 12.30 \pm 0.11$

$\overline{v_c} = (876 \pm 48)$ MHz

$\overline{\tau_F} = (182 \pm 10)$ ps

$t$ butanol with 0.299 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$v_c$/MHz</th>
<th>$\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>71</td>
<td>1,145</td>
<td>13.16</td>
</tr>
<tr>
<td>66</td>
<td>1,190</td>
<td>13.02</td>
</tr>
<tr>
<td>61</td>
<td>1,200</td>
<td>12.91</td>
</tr>
<tr>
<td>56</td>
<td>1,105</td>
<td>12.75</td>
</tr>
<tr>
<td>51</td>
<td>1,110</td>
<td>12.76</td>
</tr>
<tr>
<td>46</td>
<td>1,155</td>
<td>12.84</td>
</tr>
<tr>
<td>41</td>
<td>1,140</td>
<td>12.80</td>
</tr>
<tr>
<td>36</td>
<td>1,150</td>
<td>12.95</td>
</tr>
<tr>
<td>31</td>
<td>1,145</td>
<td>12.95</td>
</tr>
</tbody>
</table>

$\overline{\varepsilon_s} = 12.90 \pm 0.13$

$\overline{v_c} = (1,149 \pm 31)$ MHz

$\overline{\tau_F} = (139 \pm 4)$ ps
t butanol with 0.350 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_S$</th>
<th>(Dipolmeter value = 13.76)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>1,140</td>
<td>13.75</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>1,130</td>
<td>13.75</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>1,145</td>
<td>13.80</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>1,248</td>
<td>14.04</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>1,160</td>
<td>14.04</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>1,225</td>
<td>13.80</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>1,335</td>
<td>13.40</td>
<td></td>
</tr>
</tbody>
</table>

$\bar{\varepsilon_S} = 13.80 \pm 0.22$

$\bar{\nu_c} = (1,198 \pm 76)$ MHz

$\bar{\tau_F} = (133 \pm 9)$ ps

---

t butanol with 0.400 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_S$</th>
<th>(Dipolmeter value = 14.72)</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>1,220</td>
<td>14.70</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>1,215</td>
<td>14.72</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>1,175</td>
<td>14.63</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>1,240</td>
<td>14.86</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>1,645</td>
<td>15.24</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>1,450</td>
<td>14.94</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>1,455</td>
<td>14.99</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>1,400</td>
<td>14.95</td>
<td></td>
</tr>
</tbody>
</table>

$\bar{\varepsilon_S} = 14.88 \pm 0.20$

$\bar{\nu_c} = (1,350 \pm 164)$ MHz

$\bar{\tau_F} = (119 \pm 15)$ ps
Table 11
Cyclohexanol-water mixtures

Cyclohexanol

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 16.49)</th>
</tr>
</thead>
<tbody>
<tr>
<td>71</td>
<td>116</td>
<td>9.86</td>
<td></td>
</tr>
</tbody>
</table>

$\tau_F = 1,372 \text{ ps}$

Cyclohexanol with 0.098 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 15.60)</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>145</td>
<td>12.44</td>
<td></td>
</tr>
</tbody>
</table>

$\tau_F = 1,098 \text{ ps}$

Cyclohexanol with 0.148 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 15.39)</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>176</td>
<td>10.99</td>
<td></td>
</tr>
</tbody>
</table>

$\tau_F = 904 \text{ ps}$

Cyclohexanol with 0.198 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 15.30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>225</td>
<td>13.12</td>
<td></td>
</tr>
</tbody>
</table>

$\tau_F = 707 \text{ ps}$

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Cyclohexanol with 0.251 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 15.34)</th>
</tr>
</thead>
<tbody>
<tr>
<td>96</td>
<td>255</td>
<td>14.30</td>
<td></td>
</tr>
<tr>
<td>91</td>
<td>263</td>
<td>14.25</td>
<td></td>
</tr>
<tr>
<td>86</td>
<td>250</td>
<td>14.35</td>
<td></td>
</tr>
<tr>
<td>76</td>
<td>272</td>
<td>14.06</td>
<td></td>
</tr>
</tbody>
</table>

$\overline{\varepsilon_s} = 14.24 \pm 0.13$

$\overline{\nu_c} = (260 \pm 10)$ MHz

$\overline{\tau_F} = (612 \pm 24)$ ps

Cyclohexanol with 0.298 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 15.53)</th>
</tr>
</thead>
<tbody>
<tr>
<td>81</td>
<td>308</td>
<td>15.65</td>
<td></td>
</tr>
<tr>
<td>76</td>
<td>329</td>
<td>15.50</td>
<td></td>
</tr>
</tbody>
</table>

$\overline{\varepsilon_s} = 15.57 \pm 0.11$

$\overline{\nu_c} = (318 \pm 15)$ MHz

$\overline{\tau_F} = (500 \pm 24)$ ps

Cyclohexanol with 0.353 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 15.92)</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td>375</td>
<td>15.89</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>398</td>
<td>15.63</td>
<td></td>
</tr>
</tbody>
</table>

$\overline{\varepsilon_s} = 15.76 \pm 0.18$

$\overline{\nu_c} = (386 \pm 16)$ MHz

$\overline{\tau_F} = (412 \pm 18)$ ps
Cyclohexanol with 0.399 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 16.35)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>416</td>
<td>16.65</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>454</td>
<td>16.37</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>478</td>
<td>16.13</td>
<td></td>
</tr>
</tbody>
</table>

$\overline{\varepsilon_s} = 16.38 \pm 0.26$

$\overline{\nu_c} = (449 \pm 31)$ MHz

$\overline{\tau_F} = (356 \pm 25)$ ps

**Table 12**

1 butanol-water mixtures

1 butanol

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 17.31)</th>
</tr>
</thead>
<tbody>
<tr>
<td>106</td>
<td>285</td>
<td>17.61</td>
<td></td>
</tr>
<tr>
<td>96</td>
<td>292</td>
<td>17.23</td>
<td></td>
</tr>
<tr>
<td>86</td>
<td>273</td>
<td>17.26</td>
<td></td>
</tr>
<tr>
<td>76</td>
<td>320</td>
<td>16.95</td>
<td></td>
</tr>
</tbody>
</table>

$\overline{\varepsilon_s} = 17.26 \pm 0.27$

$\overline{\nu_c} = (295 \pm 24)$ MHz

$\overline{\tau_F} = (543 \pm 40)$ ps

1 butanol with 0.150 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$\nu_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 17.56)</th>
</tr>
</thead>
<tbody>
<tr>
<td>82</td>
<td>438</td>
<td>17.27</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>442</td>
<td>17.42</td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>438</td>
<td>17.58</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>396</td>
<td>18.08</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>448</td>
<td>17.53</td>
<td></td>
</tr>
</tbody>
</table>
\[ \bar{\varepsilon}_S = 17.58 \pm 0.31 \]
\[ \bar{\nu}_c = (432 \pm 21) \text{ MHz} \]
\[ \bar{\tau}_F = (387 \pm 18) \text{ ps} \]

1 butanol with 0.248 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>(\nu_c/\text{MHz} )</th>
<th>(\varepsilon_S )</th>
<th>(Dipolmeter value = 17.79)</th>
</tr>
</thead>
<tbody>
<tr>
<td>82</td>
<td>648</td>
<td>17.53</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>602</td>
<td>17.34</td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>575</td>
<td>16.90</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>552</td>
<td>17.82</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>552</td>
<td>17.73</td>
<td></td>
</tr>
</tbody>
</table>

\[ \bar{\varepsilon}_S = 17.46 \pm 0.36 \]
\[ \bar{\nu}_c = (586 \pm 40) \text{ MHz} \]
\[ \bar{\tau}_F = (272 \pm 19) \text{ ps} \]

1 butanol with 0.351 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>(\nu_c/\text{MHz} )</th>
<th>(\varepsilon_S )</th>
<th>(Dipolmeter value = 18.04)</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>690</td>
<td>18.03</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>692</td>
<td>18.01</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>688</td>
<td>18.09</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>690</td>
<td>18.11</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>720</td>
<td>18.01</td>
<td></td>
</tr>
</tbody>
</table>

\[ \bar{\varepsilon}_S = 18.05 \pm 0.05 \]
\[ \bar{\nu}_c = (696 \pm 13) \text{ MHz} \]
\[ \bar{\tau}_F = (230 \pm 6) \text{ ps} \]
Table 13
1 heptanol-water mixtures

1 heptanol

<table>
<thead>
<tr>
<th>N</th>
<th>$v_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 11.48)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>167</td>
<td>10.50</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>159</td>
<td>10.68</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>173</td>
<td>10.36</td>
<td></td>
</tr>
</tbody>
</table>

$\varepsilon_s = 10.51 \pm 0.16$

$\bar{v_c} = (166 \pm 7)$ MHz

$\bar{\tau_F} = (960 \pm 40)$ ps

1 heptanol with 0.153 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$v_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 10.52)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>204</td>
<td>10.63</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>188</td>
<td>10.82</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>220</td>
<td>10.40</td>
<td></td>
</tr>
</tbody>
</table>

$\varepsilon_s = 10.62 \pm 0.21$

$\bar{v_c} = (204 \pm 16)$ MHz

$\bar{\tau_F} = (785 \pm 62)$ ps

1 heptanol with 0.252 mf of water

<table>
<thead>
<tr>
<th>N</th>
<th>$v_c$/MHz</th>
<th>$\varepsilon_s$</th>
<th>(Dipolmeter value = 10.41)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>258</td>
<td>10.25</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>244</td>
<td>10.39</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>256</td>
<td>10.33</td>
<td></td>
</tr>
</tbody>
</table>

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4.4.3 Dielectric relaxation parameters

The dielectric dispersion curves of $\varepsilon''$ against $\varepsilon'$ for each mixture have been drawn for the value of $N$ which gave a $\tau_F$ value closest to $\overline{\tau_F}$ (Figures 10 to 22).

For all alcohol-water mixtures studied, a semi-circle can be drawn through the data points corresponding to the principal dispersion and it is therefore concluded that this dispersion is Debye-type. Deviation from the semi-circle is evident at the higher frequencies. This will be due primarily to impedance mismatch effects causing anomalous truncation (184). In addition, there are possibly contributions from higher frequency relaxation processes. The less satisfactory semi-circles for the cyclohexanol-water mixtures at low water content will be due to impedance mismatch effects in these long relaxation time dispersions.

The Fourier transform values for the dielectric relaxation parameters of the alcohol-water mixtures are given in Tables 14 to 17.
Table 14

<table>
<thead>
<tr>
<th>Mole Fraction of Water</th>
<th>Temperature °C</th>
<th>Relaxation Time τ_F/ps</th>
<th>Static Permittivity ε_s</th>
<th>High frequency limiting value of permittivity ε_∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>27.3</td>
<td>486</td>
<td>11.4</td>
<td>3.9</td>
</tr>
<tr>
<td>0.052</td>
<td>27.3</td>
<td>386</td>
<td>11.4</td>
<td>3.4</td>
</tr>
<tr>
<td>0.101</td>
<td>27.3</td>
<td>288</td>
<td>11.4</td>
<td>3.9</td>
</tr>
<tr>
<td>0.153</td>
<td>27.3</td>
<td>215</td>
<td>11.3</td>
<td>4.2</td>
</tr>
<tr>
<td>0.197</td>
<td>27.3</td>
<td>208</td>
<td>11.8</td>
<td>4.2</td>
</tr>
<tr>
<td>0.250</td>
<td>27.3</td>
<td>182</td>
<td>12.2</td>
<td>4.7</td>
</tr>
<tr>
<td>0.299</td>
<td>27.3</td>
<td>137</td>
<td>13.0</td>
<td>4.9</td>
</tr>
<tr>
<td>0.350</td>
<td>27.3</td>
<td>135</td>
<td>13.8</td>
<td>4.1</td>
</tr>
<tr>
<td>0.400</td>
<td>27.3</td>
<td>136</td>
<td>14.0</td>
<td>4.6</td>
</tr>
</tbody>
</table>

The value of $\bar{\tau}_F = 486$ ps for the pure alcohol is in fair agreement with the value of approximately 520 ps obtained by Sato et al (188) at 25°C. The 520 ps figure is approximate as it was obtained from graphical data. It should be noted that the frequency domain value of Sato et al was obtained from a Cole-Cole plot which contained only five data points, all of which were at frequencies above the relaxation frequency $\nu_C$.

The value of $\varepsilon_\infty$ for the pure alcohol is rather higher than the value of approximately 3.2 obtained by Sato et al.

Literature values for $\tau$ and $\varepsilon_\infty$ of t-butanol-water mixtures is not available.
<table>
<thead>
<tr>
<th>Mole Fraction of water</th>
<th>Temperature /°C</th>
<th>Relaxation Time τ_p/ps</th>
<th>ε_∞</th>
<th>ε_S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>25.0</td>
<td>1,372</td>
<td>10.1</td>
<td>3.6</td>
</tr>
<tr>
<td>0.098</td>
<td>25.0</td>
<td>1,098</td>
<td>12.6</td>
<td>4.9</td>
</tr>
<tr>
<td>0.148</td>
<td>24.0</td>
<td>904</td>
<td>12.3</td>
<td>4.7</td>
</tr>
<tr>
<td>0.198</td>
<td>24.2</td>
<td>707</td>
<td>13.2</td>
<td>5.5</td>
</tr>
<tr>
<td>0.251</td>
<td>24.2</td>
<td>622</td>
<td>14.4</td>
<td>4.9</td>
</tr>
<tr>
<td>0.298</td>
<td>24.1</td>
<td>500</td>
<td>15.6</td>
<td>4.9</td>
</tr>
<tr>
<td>0.353</td>
<td>24.1</td>
<td>412</td>
<td>15.9</td>
<td>4.2</td>
</tr>
<tr>
<td>0.399</td>
<td>24.5</td>
<td>356</td>
<td>16.3</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The value of \( \tau_p = 1,372 \text{ ps} \) for the pure alcohol is substantially lower than the values of 2,290 ps obtained by Garg and Smyth (20) and 2,430 ps obtained by Arnoult et al (189). Both values were obtained at 25° C. This discrepancy is to be expected, since for slower relaxations, truncation of the Fourier transform will occur before the relaxation has been completed, giving too low a value for \( \tau_p \). This effect will also give \( \varepsilon_S \) values which are too low, which was the case for the pure alcohol and for mixtures with mole fractions of water of 0.25 and below. The value of \( \varepsilon_\infty = 3.6 \) for the pure alcohol is somewhat higher than the value of 2.9 obtained by Garg and Smyth (20) and 3.4 obtained by Arnoult et al (189).

Literature data for \( \tau \) and \( \varepsilon_\infty \) for cyclohexanol-water mixtures are not available.
Table 16
1 butanol-water mixtures

<table>
<thead>
<tr>
<th>Mole Fraction of water</th>
<th>Temperature /°C</th>
<th>Relaxation Time (\bar{\tau}_F/\text{ps})</th>
<th>(\varepsilon_s)</th>
<th>(\varepsilon_\infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>25.1</td>
<td>543</td>
<td>17.3</td>
<td>3.3</td>
</tr>
<tr>
<td>0.150</td>
<td>25.0</td>
<td>387</td>
<td>17.3</td>
<td>2.8</td>
</tr>
<tr>
<td>0.245</td>
<td>25.1</td>
<td>272</td>
<td>17.8</td>
<td>4.1</td>
</tr>
<tr>
<td>0.351</td>
<td>24.9</td>
<td>230</td>
<td>18.1</td>
<td>5.5</td>
</tr>
</tbody>
</table>

The value of \(\bar{\tau}_F = 543\) ps for the pure alcohol is in satisfactory agreement with values of 561 ps obtained by Campbell et al (34) at 20° C, 575 ps obtained by Garg and Smyth (20) at 25° C and 488 ps obtained by Sagal (35) at 25° C. The value of \(\varepsilon_\infty = 3.3\) is in good agreement with the values of approximately 3.6 obtained by Campbell et al (34) and 3.3 obtained by Sagal (35).

The fall in \(\bar{\tau}_F\) for 1 butanol-water mixtures on addition of water is in disagreement with the results of Sarojini (67) who reported a monotonous increase in \(\tau\) as water was added to 1 butanol.

Table 17
1 heptanol-water mixtures

<table>
<thead>
<tr>
<th>Mole Fraction of water</th>
<th>Temperature /°C</th>
<th>Relaxation Time (\bar{\tau}_F/\text{ps})</th>
<th>(\varepsilon_s)</th>
<th>(\varepsilon_\infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>25.0</td>
<td>960</td>
<td>10.8</td>
<td>1.9</td>
</tr>
<tr>
<td>0.153</td>
<td>24.8</td>
<td>785</td>
<td>10.5</td>
<td>3.7</td>
</tr>
<tr>
<td>0.252</td>
<td>24.8</td>
<td>630</td>
<td>10.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>
The value of $\tau_F = 960$ ps for the pure alcohol is substantially lower than the value of 1,660 ps obtained by Lebrun (190) at 20° C. The value of $\varepsilon_\infty = 1.9$ is also substantially lower than the value of 3.2 obtained by Lebrun. The discrepancy in the $\tau$ values is to be expected since the slower relaxation of the pure alcohol will lead to truncation errors as observed in the pure alcohol cyclohexanol. The low $\varepsilon_s$ value confirms this view. The value of $\varepsilon_\infty = 1.9$ is clearly too low since $n^2$ (where $n$ is the refractive index) would be expected to be slightly higher than this.

The observed reduction of $\tau_F$ on addition of water to 1 heptanol is in agreement with the results of Tjia (59) on 1 heptanol-water mixtures up to 0.115 mf of water over the lower temperature range of -35 to -10° C. The value of $\varepsilon_\infty = 3.7$ for the 0.153 mf mixture is rather higher than the almost temperature independent value of 2.9 obtained by Tjia for the 0.115 mf water content mixture over the -35 to -10° C temperature range.

For all four alcohols studied, the results reveal that addition of water causes a progressive reduction in the relaxation time $\tau_F$ with the very close $\tau$ values for the 0.299 and 0.300 mf of water t butanol mixtures being a possible exception to this trend.

The results for $\varepsilon_\infty$ show considerable scatter with no trend being revealed. However, the results for the t butanol
mixture with 0.400 mf of water with the time zero reference both retarded and advanced by 3.9 ps (Figure 14b) reveal that the value of $\varepsilon_\infty$ is critically dependent on precision in the time zero reference. For this reason, the variation in $\varepsilon_\infty$ exhibited by the alcohol-water mixtures is attributed to experimental error.

It should be noted that the value of $\bar{\tau}_F$ is, in contrast, relatively insensitive to small errors in the time zero reference since the results for the 0.400 mf mixture both (i) retarded and (ii) advanced by 3.9 ps together with (iii) the actual time zero adopted give $\tau_F$ values of (i) 111 ps, (ii) 104 ps and (iii) 105 ps respectively, giving a mean value of 107 ps with a standard deviation of 4 ps.

4.5 Direct time domain methods

4.5.1 Fellner-Feldegg method, $\tau_D$

The WTW Dipolmeter data for $\varepsilon_S$ has been used. The graphs of $\ln (\varepsilon_S - \varepsilon)$ against time are given in Figures 23 to 25. The relaxation times $\tau_D$ are given by the reciprocal of the slopes of graphs.

The $\tau_D$ values are given in Tables 18 to 21.
Table 18

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Mole Fraction of Water</th>
<th>Temperature $/°C$</th>
<th>Relaxation Time $\tau_D$/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>t butanol</td>
<td>0.000</td>
<td>27.3</td>
<td>355</td>
</tr>
<tr>
<td></td>
<td>0.052</td>
<td>27.3</td>
<td>241</td>
</tr>
<tr>
<td></td>
<td>0.101</td>
<td>27.3</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>0.153</td>
<td>27.3</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>0.197</td>
<td>27.3</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>0.250</td>
<td>27.3</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>0.299</td>
<td>27.3</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>0.350</td>
<td>27.3</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>0.400</td>
<td>27.3</td>
<td>73</td>
</tr>
</tbody>
</table>

Table 19

<table>
<thead>
<tr>
<th>Cyclohexanol</th>
<th>Mole Fraction of Water</th>
<th>Temperature $/°C$</th>
<th>Relaxation Time $\tau_D$/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>25.0</td>
<td>4321</td>
<td></td>
</tr>
<tr>
<td>0.098</td>
<td>25.0</td>
<td>2664</td>
<td></td>
</tr>
<tr>
<td>0.148</td>
<td>24.0</td>
<td>1751</td>
<td></td>
</tr>
<tr>
<td>0.198</td>
<td>24.2</td>
<td>748</td>
<td></td>
</tr>
<tr>
<td>0.251</td>
<td>24.2</td>
<td>512</td>
<td></td>
</tr>
<tr>
<td>0.298</td>
<td>24.1</td>
<td>291</td>
<td></td>
</tr>
<tr>
<td>0.353</td>
<td>24.1</td>
<td>253</td>
<td></td>
</tr>
<tr>
<td>0.399</td>
<td>24.5</td>
<td>219</td>
<td></td>
</tr>
</tbody>
</table>
Table 20

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Mole Fraction of Water</th>
<th>Temperature °C</th>
<th>Relaxation Time τD/τp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 butanol</td>
<td>0.000</td>
<td>25.1</td>
<td>355</td>
</tr>
<tr>
<td></td>
<td>0.150</td>
<td>25.0</td>
<td>191</td>
</tr>
<tr>
<td></td>
<td>0.245</td>
<td>25.1</td>
<td>163</td>
</tr>
<tr>
<td></td>
<td>0.351</td>
<td>24.9</td>
<td>146</td>
</tr>
</tbody>
</table>

Table 21

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Mole Fraction of Water</th>
<th>Temperature °C</th>
<th>Relaxation Time τD/τp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 heptanol</td>
<td>0.000</td>
<td>25.0</td>
<td>1017</td>
</tr>
<tr>
<td></td>
<td>0.153</td>
<td>24.8</td>
<td>538</td>
</tr>
<tr>
<td></td>
<td>0.252</td>
<td>24.8</td>
<td>450</td>
</tr>
</tbody>
</table>

4.5.2 **Fellner Feldegg and Barnett method, τ_{FF+BB}**

As discussed in the experimental chapter, the curves appropriate to \( \frac{\rho_S - \rho(t)}{\rho_S - \rho_\infty} = 0.2 (\rho_{0.2}) \) were used wherever possible. In order to use these curves, it is necessary for the reflection coefficient to be within 20% of its low frequency value at the end of the time domain scan. This condition was fulfilled in all cases except for the cyclohexanol-water mixtures below 0.250 mole fraction of water and for the pure alcohol 1 heptanol. Use of the curves was straightforward except for two related major difficulties, namely selection of the appropriate values...
of $\rho_\infty$ and $\varepsilon_\infty$. Since the values of these two quantities are critically dependent on the accuracy of time zero referencing and, as revealed in the study of the 0.400 mf t butanol-water mixture with a 3.9 ps sampling interval, these values are subject to a high degree of uncertainty.

The problem has two aspects because in addition to affecting the value of $\rho(t)$, the value of $\rho_\infty$ (and hence $\varepsilon_\infty$) selected also determines which set of curves in the FF+B paper are to be used. The values of $\rho_\infty$ and $\varepsilon_\infty$ selected were obtained using the procedure described in the experimental chapter. The $\rho_S$ values were obtained from the Dipolmeter values of $\varepsilon_S$.

The values of $\rho_S$, $\rho_\infty$, $\rho(t)$, the scaling factor obtained from the FF+B paper and $\tau_{FF+B}$ are given in Tables 22 to 25.

Table 22

<table>
<thead>
<tr>
<th>Mole Fraction of water</th>
<th>Temperature °C</th>
<th>$\rho_S$</th>
<th>$\rho_\infty$</th>
<th>$\varepsilon_\infty$</th>
<th>$\rho_{0.2}$</th>
<th>$t_{0.2}$/ps</th>
<th>Scaling factor</th>
<th>$\tau_{FF+B}$/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>27.3</td>
<td>0.552</td>
<td>0.33</td>
<td>4.0</td>
<td>0.508</td>
<td>419</td>
<td>1.2</td>
<td>503</td>
</tr>
<tr>
<td>0.052</td>
<td>27.3</td>
<td>0.545</td>
<td>0.31</td>
<td>3.6</td>
<td>0.498</td>
<td>300</td>
<td>1.3</td>
<td>390</td>
</tr>
<tr>
<td>0.101</td>
<td>27.3</td>
<td>0.544</td>
<td>0.32</td>
<td>3.8</td>
<td>0.499</td>
<td>264</td>
<td>1.2</td>
<td>317</td>
</tr>
<tr>
<td>0.153</td>
<td>27.3</td>
<td>0.546</td>
<td>0.37</td>
<td>4.7</td>
<td>0.511</td>
<td>284</td>
<td>1.1</td>
<td>312</td>
</tr>
<tr>
<td>0.197</td>
<td>27.3</td>
<td>0.550</td>
<td>0.37</td>
<td>4.7</td>
<td>0.514</td>
<td>229</td>
<td>1.1</td>
<td>252</td>
</tr>
<tr>
<td>0.250</td>
<td>27.3</td>
<td>0.557</td>
<td>0.38</td>
<td>5.0</td>
<td>0.522</td>
<td>216</td>
<td>1.1</td>
<td>238</td>
</tr>
<tr>
<td>0.299</td>
<td>27.3</td>
<td>0.565</td>
<td>0.42</td>
<td>6.0</td>
<td>0.537</td>
<td>158</td>
<td>1.0</td>
<td>158</td>
</tr>
<tr>
<td>0.350</td>
<td>27.3</td>
<td>0.575</td>
<td>0.39</td>
<td>5.2</td>
<td>0.538</td>
<td>142</td>
<td>1.1</td>
<td>156</td>
</tr>
<tr>
<td>0.400</td>
<td>27.3</td>
<td>0.587</td>
<td>0.46</td>
<td>7.3</td>
<td>0.562</td>
<td>139</td>
<td>1.0</td>
<td>139</td>
</tr>
</tbody>
</table>
### Table 23
Cyclohexanol-water mixtures

<table>
<thead>
<tr>
<th>Mole Fraction of water</th>
<th>Temperature /°C</th>
<th>ρ_s</th>
<th>ρ_∞</th>
<th>ε_∞</th>
<th>t_{1/e} /ps</th>
<th>Scaling Factor</th>
<th>t_{FF+B} /ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>25.0</td>
<td>0.605</td>
<td>0.36</td>
<td>4.5</td>
<td>0.515</td>
<td>2360</td>
<td>2.7</td>
</tr>
<tr>
<td>0.098</td>
<td>25.0</td>
<td>0.596</td>
<td>0.40</td>
<td>5.4</td>
<td>0.524</td>
<td>1143</td>
<td>2.0</td>
</tr>
<tr>
<td>0.148</td>
<td>24.0</td>
<td>0.594</td>
<td>0.33</td>
<td>3.9</td>
<td>0.495</td>
<td>749</td>
<td>2.2</td>
</tr>
<tr>
<td>0.198</td>
<td>24.2</td>
<td>0.593</td>
<td>0.40</td>
<td>5.4</td>
<td>0.522</td>
<td>553</td>
<td>2.0</td>
</tr>
<tr>
<td>0.251</td>
<td>24.2</td>
<td>0.593</td>
<td>0.37</td>
<td>4.7</td>
<td>0.548</td>
<td>640</td>
<td>1.2</td>
</tr>
<tr>
<td>0.298</td>
<td>24.1</td>
<td>0.595</td>
<td>0.33</td>
<td>3.9</td>
<td>0.542</td>
<td>348</td>
<td>1.3</td>
</tr>
<tr>
<td>0.353</td>
<td>24.1</td>
<td>0.599</td>
<td>0.29</td>
<td>3.3</td>
<td>0.537</td>
<td>269</td>
<td>1.6</td>
</tr>
<tr>
<td>0.399</td>
<td>24.5</td>
<td>0.603</td>
<td>0.33</td>
<td>4.0</td>
<td>0.548</td>
<td>235</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### Table 24
1 butanol-water mixtures

<table>
<thead>
<tr>
<th>Mole Fraction of water</th>
<th>Temperature /°C</th>
<th>ρ_s</th>
<th>ρ_∞</th>
<th>ε_∞</th>
<th>t_{0.2} /ps</th>
<th>Scaling Factor</th>
<th>t_{FF+B} /ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>24.9</td>
<td>0.612</td>
<td>0.29</td>
<td>3.3</td>
<td>0.548</td>
<td>375</td>
<td>1.7</td>
</tr>
<tr>
<td>0.150</td>
<td>24.8</td>
<td>0.615</td>
<td>0.30</td>
<td>3.4</td>
<td>0.553</td>
<td>242</td>
<td>1.6</td>
</tr>
<tr>
<td>0.248</td>
<td>24.8</td>
<td>0.617</td>
<td>0.32</td>
<td>3.7</td>
<td>0.557</td>
<td>192</td>
<td>1.6</td>
</tr>
<tr>
<td>0.351</td>
<td>24.9</td>
<td>0.619</td>
<td>0.33</td>
<td>3.9</td>
<td>0.561</td>
<td>170</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### Table 25
1 heptanol-water mixtures

<table>
<thead>
<tr>
<th>Mole Fraction of water</th>
<th>Temperature /°C</th>
<th>ρ_s</th>
<th>ρ_∞</th>
<th>ε_∞</th>
<th>t_{0.2} /ps</th>
<th>Scaling Factor</th>
<th>t_{FF+B} /ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>24.9</td>
<td>0.545</td>
<td>0.27</td>
<td>3.0</td>
<td>0.491</td>
<td>977</td>
<td>1.35</td>
</tr>
<tr>
<td>0.153</td>
<td>24.9</td>
<td>0.530</td>
<td>0.27</td>
<td>3.0</td>
<td>0.478</td>
<td>579</td>
<td>1.25</td>
</tr>
<tr>
<td>0.252</td>
<td>24.8</td>
<td>0.527</td>
<td>0.33</td>
<td>3.9</td>
<td>0.488</td>
<td>558</td>
<td>1.1</td>
</tr>
</tbody>
</table>
4.5.3 Brehm and Stockmayer method (B+S)$_{B+S}$

Application of this method posed some difficulty since, in addition to the requirement of knowledge of the values of $\rho_{\infty}$ and $\epsilon_{\infty}$, the faster relaxation in the higher water-content mixtures resulted in the $t_3$ condition being attained very rapidly. This made the value of $t_3$ subject to rather high uncertainty, and possibly due to this effect, the ratio $t_{13}/t_{23}$ gave Cole-Davidson $\beta$-values greater than unity in many mixtures. Because of this difficulty with the $\beta$-values, it was decided to assume Debye-type dispersion as in the FF+B paper giving $\beta=1$.

Relaxation time values were then determined by two different methods. In the first ($\tau_{B+S_1}$), the values of $\epsilon_{S}$ and $\epsilon_{\infty}$ of the FF+B method were used to determine the most appropriate curve for $(\epsilon_{S}/\epsilon_{\infty})$ in the B+S paper from which the required scaling factor for $t_{13}$ was obtained.

In the second method ($\tau_{B+S_2}$), the value of $t_{13}$ was obtained from the more precisely measureable $t_{23}$ value by assuming that $t_{13} = 0.31 t_{23}$ which corresponds to $\beta = 1$ and $\epsilon_{S}/\epsilon_{\infty} = 4$ in the B+S paper. The ratio $\epsilon_{S}/\epsilon_{\infty} = 4$ was considered to be the optimum choice based on literature data for the four pure alcohols and 1 heptanol-water mixtures (185, 19, 20, 59).

The values of $t_{13}$, $t_{23}$, $\beta$, the scaling factor, $\tau_{B+S_1}$, and $\tau_{B+S_2}$ are given in Tables 26 to 29.
Table 26

**t butanol-water mixtures**

<table>
<thead>
<tr>
<th>Mole Fraction of water, x</th>
<th>$\frac{\varepsilon_s}{\varepsilon_\infty}$</th>
<th>$t_1$ /ps$^3$</th>
<th>$t_2$ /ps$^3$</th>
<th>$\beta$</th>
<th>Scaling Factor /ps</th>
<th>$^{10}B+S_1$ /ps</th>
<th>$^{10}B+S_2$ /ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>3.0</td>
<td>134</td>
<td>300</td>
<td>1.5</td>
<td>5.7</td>
<td>764</td>
<td>514</td>
</tr>
<tr>
<td>0.052</td>
<td>3.2</td>
<td>86.9</td>
<td>237</td>
<td>1.2</td>
<td>6.25</td>
<td>543</td>
<td>444</td>
</tr>
<tr>
<td>0.101</td>
<td>3.0</td>
<td>79</td>
<td>180</td>
<td>0.8</td>
<td>5.7</td>
<td>450</td>
<td>309</td>
</tr>
<tr>
<td>0.153</td>
<td>2.5</td>
<td>94.8</td>
<td>193</td>
<td>1.6</td>
<td>4.0</td>
<td>379</td>
<td>232</td>
</tr>
<tr>
<td>0.197</td>
<td>2.5</td>
<td>79</td>
<td>153</td>
<td>2.0</td>
<td>4.0</td>
<td>316</td>
<td>184</td>
</tr>
<tr>
<td>0.250</td>
<td>2.6</td>
<td>71.1</td>
<td>145</td>
<td>1.6</td>
<td>4.3</td>
<td>306</td>
<td>189</td>
</tr>
<tr>
<td>0.299</td>
<td>2.2</td>
<td>75.8</td>
<td>123</td>
<td>2</td>
<td>3.4</td>
<td>258</td>
<td>127</td>
</tr>
<tr>
<td>0.350</td>
<td>2.6</td>
<td>63.2</td>
<td>99.5</td>
<td>2</td>
<td>4.5</td>
<td>284</td>
<td>136</td>
</tr>
<tr>
<td>0.400</td>
<td>2.0</td>
<td>66.3</td>
<td>102</td>
<td>2</td>
<td>3.1</td>
<td>206</td>
<td>96</td>
</tr>
</tbody>
</table>

**Cyclohexanol-water mixtures**

<table>
<thead>
<tr>
<th></th>
<th>$\frac{\varepsilon_s}{\varepsilon_\infty}$</th>
<th>$t_1$ /ps$^3$</th>
<th>$t_2$ /ps$^3$</th>
<th>$\beta$</th>
<th>Scaling Factor /ps</th>
<th>$^{10}B+S_1$ /ps</th>
<th>$^{10}B+S_2$ /ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>3.7</td>
<td>827</td>
<td>*</td>
<td>-</td>
<td>7.1</td>
<td>5871</td>
<td>-</td>
</tr>
<tr>
<td>0.098</td>
<td>2.9</td>
<td>394</td>
<td>1280</td>
<td>0.95</td>
<td>5.3</td>
<td>2088</td>
<td>2021</td>
</tr>
<tr>
<td>0.148</td>
<td>2.9</td>
<td>433</td>
<td>1615</td>
<td>0.8</td>
<td>5.3</td>
<td>2294</td>
<td>1796</td>
</tr>
<tr>
<td>0.198</td>
<td>2.8</td>
<td>205</td>
<td>616</td>
<td>0.94</td>
<td>4.8</td>
<td>984</td>
<td>881</td>
</tr>
<tr>
<td>0.251</td>
<td>3.3</td>
<td>134</td>
<td>382</td>
<td>1.1</td>
<td>6.25</td>
<td>837</td>
<td>719</td>
</tr>
<tr>
<td>0.298</td>
<td>4.0</td>
<td>83.7</td>
<td>218</td>
<td>1.3</td>
<td>7.9</td>
<td>661</td>
<td>515</td>
</tr>
<tr>
<td>0.353</td>
<td>4.8</td>
<td>69.5</td>
<td>166</td>
<td>1.6</td>
<td>10.0</td>
<td>695</td>
<td>498</td>
</tr>
<tr>
<td>0.399</td>
<td>4.1</td>
<td>45.8</td>
<td>111</td>
<td>1.4</td>
<td>8.3</td>
<td>380</td>
<td>277</td>
</tr>
</tbody>
</table>

**1 butanol-water mixtures**

<table>
<thead>
<tr>
<th></th>
<th>$\frac{\varepsilon_s}{\varepsilon_\infty}$</th>
<th>$t_1$ /ps$^3$</th>
<th>$t_2$ /ps$^3$</th>
<th>$\beta$</th>
<th>Scaling Factor /ps</th>
<th>$^{10}B+S_1$ /ps</th>
<th>$^{10}B+S_2$ /ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>5.2</td>
<td>91</td>
<td>235</td>
<td>1.2</td>
<td>10.0</td>
<td>910</td>
<td>705</td>
</tr>
<tr>
<td>0.150</td>
<td>5.1</td>
<td>69.8</td>
<td>161</td>
<td>1.3</td>
<td>10.0</td>
<td>698</td>
<td>483</td>
</tr>
<tr>
<td>0.245</td>
<td>4.8</td>
<td>60.9</td>
<td>123</td>
<td>1.8</td>
<td>9.1</td>
<td>554</td>
<td>337</td>
</tr>
<tr>
<td>0.351</td>
<td>4.5</td>
<td>28.6</td>
<td>93.1</td>
<td>1.1</td>
<td>7.7</td>
<td>220</td>
<td>215</td>
</tr>
</tbody>
</table>
1 heptanol-water mixtures

<table>
<thead>
<tr>
<th>Mole Fraction of water, x</th>
<th>$\epsilon S/\epsilon_\infty$ /ps</th>
<th>$t_1$ /ps</th>
<th>$t_2$ /ps</th>
<th>$\tau_{B+S_1}$ /ps</th>
<th>$\tau_{B+S_2}$ /ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>3.7</td>
<td>279</td>
<td>639</td>
<td>7.1</td>
<td>1980</td>
</tr>
<tr>
<td>0.153</td>
<td>3.5</td>
<td>139.6</td>
<td>384</td>
<td>6.7</td>
<td>935</td>
</tr>
<tr>
<td>0.252</td>
<td>2.6</td>
<td>174.5</td>
<td>387</td>
<td>4.3</td>
<td>750</td>
</tr>
</tbody>
</table>

NB All values for $\beta > 1.0$ are approximate since extrapolation of the $B+S$ curves had to be applied.

4.6 Estimation of experimental error in relaxation time values

4.6.1 Fourier transform method

The experimental technique has errors arising from the following:

(a) non-linearity in the X-Y plotter,
(b) amplitude uncertainty for both the dielectric and short circuit terminated coaxial line,
(c) truncation errors due to impedance mismatches,
(d) time zero reference uncertainty,
(e) sampling interval uncertainty due to uncertainty in the calibration of (i) the 180 CRO "mainframe" and (ii) the time-base for the X-Y plots,

and

(f) errors due to too early truncation of the Fourier transform when the relaxation time is long.

The operating manuals quote a figure of $\pm 0.1\%$ for X-Y plotter non-linearity, $\pm 0.2\%$ for full-scale Y deflection
and ± 3% for the CRO "mainframe" calibration.

The ± 0.1% quoted for (a) is considered negligible. Since the effect of amplitude uncertainties in (b) have been included in the procedure adopted to account for truncation effects, the value $\tau_F$ is considered to include the contributions from both (b) and (c). The effect of time zero reference uncertainty is indicated in the results for the t butanol water mixture at 0.400 mf of water for which a ± 4% spread in $\tau$ was revealed for the time zero reference shift of ± 3.9 ps. Since an uncertainty of ± 2 ps is considered appropriate, a figure of ± 2% has been adopted for the effect of (d).

For the t butanol-, 1 butanol- and 1 heptanol-water mixtures both the CRO mainframe setting (0.2 ns/cm for t and 1 butanol-water mixtures, 0.5 ns/cm for 1 heptanol-water mixtures) and the X sensitivity of the recorder were maintained constant for each set of alcohol-water mixtures. Thus for each of these sets of mixtures, errors in the sampling interval will not affect the relative values of $\tau_F$. In addition, since the experimental values for the pure alcohols t butanol and 1 butanol agree with literature data within uncertainty limits set by addition of the truncation and time zero reference error contributions, it will be presumed that the sampling interval error (e) is negligible.
For the cyclohexanol-water mixtures, the CRO "mainframe" setting was 0.5 ns/cm at up to and including 0.148 mf of water and 0.2 ns/cm for the higher water content mixtures. This change of setting will introduce additional error but study of the relative precision of these two main-frame settings has shown that they agree within 1%. This 1% figure has been added to the contributions from (b) and (c) for the cyclohexanol-water mixtures.

The longest relaxation time, $\tau_{max}$, above which errors arise due to too early truncation of the transform ($f$) can be estimated by determining the maximum value of $\tau$ for which the transform interpolated static permittivity $\varepsilon_s$, truncates to the Dipolmeter value. Inspection of the $\bar{\tau}_F$ and $\varepsilon_s$ values for the cyclohexanol-water mixtures reveals that the transform truncates to the published value of $\varepsilon_s$ when the mole fraction of water is 0.298 for which $\bar{\tau}_F$ is 500 ps, whereas the 0.251 mixture which has a $\bar{\tau}_F$ value of 622 ps exhibits truncation limitations. Satisfactory truncation was also obtained for the pure alcohol 1 butanol with a $\bar{\tau}_F$ value of 551 ps. It is therefore suggested that with the experimental procedure adopted in this work, the Fourier transform values should be free of too-early-truncation limitations for relaxation times $\tau \leq 600$ ps.

In order to correct the transform values for relaxation times longer than 600 ps, a scaling procedure has been
adopted since the Fourier transform values will give an increasing difference between measured and 'correct' values as the $\tau$ value increases above the 600 ps figure. A simple method has been adopted in which a graph of corrected $\tau$ value against measured $\tau$ value has been plotted (Figure 26) based on the assumption that for $\tau_F \leq 600$ ps the scaling factor is unity. Two other points have been used to set the position of this calibration line. The first is based on a mean of the two literature values for cyclohexanol at 25° C (20,189) which was taken as 2,360 ps. The second is based on literature data for 1 heptanol at 20° C (190) where adjustment to the $\tau$ value at 25° C has been obtained using an activation enthalpy value of 33.2 kJ mol$^{-1}$ (35). Applying this figure gives a value 1,320 ps for 1 heptanol at 25° C.

The above figures thus give values as in Table 30.

Table 30

<table>
<thead>
<tr>
<th>Measured Relaxation Time/ps</th>
<th>Corrected Relaxation Time/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>960</td>
<td>1320</td>
</tr>
<tr>
<td>1372</td>
<td>2360</td>
</tr>
</tbody>
</table>

Applying linear regression analysis to the above relation between measured and corrected values for $\tau_F > 600$ ps gives corrected values for the cyclohexanol-water mixtures as in Table 31.
(The higher water content mixtures containing this alcohol will not be significantly affected.)

The corrected values for the 1 heptanol-water mixtures are given in Table 32.

Table 32

<table>
<thead>
<tr>
<th>Mole Fraction of Water</th>
<th>Temperature /°C</th>
<th>Corrected Relaxation Time τp/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>25.0</td>
<td>1,387</td>
</tr>
<tr>
<td>0.153</td>
<td>24.8</td>
<td>987</td>
</tr>
<tr>
<td>0.252</td>
<td>24.8</td>
<td>633</td>
</tr>
</tbody>
</table>

The relaxation times of the alcohol-water mixtures together with the uncertainty limits are given in Table 33.

Table 33

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Mole Fraction of Water</th>
<th>Relaxation Time τp/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>t butanol</td>
<td>0.000</td>
<td>486 ± 42</td>
</tr>
<tr>
<td></td>
<td>0.052</td>
<td>386 ± 20</td>
</tr>
<tr>
<td></td>
<td>0.101</td>
<td>288 ± 25</td>
</tr>
<tr>
<td></td>
<td>0.153</td>
<td>215 ± 14</td>
</tr>
<tr>
<td></td>
<td>0.197</td>
<td>208 ± 10</td>
</tr>
<tr>
<td>Alcohol</td>
<td>Mole fraction of water</td>
<td>Relaxation time $\tau_p$/ps</td>
</tr>
<tr>
<td>-------------</td>
<td>------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td></td>
<td>0.250</td>
<td>182 ± 14</td>
</tr>
<tr>
<td></td>
<td>0.299</td>
<td>137 ± 12</td>
</tr>
<tr>
<td></td>
<td>0.350</td>
<td>135 ± 12</td>
</tr>
<tr>
<td></td>
<td>0.400</td>
<td>136 ± 20</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>0.000</td>
<td>2329 ± 279</td>
</tr>
<tr>
<td></td>
<td>0.098</td>
<td>1702 ± 204</td>
</tr>
<tr>
<td></td>
<td>0.148</td>
<td>1259 ± 151</td>
</tr>
<tr>
<td></td>
<td>0.198</td>
<td>809 ± 97</td>
</tr>
<tr>
<td></td>
<td>0.251</td>
<td>622 ± 43</td>
</tr>
<tr>
<td></td>
<td>0.298</td>
<td>500 ± 39</td>
</tr>
<tr>
<td></td>
<td>0.353</td>
<td>412 ± 30</td>
</tr>
<tr>
<td></td>
<td>0.399</td>
<td>366 ± 37</td>
</tr>
<tr>
<td>1 butanol</td>
<td>0.000</td>
<td>543 ± 51</td>
</tr>
<tr>
<td></td>
<td>0.150</td>
<td>387 ± 26</td>
</tr>
<tr>
<td></td>
<td>0.245</td>
<td>272 ± 24</td>
</tr>
<tr>
<td></td>
<td>0.351</td>
<td>230 ± 11</td>
</tr>
<tr>
<td>1 heptanol</td>
<td>0.000</td>
<td>1387 ± 153</td>
</tr>
<tr>
<td></td>
<td>0.153</td>
<td>987 ± 109</td>
</tr>
<tr>
<td></td>
<td>0.252</td>
<td>633 ± 51</td>
</tr>
</tbody>
</table>

It can be seen that the highest error occurs for the longest relaxation time mixtures; this is due to the scatter in the graph for conversion from measured to corrected values.

Rather higher error would also be expected in the faster relaxations of the higher water content t butanol mixtures. This is observed to occur in the relatively high uncertainty in the 0.400 mf t butanol mixture. The quoted uncertainty for the 0.299 and 0.350 mf mixtures is possibly too low. The variation of relaxation time determined by the Fourier transform method for the alcohol-water mixtures is given in Figures 27 and 28.
4.6.2 **Fellner-Feldegg method**

Experimental errors have not been estimated here but the relatively high scatter in the \( \ln(\varepsilon_s - \varepsilon) \) against time graphs reveals that the uncertainty in \( \tau_D \) will be significantly higher than for the Fourier transform value \( \tau_F \).

4.6.3 **Fellner-Feldegg and Barnett method**

The relatively high uncertainty of about 25% in the value of \( \rho_\infty \) contributes significant uncertainty in the appropriate value of \( \rho_{0.2} \). Determination of the required \( t_{0.2} \) value and the scaling factor introduces additional error. The error in \( t_{0.2} \) will be typically about \( \pm 10\% \) and that in the scaling factor about \( \pm 5\% \). The error in \( \rho_{0.2} \) is not easy to estimate since the value selected for \( \rho_{0.2} \) also affects both \( t_{0.2} \) and the scaling factor, but investigation has shown that a figure of \( \pm 5\% \) is realistic giving a net uncertainty of \( \pm 20\% \) which is again substantially higher than that for the Fourier transform value.

4.6.4 **Brehm and Stockmayer method**

The uncertainty in \( \tau_{B+S} \) will be even higher than that for \( \tau_{FF+B} \) due to the requirement of knowledge of two times \( t_1 \) and \( t_2 \) instead of the single value (e.g. \( t_{0.2} \)) for the \( FF+B \) method. The scaling factor will also have a higher uncertainty giving a net uncertainty significantly larger than the \( \pm 20\% \) assigned to the \( FF+B \) method.
4.7 **Comparison of the methods used for determination of \( \tau \)**

Both the FF+B and B+S\(_1\) methods give \( \tau \) values for the pure alcohol cyclohexanol which are about a factor of 2.5 higher than literature values, which suggests that, in practice, these two methods are not suitable for studying slow relaxations where the Fourier transform data will be unreliable due to truncation effects. Similarly the direct time domain method \( \tau_D \) gives a value of \( \tau \) for cyclohexanol which is about a factor of 2 too high, revealing that this method is also unsuitable in the study of slow relaxations.

For \( \tau \leq 600 \text{ ps} \), comparison with literature values for the pure alcohols \( t \) butanol and 1 butanol, both of which have \( \tau \) values lower than 600 ps reveals that, of the various methods of calculation used in this work, the Fourier transform values \( \tau_F \) give closest agreement with literature values. For both \( t \) butanol and 1 butanol, the \( \tau_D \) method gives \( \tau \) values which are too low. The FF+B method gives good agreement with literature values for \( t \) butanol but the value for 1 butanol is about 25% too high.

The B+S\(_1\) method gives \( \tau \) values which are too high for both \( t \) and 1 butanol whereas the B+S\(_2\) method proposed in this work gives much closer agreement with literature values than the B+S\(_1\) method but the \( \tau \) value for 1 butanol is still too high. In addition, the B+S\(_1\) method gives in many cases \( \beta > 1 \) which is physically meaningless.
Of the direct methods studied, FF+B appears most suitable in terms of correlation with $\bar{\tau}_F$, although the B+S$_2$ method is only marginally poorer. In contrast, B+S$_1$ gives such highly inaccurate values that it is considered to be of no use.

Since the Fourier transform method is considered to give the most accurate relaxation time values, the discussion in Chapter 5 will be restricted to the $\bar{\tau}_F$ values.

4.8 Dielectric properties of surfactants

Dielectric dispersion was not observed in the frequency range 30 kHz to 15 MHz. The static permittivity values were obtained from Dipolmeter data using the MFL 2 cell.

4.8.1 Static Permittivity

Static permittivity values as a function of temperature for all the surfactants are given in Tables 34 to 37 and Figure 29.

Table 34

<table>
<thead>
<tr>
<th>Brij 30</th>
<th>Temperature/°C</th>
<th>Static Permittivity $\varepsilon_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>6.28</td>
<td></td>
</tr>
<tr>
<td>29.8</td>
<td>6.18</td>
<td></td>
</tr>
<tr>
<td>34.9</td>
<td>6.07</td>
<td></td>
</tr>
<tr>
<td>40.2</td>
<td>5.96</td>
<td></td>
</tr>
<tr>
<td>45.2</td>
<td>5.86</td>
<td></td>
</tr>
<tr>
<td>49.8</td>
<td>5.78</td>
<td></td>
</tr>
<tr>
<td>54.4</td>
<td>5.69</td>
<td></td>
</tr>
<tr>
<td>60.3</td>
<td>5.58</td>
<td></td>
</tr>
<tr>
<td>65.7</td>
<td>5.48</td>
<td></td>
</tr>
</tbody>
</table>
Temperature coefficient $d\varepsilon_s/dT = -1.96 \times 10^{-2} \, ^\circ\text{C}^{-1}$

Table 35

<table>
<thead>
<tr>
<th>$C_{12}E_4$</th>
<th>Temperature/°C</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Lot 80928)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.5</td>
<td>6.00</td>
<td></td>
</tr>
<tr>
<td>30.2</td>
<td>5.88</td>
<td></td>
</tr>
<tr>
<td>35.1</td>
<td>5.78</td>
<td></td>
</tr>
<tr>
<td>40.2</td>
<td>5.68</td>
<td></td>
</tr>
<tr>
<td>45.2</td>
<td>5.58</td>
<td></td>
</tr>
<tr>
<td>50.0</td>
<td>5.49</td>
<td></td>
</tr>
<tr>
<td>54.6</td>
<td>5.40</td>
<td></td>
</tr>
<tr>
<td>60.5</td>
<td>5.30</td>
<td></td>
</tr>
<tr>
<td>66.1</td>
<td>5.20</td>
<td></td>
</tr>
</tbody>
</table>

Temperature coefficient $d\varepsilon_s/dT = -1.83 \times 10^{-2} \, ^\circ\text{C}^{-1}$

Table 36

<table>
<thead>
<tr>
<th>$C_{12}E_6$</th>
<th>Temperature/°C</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Lot 81002)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td>6.21</td>
<td></td>
</tr>
<tr>
<td>35.0</td>
<td>6.11</td>
<td></td>
</tr>
<tr>
<td>40.2</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>45.4</td>
<td>5.91</td>
<td></td>
</tr>
<tr>
<td>50.1</td>
<td>5.82</td>
<td></td>
</tr>
<tr>
<td>55.1</td>
<td>5.74</td>
<td></td>
</tr>
<tr>
<td>60.8</td>
<td>5.64</td>
<td></td>
</tr>
<tr>
<td>66.6</td>
<td>5.54</td>
<td></td>
</tr>
</tbody>
</table>

Temperature coefficient $d\varepsilon_s/dT = -1.83 \times 10^{-2} \, ^\circ\text{C}^{-1}$
Table 37

<table>
<thead>
<tr>
<th>C_{12}E_8</th>
<th>Temperature/°C</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Lot 81024)</td>
<td>35.4</td>
<td>6.36</td>
</tr>
<tr>
<td></td>
<td>40.2</td>
<td>6.27</td>
</tr>
<tr>
<td></td>
<td>45.2</td>
<td>6.17</td>
</tr>
<tr>
<td></td>
<td>50.2</td>
<td>6.07</td>
</tr>
<tr>
<td></td>
<td>55.0</td>
<td>5.98</td>
</tr>
<tr>
<td></td>
<td>60.8</td>
<td>5.87</td>
</tr>
<tr>
<td></td>
<td>66.4</td>
<td>5.78</td>
</tr>
</tbody>
</table>

Temperature coefficient $d\varepsilon_s/dT = -1.89 \times 10^{-2} \degree \text{C}^{-1}$

These results reveal an increase of $\varepsilon_s$ at any given temperature as the oxyethylene chain length is increased. The commercial product Brij 30 has a slightly higher permittivity than its pure counterpart $C_{12}E_4$. All surfactants exhibit an almost linear temperature dependence for $\varepsilon_s$ with almost identical values for the temperature coefficient.

4.8.2 Time domain data for surfactant Brij 30

The TDR system revealed that a rapid but measurable dielectric relaxation occurred in Brij 30. The relaxation was studied at the two temperatures 44 and 70° C and the relaxation time was determined using both the $\tau_D$ and FF+B methods. In both methods, the static permittivity $\varepsilon_s$ was obtained from Dipolmeter values. The graphs of $\ln(\varepsilon_s - \varepsilon)$ against time are given in Figure 30. Linear regression analysis of the values of $\ln(\varepsilon_s - \varepsilon)$
against time gave $\tau_D$ values of 46 ps at 44°C and 39 ps at 70°C.

The FF+B method gave the values appearing in Table 38.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\rho_S$</th>
<th>$\rho_\infty$</th>
<th>$\rho_{0.2}$</th>
<th>$\tau_{u-2}$ /ps</th>
<th>Scaling Factor</th>
<th>$\tau_{FF+B}$ /ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>0.415</td>
<td>0.29</td>
<td>0.390</td>
<td>97</td>
<td>0.9</td>
<td>87</td>
</tr>
<tr>
<td>70</td>
<td>0.396</td>
<td>0.29</td>
<td>0.375</td>
<td>92</td>
<td>0.9</td>
<td>83</td>
</tr>
</tbody>
</table>

As in the alcohol-water mixtures, $\tau_D$ is lower than $\tau_{FF+B}$. The relaxation time determinations reveal a slightly lower $\tau$ at the higher temperature. However, there will be a high uncertainty in both the $\tau_D$ and $\tau_{FF+B}$ values due to the relaxation being very rapid and therefore being very sensitive to both time zero reference and impedance mismatch errors. In view of the high uncertainty in these results, it is considered that the difference in $\tau_D$ values at 44 and 70°C may be wholly accounted for by experimental error.

4.9 Densities of surfactants

In order to compare the dielectric properties of the binary and ternary mixtures of the surfactants with values predicted by the various dielectric mixture equations, the density values of each of the surfactants were required as the mixture equations involve the use of volume fraction $\phi$ rather than mass fraction $p$. 

- 176 -
The density values were determined with a standard 10 ml SG bottle, and are given in Table 39.

**Table 39**

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Temperature /°C</th>
<th>Density /10³ kgm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brij 30</td>
<td>23</td>
<td>0.947</td>
</tr>
<tr>
<td>C₁₂E₄</td>
<td>23</td>
<td>0.942</td>
</tr>
<tr>
<td>C₁₂E₆</td>
<td>63</td>
<td>0.912</td>
</tr>
<tr>
<td>C₁₂E₈</td>
<td>29</td>
<td>0.971</td>
</tr>
<tr>
<td>C₁₂E₈</td>
<td>32</td>
<td>0.990</td>
</tr>
</tbody>
</table>

An uncertainty of ± 0.003 in these density values is considered appropriate. The density data for C₁₂E₄ at two temperatures gives a temperature dependence value of \(-7.5 \times 10^{-4} \text{ kgm}^{-3} \text{ °C}^{-1}\). The results reveal an increase in density as the oxyethylene chain length is increased which is in agreement with the trend revealed in the literature values reported by Mulley (191) for C₁₂E₁ to C₁₂E₅. The value of 0.942 compares fairly satisfactorily with the value of 0.9502 at the same temperature reported by Mulley. Brij 30 has a density similar to that of its pure counterpart C₁₂E₄.

**4.10 Static Permittivity of tetraethylene glycol (E₄)**

As with the surfactants, the static permittivity of E₄ as a function of temperature was studied using the Dipolmeter with the MFL2 cell. The results are given in Table 40 and Figure 31.
Table 40

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>Static Permittivity $\varepsilon_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>20.12</td>
</tr>
<tr>
<td>35.3</td>
<td>19.09</td>
</tr>
<tr>
<td>44.8</td>
<td>18.18</td>
</tr>
<tr>
<td>54.6</td>
<td>17.32</td>
</tr>
<tr>
<td>65.4</td>
<td>16.44</td>
</tr>
</tbody>
</table>

Temperature coefficient of $\varepsilon_S$, $d\varepsilon_S/dT = -9.12 \times 10^{-2}$ °C⁻¹

The $\varepsilon_S$ values compare very favourably with the value of 21.1 at 21.4 °C obtained by Davies et al (192).

This exhibits higher values of both $\varepsilon_S$ and $d\varepsilon_S/dT$ than any of the surfactants studied. The lower values in the surfactants will be due to the depolarising effect of the non-polar alkyl ether chain.

4.11 Dielectric properties of surfactant-water binary mixtures

Dielectric dispersion was not observed in the frequency range of 30 kHz to 15 MHz. Dipolmeter values could not be obtained due to the dielectric behavior being too high and the static permittivity values were thus obtained from the RF bridge. The measurement frequency adopted was 2 MHz.

The temperature was adjusted so that all measurements were performed on transparent solutions and, with the exception of the C₁₂E₆-water mixtures, it was not possible to study all compositions at the same temperature.
4.11.1 Static Permittivity

The static permittivity values as a function of mass fraction $p$ of surfactant together with the measurement temperatures are given in Tables 41 to 44 and Figures 32 to 35.

Table 41
Brij 30-water mixtures

<table>
<thead>
<tr>
<th>Mass fraction of surfactant, $p$</th>
<th>Temperature/$^\circ$C</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.101</td>
<td>56.8</td>
<td>54.7</td>
</tr>
<tr>
<td>0.202</td>
<td>61.3</td>
<td>44.7</td>
</tr>
<tr>
<td>0.300</td>
<td>63.2</td>
<td>37.5</td>
</tr>
<tr>
<td>0.400</td>
<td>68.8</td>
<td>32.0</td>
</tr>
<tr>
<td>0.500</td>
<td>68.8</td>
<td>27.1</td>
</tr>
<tr>
<td>0.600</td>
<td>69.7</td>
<td>22.1</td>
</tr>
<tr>
<td>0.700</td>
<td>69.7</td>
<td>17.4</td>
</tr>
<tr>
<td>0.802</td>
<td>69.7</td>
<td>12.5</td>
</tr>
<tr>
<td>0.897</td>
<td>69.7</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Table 42
$C_{12}E_4$ -water mixtures

<table>
<thead>
<tr>
<th>Mass fraction of surfactant, $p$</th>
<th>Temperature/$^\circ$C</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.099</td>
<td>60.0</td>
<td>51.0</td>
</tr>
<tr>
<td></td>
<td>5.6</td>
<td>72.7</td>
</tr>
<tr>
<td>0.198</td>
<td>64.2</td>
<td>41.2</td>
</tr>
<tr>
<td></td>
<td>8.4</td>
<td>61.9</td>
</tr>
<tr>
<td>0.301</td>
<td>67.3</td>
<td>34.1</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td>51.2</td>
</tr>
<tr>
<td>0.400</td>
<td>70.5</td>
<td>28.4</td>
</tr>
<tr>
<td></td>
<td>11.9</td>
<td>43.7</td>
</tr>
<tr>
<td>0.500</td>
<td>72.6</td>
<td>24.5</td>
</tr>
<tr>
<td>(0.600)</td>
<td>(72.6)</td>
<td>(20.1)</td>
</tr>
</tbody>
</table>

- 179 -
0.700  69.6  16.3  
0.802  43.7  12.4  
0.904  68.0  8.9  

For mass fractions up to and including p = 0.4, two permitivity values are given due to the existence of two separate clear regions. The p = 0.6 data is given in brackets as the transparency could not be attained for this composition. At the temperature quoted the translucent mixture was as close to transparency as could be achieved.

Table 43

$C_{12}E_6$-water mixtures

<table>
<thead>
<tr>
<th>Mass fraction of surfactant, $p$</th>
<th>Temperature/°C</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.097</td>
<td>25.4</td>
<td>69.0</td>
</tr>
<tr>
<td>0.201</td>
<td>24.8</td>
<td>60.5</td>
</tr>
<tr>
<td>0.300</td>
<td>35.2</td>
<td>49.3</td>
</tr>
<tr>
<td>0.400</td>
<td>43.1</td>
<td>39.5</td>
</tr>
<tr>
<td>0.500</td>
<td>44.7</td>
<td>32.7</td>
</tr>
<tr>
<td>0.600</td>
<td>66.5</td>
<td>23.5</td>
</tr>
<tr>
<td>0.699</td>
<td>66.5</td>
<td>18.7</td>
</tr>
<tr>
<td>0.798</td>
<td>51.1</td>
<td>15.4</td>
</tr>
<tr>
<td>0.880</td>
<td>51.1</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Table 44

$C_{12}E_8$-water mixtures

<table>
<thead>
<tr>
<th>Mass fraction of surfactant, $p$</th>
<th>Temperature/°C</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>66.1</td>
<td>57.6</td>
</tr>
<tr>
<td>0.200</td>
<td>66.1</td>
<td>50.6</td>
</tr>
</tbody>
</table>
A general trend of decrease in $\varepsilon_s$ as the mass fraction of surfactant is increased is revealed. The necessity of changing the temperature for the Brij 30, C$_{12}$E$_4$ and C$_{12}$E$_6$ mixtures precludes conclusions based simply on the graphs. One notable feature however, is that there is a significant difference between C$_{12}$E$_4$ and Brij 30 in that at low surfactant concentration C$_{12}$E$_4$ forms transparent solutions in two separate temperature ranges whereas Brij 30 only exhibits transparency in one temperature range.

4.11.2 Temperature dependence of $\varepsilon_s$ for binary mixtures

The temperature dependence of $\varepsilon_s$ for some of the aqueous mixtures which were transparent over a wide range of temperature are given in Tables 45 to 48 and Figure 36. The $C_{12}E_n$–water mixtures with $p = 0.900$ were measured with the Dipolmeter. The other mixtures were measured with the RF bridge operating at 2 MHz.
Table 45
\[ C_{12}E_4 \text{-water with } p = 0.900 \]

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>Static Permittivity ( \varepsilon_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>10.88</td>
</tr>
<tr>
<td>46.0</td>
<td>10.05</td>
</tr>
<tr>
<td>64.0</td>
<td>9.29</td>
</tr>
</tbody>
</table>

Temperature coefficient \( d\varepsilon_s/dT = 4.08 \times 10^{-2} \, °C^{-1} \)

Table 46
\[ C_{12}E_6 \text{-water with } p = 0.097 \]

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>Static Permittivity ( \varepsilon_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.9</td>
<td>72.4</td>
</tr>
<tr>
<td>20.2</td>
<td>71.1</td>
</tr>
<tr>
<td>25.4</td>
<td>69.0</td>
</tr>
<tr>
<td>29.6</td>
<td>67.7</td>
</tr>
<tr>
<td>34.8</td>
<td>66.1</td>
</tr>
<tr>
<td>40.0</td>
<td>64.5</td>
</tr>
</tbody>
</table>

Temperature coefficient \( d\varepsilon_s/dT = -0.32 \, °C^{-1} \)

Table 47
\[ C_{12}E_8 \text{-water with } p = 0.100 \]

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>Static Permittivity ( \varepsilon_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>69.6</td>
</tr>
<tr>
<td>35.3</td>
<td>66.2</td>
</tr>
<tr>
<td>45.4</td>
<td>63.3</td>
</tr>
<tr>
<td>55.0</td>
<td>60.55</td>
</tr>
<tr>
<td>66.1</td>
<td>57.6</td>
</tr>
</tbody>
</table>
Temperature coefficient \( d\varepsilon_S/dT = -0.29 \; ^\circ\text{C}^{-1} \)

### Table 48

\( C_{12}E_8 \)-water with \( p = 0.901 \)

<table>
<thead>
<tr>
<th>Temperature / (^\circ\text{C})</th>
<th>Static Permittivity ( \varepsilon_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.4</td>
<td>11.85</td>
</tr>
<tr>
<td>46.8</td>
<td>10.95</td>
</tr>
<tr>
<td>66.2</td>
<td>9.35</td>
</tr>
</tbody>
</table>

Temperature coefficient \( d\varepsilon_S/dT = -7.02 \times 10^{-2} \; ^\circ\text{C}^{-1} \)

The variation of \( \varepsilon_S \) with temperature for both \( C_{12}E_4 \)- and \( C_{12}E_8 \)-water mixtures for mass fraction of surfactant \( p = 0.9 \) is almost linear but the \( C_{12}E_8 \) mixture has a temperature coefficient almost twice that of the \( C_{12}E_4 \) mixture.

The variation of \( \varepsilon_S \) with temperature for both \( C_{12}E_6 \)- and \( C_{12}E_8 \)-water mixtures for mass fraction of surfactant \( p = 0.10 \) is again almost linear with the temperature coefficient of \( \varepsilon_S \) for both surfactants being notably very similar.

### 4.11.3 Time domain data for Brij 30-water binary mixtures

Mixtures of Brij 30 with water at mass fractions of surfactant \( p = 0.90 \) and 0.70 were studied. As with the surfactant Brij 30 alone, the dielectric relaxation was again rapid and, in addition, the high dc conductivity of both mixtures was manifested in the TDR system as a
superimposed apparent slow relaxation causing the reflection coefficient to exhibit a monotonous increase for the whole duration of the time domain scan.

The high conductivity precluded use of the Dipolmeter for \( \varepsilon_s \) determination, and instead the less precise RF bridge method was used. The relaxation time was determined by the \( \tau_D \) and FF+B methods. The graphs of \( \ln(\varepsilon_s - \varepsilon) \) against time are given in Figure 37. Linear regression analysis of the values of \( \ln(\varepsilon_s - \varepsilon) \) against time gave a value of \( \tau_D = 64 \) ps for \( p = 0.90 \) at \( 44^\circ C \) and \( 50 \) ps for \( p = 0.70 \) at \( 70^\circ C \).

The FF+B method gave values as tabulated:

<table>
<thead>
<tr>
<th>Mass fraction of surfactant, ( p )</th>
<th>Temperature ( ^\circ C )</th>
<th>( \rho_s )</th>
<th>( \rho_\infty )</th>
<th>( \rho_{0.2} )/ps</th>
<th>Scaling Factor</th>
<th>( \tau_{FF+B} )/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>44</td>
<td>0.525</td>
<td>0.358</td>
<td>0.492</td>
<td>107</td>
<td>1.0</td>
</tr>
<tr>
<td>0.7</td>
<td>70</td>
<td>0.613</td>
<td>0.400</td>
<td>0.570</td>
<td>82</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Although the FF+B method is considered to give relaxation time values which are closer in magnitude to the correct values, the significant dc conductivity will cause the FF+B values to be more susceptible to error. These results reveal a similarly rapid relaxation to that observed for Brij 30.

4.12 Static permittivity of tetra ethylene glycol (\( E_n \))-water mixtures

The results are given in Table 50 and Figure 38.
Table 50

<table>
<thead>
<tr>
<th>Mass fraction of E₄₀</th>
<th>Temperature /°C</th>
<th>Static Permittivity εₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>25.0</td>
<td>74.2</td>
</tr>
<tr>
<td>0.200</td>
<td>25.0</td>
<td>69.6</td>
</tr>
<tr>
<td>0.300</td>
<td>25.0</td>
<td>65.3</td>
</tr>
<tr>
<td>0.400</td>
<td>25.0</td>
<td>60.3</td>
</tr>
<tr>
<td>0.500</td>
<td>25.0</td>
<td>55.3</td>
</tr>
<tr>
<td>0.600</td>
<td>25.0</td>
<td>49.5</td>
</tr>
<tr>
<td>0.700</td>
<td>25.0</td>
<td>43.4</td>
</tr>
<tr>
<td>0.800</td>
<td>25.0</td>
<td>36.7</td>
</tr>
<tr>
<td>0.900</td>
<td>25.0</td>
<td>28.8</td>
</tr>
</tbody>
</table>

As with the surfactants, a general trend of decrease in εₛ as the mass fraction of E₄₀ is increased is revealed.

4.13 Static permittivity of Brij 30-heptane binary mixtures

Static permittivity values for mixtures of Brij 30 with heptane were determined from Dipolmeter data using the DFL2 cell. The results are given in Table 51 and Figure 39.

Table 51

<table>
<thead>
<tr>
<th>Mass fraction of Brij 30</th>
<th>Static Permittivity εₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>2.29</td>
</tr>
<tr>
<td>0.40</td>
<td>2.82</td>
</tr>
<tr>
<td>0.60</td>
<td>3.62</td>
</tr>
<tr>
<td>0.80</td>
<td>4.55</td>
</tr>
</tbody>
</table>

The results reveal a monotonous increase in εₛ as the proportion of the non-polar solvent heptane is decreased.
4.14 Dielectric properties of surfactant, water and a hydrocarbon ternary mixtures

In ternary mixtures which were transparent, dielectric dispersion was not observed in the frequency range 30 kHz to 15 MHz. In addition, dielectric dispersion was not in general observed in the higher frequency range of the TDR system and the static permittivity values given by the TDR system agreed with the RF range values within experimental error limits of ±3%. It is thus concluded that dielectric dispersion does not occur within the frequency range of 30 kHz to approximately 3 GHz.

The exceptions to this general trend were surfactant rich ternary mixtures of Brij 30 which exhibited dielectric dispersion in the TDR range.

4.14.1 Static permittivity

Static permittivity values of Brij 30 mixtures were obtained from RF bridge data at a measurement frequency of 2 MHz. The static permittivity values of C_{12}E_4 mixtures were obtained using the Dipolmeter when the permittivity was within the range of the MFL2 cell (3.60 to 22.0), and for permittivity values outside this range the RF bridge operating at 2 MHz was again used.

The values of $\varepsilon_s$ for a range of ternary mixtures of both C_{12}E_4 and Brij 30, together with the measurement temperatures are given in Tables 52 and 53.
Table 52

$C_{12}E_4$-water-n-alkane systems

<table>
<thead>
<tr>
<th>Mass fraction of water</th>
<th>Mass fraction of heptane</th>
<th>Temperature $^\circ C$</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.70</td>
<td>17.2</td>
<td>3.7</td>
</tr>
<tr>
<td>0.10</td>
<td>0.60</td>
<td>17.7</td>
<td>4.3</td>
</tr>
<tr>
<td>0.10</td>
<td>0.40</td>
<td>17.4</td>
<td>5.7</td>
</tr>
<tr>
<td>0.10</td>
<td>0.20</td>
<td>17.4</td>
<td>7.8</td>
</tr>
<tr>
<td>0.30</td>
<td>0.50</td>
<td>16.9</td>
<td>7.0</td>
</tr>
<tr>
<td>0.40</td>
<td>0.50</td>
<td>4.2</td>
<td>20.3</td>
</tr>
<tr>
<td>0.40</td>
<td>0.50</td>
<td>13.0</td>
<td>7.3</td>
</tr>
<tr>
<td>0.70</td>
<td>0.10</td>
<td>20.2</td>
<td>32.3</td>
</tr>
</tbody>
</table>

Mass fraction of decane

<table>
<thead>
<tr>
<th>Mass fraction of decane</th>
<th>Temperature $^\circ C$</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>0.34</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.6</td>
</tr>
</tbody>
</table>

Mass fraction of hexadecane

<table>
<thead>
<tr>
<th>Mass fraction of hexadecane</th>
<th>Temperature $^\circ C$</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.49</td>
<td>0.33</td>
<td>24.3</td>
</tr>
<tr>
<td></td>
<td>33.3</td>
<td>28.1</td>
</tr>
<tr>
<td>0.52</td>
<td>0.35</td>
<td>28.4</td>
</tr>
<tr>
<td></td>
<td>31.4</td>
<td>26.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.1</td>
</tr>
</tbody>
</table>
Table 53

Brij 30-water-n-heptane systems

<table>
<thead>
<tr>
<th>Mass fraction of water</th>
<th>Mass fraction of heptane</th>
<th>Temperature °C</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.60</td>
<td>27.5</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>27.5</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>30.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>27.0</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>23.2</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>40.0</td>
<td>9.1</td>
</tr>
<tr>
<td>0.20</td>
<td>0.60</td>
<td>33.5</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>34.5</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>32.4</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>30.0</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>29.0</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>40.0</td>
<td>11.3</td>
</tr>
<tr>
<td>0.30</td>
<td>0.50</td>
<td>27.5</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>23.0</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>26.4</td>
<td>9.6</td>
</tr>
<tr>
<td>0.35</td>
<td>0.50</td>
<td>27.5</td>
<td>6.0</td>
</tr>
<tr>
<td>0.40</td>
<td>0.40</td>
<td>21.2</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>21.2</td>
<td>8.8</td>
</tr>
</tbody>
</table>

A general trend of an increase in $\varepsilon_s$ as either the proportion of water is increased or the proportion of heptane is decreased is revealed.

Comparison of the C$_{12}$E$_4$ with the Brij 30 ternary mixture results reveals in a number of cases, similarity in $\varepsilon_s$. 

- 188 -
values, but there are important differences between the two surfactants. In certain \( C_{12}E_4 \) mixtures, two separate clear regions with a relatively small temperature difference between these two regions were observed, whereas in Brij 30 only one clear region appeared.

Inspection of the \( \varepsilon_s \) values for these \( C_{12}E_4 \) mixtures reveals a large reduction in \( \varepsilon_s \) for a relatively small temperature change. The effect is possibly most marked for the \( C_{12}E_4 \) mixture with mass fraction of water = 0.40 and mass fraction of heptane = 0.50 where for a temperature change from 4.2 to 13° C the static permittivity falls from 20.3 to 7.3.

4.14.2 Temperature dependence of \( \varepsilon_s \) for ternary mixtures of \( C_{12}E_4 \) with mass fraction of water = 0.10

With the exception of the mass fraction of heptane = 0.70 mixture above 18° C, all measurements were performed with the Dipolmeter with MFL2 cell. The results are given in Tables 54 to 57 and Figure 40.

Table 54

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>Static Permittivity ( \varepsilon_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.2</td>
<td>3.70</td>
</tr>
<tr>
<td>20.0</td>
<td>3.41</td>
</tr>
<tr>
<td>21.8</td>
<td>3.22</td>
</tr>
<tr>
<td>25.0</td>
<td>2.93</td>
</tr>
</tbody>
</table>

Temperature coefficient \( d\varepsilon_s /dT = -9.9.10^{-2} \) °C⁻¹
Table 55
Mass fraction of heptane = 0.60

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>Static Permittivity ε_s</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.9</td>
<td>4.82</td>
</tr>
<tr>
<td>13.5</td>
<td>4.61</td>
</tr>
<tr>
<td>17.7</td>
<td>4.29</td>
</tr>
<tr>
<td>22.0</td>
<td>3.99</td>
</tr>
<tr>
<td>26.4</td>
<td>3.66</td>
</tr>
</tbody>
</table>

Temperature coefficient $dε_s/dT = -7.43 \times 10^{-2} \ °C^{-1}$

Comparison of these four sets of results for mass fraction of water = 0.10 reveals that as the proportion of the non-polar heptane is decreased, the static permittivity $ε_s$ increases but its temperature coefficient decreases from $-9.9 \times 10^{-2} \ °C^{-1}$ at 70% by mass of heptane to $-3.2 \times 10^{-2} \ °C^{-1}$ at 40% and then remaining unchanged at 20% of heptane.

Table 56
Mass fraction of heptane = 0.40

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>Static Permittivity ε_s</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.6</td>
<td>6.01</td>
</tr>
<tr>
<td>13.2</td>
<td>5.87</td>
</tr>
<tr>
<td>17.4</td>
<td>5.71</td>
</tr>
<tr>
<td>21.0</td>
<td>5.58</td>
</tr>
<tr>
<td>25.6</td>
<td>5.44</td>
</tr>
<tr>
<td>31.8</td>
<td>5.24</td>
</tr>
</tbody>
</table>
Temperature coefficient $d\varepsilon_s/dT = -3.20 \times 10^{-2} \, ^\circ\text{C}^{-1}$

Table 57

<table>
<thead>
<tr>
<th>Mass fraction of heptane = 0.20</th>
<th>Static Permittivity $\varepsilon_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature / °C</td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>8.33</td>
</tr>
<tr>
<td>12.5</td>
<td>8.16</td>
</tr>
<tr>
<td>17.4</td>
<td>7.97</td>
</tr>
<tr>
<td>23.8</td>
<td>7.75</td>
</tr>
<tr>
<td>31.5</td>
<td>7.49</td>
</tr>
<tr>
<td>39.2</td>
<td>7.26</td>
</tr>
<tr>
<td>45.7</td>
<td>7.06</td>
</tr>
<tr>
<td>52.8</td>
<td>6.86</td>
</tr>
<tr>
<td>61.3</td>
<td>6.64</td>
</tr>
</tbody>
</table>

Temperature coefficient $d\varepsilon_s/dT = -3.18 \times 10^{-2} \, ^\circ\text{C}^{-1}$

4.14.3 **Time domain data for surfactant, water and heptane ternary mixtures**

For nearly all mixtures studied, the TDR system did not reveal dielectric relaxation. Exceptions to this trend were surfactant-rich ternary mixtures, which revealed a rapid but measurable relaxation. The slowest relaxation observed was in the ternary mixture 0.70 Brij 30, 0.10 heptane and 0.20 water. This was given detailed attention and the relaxation time values were determined by the
Fourier transform, $\tau_D$ and FF+B methods, at three different temperatures.

The dielectric dispersion curves given by the Fourier transform value data given in Figure 41 reveal Debye-type relaxation. The $\tau_D$ values were obtained from a linear regression analysis of the $\ln(\varepsilon_S - \varepsilon)$ against time graphs given in Figure 41.

The relaxation data obtained by the three methods is given in Table 58.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$\tau_F$ /ps</th>
<th>$\tau_D$ /ps</th>
<th>$\rho_S$</th>
<th>$\rho_\infty$</th>
<th>$\rho_{0.2}$ /ps</th>
<th>$t_{0.2}$</th>
<th>Scaling Factor</th>
<th>$\tau_{FF+B}$ /ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.7</td>
<td>93</td>
<td>64</td>
<td>0.54</td>
<td>0.36</td>
<td>0.505</td>
<td>107</td>
<td>1.10</td>
<td>118</td>
</tr>
<tr>
<td>37.3</td>
<td>95</td>
<td>49</td>
<td>0.54</td>
<td>0.32</td>
<td>0.496</td>
<td>99</td>
<td>1.10</td>
<td>109</td>
</tr>
<tr>
<td>46.0</td>
<td>76</td>
<td>49</td>
<td>0.54</td>
<td>0.40</td>
<td>0.510</td>
<td>102</td>
<td>1.05</td>
<td>107</td>
</tr>
</tbody>
</table>

Comparison of the $\tau$ values obtained by the three methods reveals a slight fall in relaxation time with increasing temperature. As in the studies detailed earlier in this chapter, the $\tau_D$ values are somewhat lower than those of both $\tau_F$ and $\tau_{FF+B}$. The apparent difference in the temperature dependence of $\tau_F$ compared with that of $\tau_D$ and $\tau_{FF+B}$ is attributed to the high experimental uncertainty which occurs in the TDR method for fast relaxations, and the principal conclusion drawn here is simply that the dielectric relaxation is very rapid with $\tau$ values comparable to the surfactant only and surfactant-water
4.14.4 **Dielectric properties of ternary mixtures at temperatures outside the limits for transparent solutions**

When the temperature was raised to just above the cloud point, dielectric dispersion in the frequency range 30 kHz to 10 MHz was not observed. In contrast, when the temperature was lowered to just below the lower limit for transparency, dielectric dispersion in the above frequency range was a general feature. A representative selection of the results for four compositions is given in Tables 59 to 62 and Figure 42. The lower temperature limit for transparent solutions is given in brackets.

**Table 59**

<table>
<thead>
<tr>
<th></th>
<th>Frequency /MHz</th>
<th>ε'</th>
<th>ε''</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.07</td>
<td>9.7</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>8.9</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>7.6</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>6.2</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>5.6</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>5.2</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>15.00</td>
<td>5.1</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The dispersion curve is Cole-Cole arc type with $\alpha = 0.24$ and $\tau = 5.3 \times 10^{-7}$ s
Table 60
0.20 Brij 30 : 0.40 hexane : 0.40 water

Temperature = 19.0° C (lower limit for transparency = 20° C)

<table>
<thead>
<tr>
<th>Frequency /MHz</th>
<th>ε'</th>
<th>ε&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>14.1</td>
<td>1.02</td>
</tr>
<tr>
<td>0.15</td>
<td>13.8</td>
<td>1.7</td>
</tr>
<tr>
<td>0.30</td>
<td>12.5</td>
<td>2.5</td>
</tr>
<tr>
<td>0.50</td>
<td>11.6</td>
<td>2.7</td>
</tr>
<tr>
<td>0.70</td>
<td>10.9</td>
<td>2.6</td>
</tr>
<tr>
<td>1.00</td>
<td>10.6</td>
<td>2.55</td>
</tr>
<tr>
<td>1.50</td>
<td>9.9</td>
<td>2.4</td>
</tr>
<tr>
<td>2.00</td>
<td>9.4</td>
<td>2.1</td>
</tr>
<tr>
<td>7.00</td>
<td>8.25</td>
<td>1.3</td>
</tr>
<tr>
<td>15.00</td>
<td>8.1</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The dispersion curve is Cole-Cole arc type with \( \alpha = 0.20 \)
and \( \tau = 2.7 \times 10^{-7} \) s.

Table 61
0.60 Brij 30 : 0.20 hexane : 0.20 water

Temperature = 29.5° C (lower limit for transparency = 30° C)

dc conductance = 6.0 \( \mu \)S

<table>
<thead>
<tr>
<th>Frequency /MHz</th>
<th>ε'</th>
<th>ε&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>11.6</td>
<td>0.85</td>
</tr>
<tr>
<td>0.15</td>
<td>10.9</td>
<td>1.3</td>
</tr>
<tr>
<td>0.30</td>
<td>10.2</td>
<td>1.5</td>
</tr>
<tr>
<td>0.50</td>
<td>9.6</td>
<td>1.44</td>
</tr>
<tr>
<td>0.70</td>
<td>9.1</td>
<td>1.3</td>
</tr>
<tr>
<td>1.50</td>
<td>8.8</td>
<td>0.9</td>
</tr>
<tr>
<td>3.00</td>
<td>8.7</td>
<td>0.64</td>
</tr>
<tr>
<td>7.00</td>
<td>8.5</td>
<td>0.4</td>
</tr>
<tr>
<td>15.00</td>
<td>8.5</td>
<td>0.12</td>
</tr>
</tbody>
</table>
The dispersion curve is Cole-Cole arc type with $\alpha = 0.11$ and $\tau = 4.5\times10^{-7}$ s.

Table 62

0.30 Brij 30 : 0.30 hexane : 0.40 water

Temperature = 21.0°C (lower limit for transparency = 22°C)

<table>
<thead>
<tr>
<th>Frequency /MHz</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>12.2</td>
<td>0.95</td>
</tr>
<tr>
<td>0.50</td>
<td>11.9</td>
<td>1.3</td>
</tr>
<tr>
<td>0.70</td>
<td>11.7</td>
<td>1.4</td>
</tr>
<tr>
<td>1.00</td>
<td>11.2</td>
<td>1.5</td>
</tr>
<tr>
<td>1.50</td>
<td>10.9</td>
<td>1.5</td>
</tr>
<tr>
<td>3.00</td>
<td>10.2</td>
<td>1.3</td>
</tr>
<tr>
<td>7.00</td>
<td>9.7</td>
<td>0.9</td>
</tr>
<tr>
<td>15.00</td>
<td>9.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>

The dispersion curve is Cole-Cole arc type with $\alpha = 0.18$ and $\tau = 1.2\times10^{-7}$ s.

For all four compositions the relaxation times are of a similar order. The dispersion parameter values are similar with $\alpha = 0.21 \pm 0.03$ for three of the mixtures but a lower value of $0.11 \pm 0.06$ is obtained for the mixture with high surfactant content. This difference could be associated with the liquid crystalline structure which forms at lower temperatures in this composition, in contrast with the other three which behave as two phase emulsions at lower temperatures. However the uncertainty in the $\alpha$ value is higher in the high surfactant content mixture due to the presence of a relatively high dc conductivity. In view
of this uncertainty, it is considered that conclusions based on distinction between liquid crystalline and two phase emulsion formation are precluded.
Calibration curve for cell constant of B601 RF bridge
FIGURE 10

Cole-Cole plots (Indicated frequencies are in GHz)

a) t butanol

b) t butanol with 0.052 mf of water
FIGURE 11
Cole-Cole Plots (Indicated frequencies are in GHz)
a) t-butanol with 0.101 mf of water

b) t-butanol with 0.153 mf of water
FIGURE 12
Cole-Cole plots (Indicated frequencies are in GHz)
a) t-butanol with 0.197 wt % of water

b) t-butanol with 0.250 wt % of water
FIGURE 13
Cole-Cole plots (Indicated frequencies are in GHz)
a) t butanol with 0.299 mf of water

b) t butanol with 0.350 mf of water
FIGURE 14
Cole-Cole plots (Indicated frequencies are in GHz)

a) t-butanol with 0.400 ml of water

b) t-butanol with 0.400 ml of water

Effect of time zero reference change

- Zero advanced by 3.9 ps
- Actual zero used
- Zero retarded by 3.9 ps
FIGURE 15
Cole-Cole plots (Indicated: frequencies are in GHz)
a) cyclohexanol

b) cyclohexanol with 0.098 mF of water
FIGURE 16

Cole-Cole plots (Indicated frequencies are in GHz)

a) cyclohexanol with 0.148 Mf of water

b) cyclohexanol with 0.198 Mf of water
FIGURE 17
Cole-Cole plots (Indicated frequencies are in GHz)

a) cyclohexanol with 0.251 mf of water

b) cyclohexanol with 0.298 mf of water
FIGURE 18
Cole-Cole plots (Indicated frequencies are in GHz)

a) cyclohexanol with 0.353 mf of water

b) cyclohexanol with 0.399 mf of water
FIGURE 19

Cole-Cole plots (Indicated frequencies are in GHz)

a) 1 butanol

b) 1 butanol with 0.150 mf of water
FIGURE 20

Cole-Cole plots (Indicated frequencies are in GHz)

a) 1 butanol with 0.245 mf of water

b) 1 butanol with 0.351 mf of water
FIGURE 21
Cole-Cole plots (Indicated frequencies are in GHz)
a) 1 heptanol

b) 1 heptanol with 0.153 mf of water
FIGURE 22
Cole-Cole plots (Indicated frequencies are in GHz)
a) 1 heptanol with 0.252 m\(\text{f}\) of water
The time marker defines the time scale used on the time axis.

(a) $\Delta \equiv 0.000 \text{ mf}$
$O \equiv 0.052 \text{ mf}$
$\times \equiv 0.101 \text{ mf}$
$\triangle \equiv 0.153 \text{ mf}$

(b) $O \equiv 0.197 \text{ mf}$
$\triangle \equiv 0.250 \text{ mf}$
$\times \equiv 0.299 \text{ mf}$
$\square \equiv 0.350 \text{ mf}$
$\triangledown \equiv 0.400 \text{ mf}$
Direct time domain plots for cyclohexanol-water mixtures

The time marker defines the time scale on the time axis.
Direct time domain plots

(a) 1 butanol-water mixtures

(b) 1 heptanol-water mixture

The time marker defines the time scale on the time axis

\[ \ln(\xi^-) \]

\[ 0 \quad 0.5 \quad 1.0 \quad 1.5 \quad 2.0 \]

\[ 1396\text{ps} \]

\[ 588\text{ps} \]
FIGURE 26
Correction curve for $\tau_f$ values in slower relaxations

Corrected value $s/10^{-9}$

Measured value $s/10^{-9}$
Figure 27
Relaxation time $\tau$ against mole fraction of water $x$ for alcohol-water mixtures:

- $\triangle$ butanol-water mixtures
- $\circ$ 1-butanol-water mixtures

Values:
- $\tau$ for alcohol-water mixtures:
  - 600
  - 400
  - 200
Figure 28: Relaxation time $\tau$ against mole fraction of water $x$ for alcohol-water mixtures.

$\bigcirc$ = cyclohexanol-water mixtures

$\bigtriangleup$ = n-heptanol-water mixtures

$s/10^{-9}$ vs $\tau$

$x$ vs $s/10^{-9}$
FIGURE 29
Temperature dependence of static permittivity for C₁₂₄ and Brij 30 surfactants

- $\times$ = C₁₂₄
- $\square$ = C₁₂E₆
- $\bigtriangleup$ = C₁₂E₈
- $\bigcirc$ = Brij 30

Temperature

50  55  60

20  30  40  50

Temperature dependence graph for various surfactants.
FIGURE 30

Direct time domain plots for Brij 30

- 44°C
- 70°C

The time marker defines the time scale used on the time axis.
FIGURE 31

Temperature dependence of static permittivity
for tetra ethylene glycol
FIGURE 32

Static permittivity of C<sub>12</sub>E<sub>4</sub> mixtures (predicted and measured values)

- • measured values
- - - • Hanai O/W equation
- - - - Rayleigh O/W equation

(The values on any curve do not necessarily refer to the same temperature.)

Mass fraction of C<sub>12</sub>E<sub>4</sub>
FIGURE 33

Static permittivity of Brij 30-water mixtures (predicted and measured values)

○ = measured values
- - - - = Hanai O/W equation
- - - - - = Rayleigh O/W equation
- - - - - = Bottcher equation
- - - - - = Looyenga equation

(The values on any curve do not necessarily refer to the same temperature.)
Static permittivity of $\text{C}_{12}\text{E}_6$-water mixtures
(predicted and measured values)

- $\circ$ = measured values
- $\ldots$ = Hanai O/W equation
- $\ldots\ldots$ = Rayleigh O/W equation

(The values on any curve do not necessarily refer to the same temperature.)
FIGURE 35

Static permittivity of C_{12}E_8-water mixtures
(predicted and measured values)

○ = Measured values
--- = Hanai O/W equation
- - - = Rayleigh O/W equation
- - - - = Ideal mixing equation

\( \varepsilon_s \)

Mass fraction of C_{12}E_8
Temperature dependence of static permittivity for surfactant-water binary mixtures

(a) Mass fraction of surfactant, $p = 0.9$

$\Delta \equiv C_{12}E_4$

$\circ \equiv C_{12}E_6$

(b) Mass fraction of surfactant, $p = 0.1$

$\circ \equiv C_{12}E_6$

$\Delta \equiv C_{12}E_8$
Direct time domain plots for Brij 30-water mixtures

(a) Mass fraction of surfactant
\[ p = 0.9 \]

(b) Mass fraction of surfactant
\[ p = 0.7 \]

The time marker defines the time scale on the time axis.
Static permittivity of tetra ethylene glycol (E₄)-water mixtures

○ = Measured values
△ = Ideal mixing equation
Static permittivity of Brij-30 heptane mixtures
(predicted and measured values)

- - - - Rayleigh O/W
- - - - Rayleigh W/O

Mass fraction of surfactant
Temperature dependence of the static permittivity of ternary mixtures containing 10% by mass of water

(a) \( \Delta \equiv 60\% \) by mass of heptane
\( \square \equiv 70\% \) by mass of heptane

(b) \( \circ \equiv 20\% \) by mass of heptane
\( \times \equiv 40\% \) by mass of heptane
FIGURE 41

Ternary mixture 70% Brij 30, 20% water and 10% heptane

(a) Cole-Cole plots (Indicated frequencies are in GHz)
- ○ = 31.7° C
- △ = 37.3° C
- □ = 46.0° C

(b) Direct time domain plots
- ○ = 31.7° C
- △ = 37.3° C
- □ = 46.0° C

The time mark defines the time scale on the time axis
FIGURE 42

Cole-Cole plots for Brij 30 ternary mixtures at temperatures below lower limit for transparency (Indicated frequencies are in MHz)

(a) ○ = 20% Brij 30, 60% heptane and 20% water at 29.2° C
(b) ▲ = 20% Brij 30, 40% heptane and 40% water at 19.0° C
(c) □ = 30% Brij 30, 30% heptane and 40% water at 21.0° C
(d) × = 60% Brij 30, 20% heptane and 20% water at 29.5° C
5.1 Alcohol-water mixtures

5.1.1 Summary of Results

The results for t butanol-, cyclohexanol-, 1 butanol- and 1 heptanol-water mixtures reveal that addition of water to all four alcohols causes a reduction in the relaxation time, $\tau$, of the principal dispersion and that the relaxation is Debye-type for all mixtures, as shown in Figures 10 to 22. These observations follow the trend revealed in the results of Chekalin and Shakhparonov (65) for methanol- and 1 propanol-water mixtures, Buck (68) for ethanol-water mixtures and Tjia (59) for 1, 2, 3 and 4 heptanol-water mixtures; 3 heptanol-water mixtures at $-70^\circ$ C being the only exception. They confirm the present proposal given in Chapter 1 that addition of water to an alcohol generally causes a reduction of relaxation time irrespective of the sign of the variation of static permittivity, $\epsilon_s$, with water content. The results of Sarojini (67) for 1 butanol-water mixtures, in which an increase in $\tau$ on addition of water was reported, are therefore considered to be erroneous.

The observation of Debye-type dispersion for all mixtures is in accord with the comment of Davies (60) that "compatible pairs of liquids appear to merge molecularly giving a single relaxation time". It should be noted that the only reported exception to Debye-type dispersion in alcohol-water mixtures is the data of Peyrelasse (66)
for methanol-water mixtures for which Cole-Cole arc behaviour was suggested with parameter \( \alpha \) increasing from 0.046 at 44% by mass of alcohol to an approximately constant value of 0.08 at and above 60% by mass of alcohol. However, this interpretation of Peyrelasse is based on Cole-Cole plots containing a similarly small number of four or five data points to those of Chekalin and Shakhparonov for methanol-water mixtures (65) and both sets of results lie on the Cole-Cole arc plot drawn by Peyrelasse for this mixture. Since the latter authors favoured an interpretation based on two Debye-type relaxations rather than a distribution of relaxation times, it is considered that for all alcohol-water mixtures studied, there is not yet sufficient justification for considering the principal dispersion to be other than Debye-type.

5.1.2 Interpretation of the relaxation time variation

When small quantities of water are added to an alcohol, the specific structure of water can be regarded as entirely lost and the presumed chain-like structure of the pure alcohol will be modified. Although a chain-like structure involving mixed water-alcohol molecules has been suggested by Chekalin and Shakhparonov (64, 65) for methanol-water mixtures, this model is not favoured since such a structure involves an alcohol oxygen atom being H-bonded to two other molecules, which is not supported by any other data.
In this work, a mechanism based on alcohol chain breakage by water molecules is considered more appropriate and addition of water to a pure alcohol with its presumed chains of indefinite length is assumed to cause a progressive reduction in average chain length.

The fall of relaxation time with increasing water content can be explained using the 'switch' model of Campbell et al (34) which was based on the proposals of Sagal (35). In this model dielectric relaxation is attributed to H-bond rupture and dipole orientation, which occurs when a hydroxyl group approaches the associated alcohol chain with its oxygen atom favourably oriented for a switch (Fig 2, p 12). The oxygen may be present in a monomer or at the end of another alcohol chain. With this model, the increase in relaxation time of the principal dispersion in pure alcohols as the length of the hydrocarbon chain is increased occurs because the total concentration of hydroxyl groups decreases with increasing hydrocarbon chain length, thus decreasing the probability that an oxygen atom will be favourably oriented for a switch.

When water is added to an alcohol, as the alcohol chains are shortened, there will be more chain ends and thus more oxygen atoms available for a switch. In addition, the presence of water molecules causes an increased density of hydroxyl groups which will further enhance the probability of an oxygen atom being favourably
oriented for a switch. This combination of increased chain ends and increased density of hydroxyl groups would be expected to lead to a progressive reduction in relaxation time when water is added to an alcohol.

Although it has been suggested that steric factors limit the association in t butanol to small size complexes (69), in contrast with the chain-association model proposed for cyclohexanol (17), the relaxation data for these two alcohols does not support this proposal. The variation of $\tau$ with water content for both cyclohexanol and t butanol is similar except for the substantially higher $\tau$ value of cyclohexanol, which on the basis of the Sagal model, will be due to the lower concentration of hydroxyl groups in this alcohol. Both of these alcohols also have similar values for both $\epsilon_s$ and the Kirkwood $g$ factor for which $g$ values of 2.12 for t butanol (18) and 2.50 for cyclohexanol (17) have been reported. When account is taken of the uncertainty in the value of $\epsilon_\infty$ and thus of $g$ for both of these alcohols, the correct $g$-values for these two alcohols could be very similar. Since chain association has been proposed for the pure alcohol cyclohexanol, it is suggested that a similar mode of association occurs in t butanol.

5.1.3 Comparison with other data

The rather limited literature data on the relaxation times of alcohol-water mixtures reveal an almost linear variation of $\tau$ with mole fraction of water, $x$, in
Relaxation time $\tau$, against mole fraction of water, $x$, for methanol and 1-propanol-water mixtures.

$\triangle$ = methanol-water mixtures

$\circ$ = 1 propanol-water mixtures
methanol-water mixtures at 20° C (65). In contrast, 1 propanol-water mixtures at 20° C show a rapid fall in \( \tau \) with \( x \) up to about 0.3 mf above which \( d\tau/dx \) is much lower (65, 171). The graphs of \( \tau \) against \( x \) for methanol- and 1 propanol-water mixtures given in Figure 43 reveal that, although the dependence of \( \tau \) on \( x \) in 1 propanol-water mixtures is significantly different from that in methanol-water mixtures, there is no evidence of deviation from a single function. The data of Tjia (59) on 1 heptanol-water mixtures at up to 0.115 mf of water at -10° C reveal a very small change in \( \tau \) for \( x \) between zero and 0.05 mf above which \( d\tau/dx \) is rather higher up to the highest water content studied. There is no evidence of deviation from a single function in Tjia's 1 heptanol-water data.

The graphs of relaxation time \( \tau \) against mole fraction of water \( x \) for the alcohol-water mixtures studied in this work (Figures 27 and 28) reveal that the relaxation behaviour of cyclohexanol-water mixtures may be described by two separate functions which meet at about 0.20 mf of water. It is also possible that there is similar behaviour in the t butanol-water mixtures at about 0.15 mf of water.

5.1.4 Evidence for associated species

It is worthy of note that aqueous mixtures of both t butanol and cyclohexanol exhibit a minimum in the static permittivity, \( \epsilon_s \), which at the measurement
FIGURE 43B

The 4A/W Species
temperature of 25° C used in these relaxation studies, is at 0.14 mf of water for t butanol (7) and 0.20 mf for cyclohexanol (8). It is thus evident that the possible change in relaxation behaviour for both t butanol- and cyclohexanol-water mixtures occurs at a similar composition to that at which \( \varepsilon_s \) is a minimum.

The occurrence of a minimum in \( \varepsilon_s \) in both t butanol- and cyclohexanol-water mixtures has been attributed to the formation of an associated species in which four alcohol molecules are H-bonded to one water molecule (7,8), and additional support for this 4A/W species interpretation has been obtained from nmr and viscosity data (8). In view of the correlation between the possible change in relaxation behaviour and the \( \varepsilon_s \) minimum, it is suggested that the relaxation behaviour could similarly be due to the formation of a 4A/W species.

5.1.5 **Effect of associated species on relaxation time**

The \( \frac{d\tau}{dx} \) value in alcohol-water mixtures should be affected if specific associated species are formed. Since the 4A/W model of Brown and Ives (7) for the t butanol-water system was also favoured by Lawrence et al (8) for the cyclohexanol-water system, an effect on the relaxation behaviour by this species would be expected here. The model favoured by these authors is given in Figure 43B.
In this associated species, there will be more shielding of the two alcohol hydrogen atoms which are H-bonded to the oxygen atom of the water molecule (A₃ and A₄) than for the other two H-bonded alcohol atoms. This shielding effect would be expected to reduce the likelihood of a switch and thus for alcohols in which such an associated species is present, a change in the variation of relaxation with water content would be expected in that dτ/dx will be lower at mole fractions of water above that required for formation of the 4A/W complex. The observed lower value of dτ/dx at values above that corresponding to the minimum in εₛ is thus consistent with such a 4A/W model proposed for both t butanol- and cyclohexanol-water mixtures. It should be added that since a variety of species are likely to be formed on addition of water to an alcohol, it is not surprising that the dτ/dx change is not well defined.

The more limited relaxation data for the 1 butanol- and 1 heptanol-water mixtures studied in this work show a monotonous fall in relaxation time on addition of water and thus the presence of specific complexes such as the 4A/W associated species is not revealed, although there is possibly slight evidence for complex formation in the 0.35 mf 1 butanol mixture. Specific association complexes in 1 butanol-water mixtures have not been proposed but the presence of a 4A/W complex in 1 heptanol-water mixtures was proposed by Lawrence et al (8), even
though at temperatures below 35° C a continuing decrease in $\varepsilon_s$ was observed at mole fractions of water higher than 0.2 mf. This effect was attributed to reduction of the average dipole moment of the species by additional H-bonding of the peripheral alcohol molecules of the 4A/W complex causing the water to effectively cross-link alcohol molecule chains. With this model, even more shielding than that exhibited by the single 4A/W complex would be expected causing a further reduction in the likelihood of a switch and thus giving a possibly almost constant value of $d\tau/dx$ at compositions above 0.2 mf of water. Since such behaviour is not exhibited in the results in this work, these proposals of Lawrence et al concerning 4A/W complex formation in 1 heptanol must be considered to be open to doubt. However, it is difficult to be unequivocal in describing complex formation in alcohols because in addition to linear species, it is agreed that cyclic species are also present in pure alcohols (2). It should be added that for 1 heptanol in particular, Bordewijk et al (3) considered effects due to cyclic species to be important. If indeed in addition to linear species, cyclic species are also present in the pure alcohol 1 heptanol it is not surprising that rather different relaxation behaviour is observed.

Since the longer alkyl chain n alcohols generally exhibit a fall in permittivity on addition of water, the association between the water and alcohol molecules in
these alcohols could be related to the formation of a low dipole moment species rather than to the high dipole moment 4A/W type proposed by Brown and Ives (7) and Lawrence et al (8). Tjia (59) suggested that in describing the behaviour of alcohol-water mixtures allowance should be made for the existence of at least two kinds of complexes where one has a relatively high dipole moment and the other a relatively low dipole moment. If the association between 1 heptanol and water does involve more than one type of associated species, then on the basis of the 'switch' model, there is likely to be a contribution to the dielectric relaxation due to shielding arising from the structure of the various species. Since there is no information available on the structure of any other species in 1 heptanol-water mixtures, it is impossible to assess the effect of such species on the relaxation behaviour. However, if there are contributions by other species, then the 4A/W contribution to the relaxation might well be masked by these other species and thus the apparent discrepancy between the relaxation data in this work and the results of Lawrence et al (8) could be resolved.

The results of Tjia for 3 heptanol-water mixtures at -70° C in which \( \tau \) remained constant for mole fractions of water between 0.020 and 0.086 also exhibit a minimum in \( \varepsilon_s \) at about 0.04 mf of water. It is tempting to
suggest that the relaxation time variation with water content, $\frac{d\tau}{dx}$, is linked with the occurrence of an $\epsilon_s$ minimum. In this case, it is hardly likely to be due to the formation of a 4A/W associated species, but it is possible that a complex involving association of water with a rather larger number of alcohol molecules has been formed and since the behaviour of $\frac{d\tau}{dx}$ and $\epsilon_s$ resembles that of the t butanol- and cyclohexanol-water mixtures studied in this work, it is suggested that these low temperature results of Tjia are more likely to be due to the formation of an associated species than to inhomogeneity in the liquid as Tjia proposed. If this behaviour is due to the formation of an associated species, it further reinforces proposals that alcohol-water mixtures can contain a number of associated species of different types.

Although, as already noted, it is considered that the variation of $\tau$ with mole fraction of water $x$ in 1 propanol-water mixtures at $20^\circ$ C does not exhibit any deviation from a single function, there is some similarity in the $\frac{d\tau}{dx}$ variation with the data in this work for t butanol- and cyclohexanol-water mixtures. It might therefore be considered possible that there is evidence for the 4A/W species in 1 propanol-water mixtures. However, since there is no minimum in $\epsilon_s$ in these mixtures at $20^\circ$ C, it must be presumed that either there is no 4A/W associated species present or that there are
a number of different species occurring which effectively mask the contribution by the 4A/W type.

Since 1 propanol has a short alkyl chain, a greater number of associated species in aqueous mixtures can be expected. Assuming the pure alcohol contains chains of indefinite length, addition of water is considered to cause chain breakage and thus, whether or not a 4A/W species is formed, an initial rapid fall of $\tau$ with increasing water content is expected. If it is supposed that a 4A/W species is formed, then because the alcohol is miscible with water, it must also be presumed that further addition of water above that required for the 4A/W species leads to the formation of small sized species such as 3A/W and 2A/W types. A possible 3A/W species is one which is similar to the 4A/W already discussed but without one of the peripheral alcohol molecules ($A_1$ or $A_2$ in Fig 43B). A 2A/W species would then be one in which both peripheral alcohol molecules are absent. Comparing this 2A/W species with the 4A/W type and noting that, in a given volume, a mixture containing only the 4A/W type (0.2 mf of water) will contain a smaller number of such species than one which contains only the 2A/W type (0.33 mf of water), it can be argued that the number of oxygen atoms favourably oriented for a switch is significantly higher in the 2A/W mixture. It would thus be expected that the 0.33 mf mixture will have a significantly lower
relaxation time than the 0.2 mf one which is not in agreement with the experimental data which shows a relatively small change in $\tau$ over this concentration range. It is thus concluded that the presence of specific species such as the 4A/W type in 1 propanol-water mixtures is difficult to maintain even if $d\tau/dx$ is not describable by a single function.

5.1.6 Conclusions on alcohol-water mixtures

It is concluded that if the variation of relaxation time with water content for both t butanol- and cyclohexanol-water mixtures is describable by two separate functions and that, in addition, the data for 1 propanol-water mixtures is describable by a single function, then there is evidence that the relaxation behaviour is modified by the formation of the 4A/W complex proposed by other workers for the t butanol- and cyclohexanol-water systems. This is because the change in behaviour of $d\tau/dx$ occurs at a similar composition to that at which the $\varepsilon_S$ minimum occurs. The results for 1 butanol- and 1 heptanol-water mixtures do not reveal the presence of the 4A/W aggregate.

The fall of relaxation time when water is added to an alcohol is considered to be satisfactorily accounted for by a switch model based on the proposals of Sagal (35).

5.1.7 Further work

In order to gain more information on the contribution or otherwise of the proposed 4A/W aggregate to the dielectric
relaxation, it is highly desirable that studies be made using frequency domain measuring equipment which is capable of giving more precise values for relaxation times. In addition, further investigation is required to determine the correct values of $\varepsilon_\infty$ for both pure alcohols and alcohol-water mixtures. If this is done, it will open the higher frequency behaviour of the dielectric dispersion of these systems to more certain interpretation. This will also enable a more precise value for the $g$ factor to be obtained, and thus perhaps give more information on association behaviour. Further information on this behaviour may possibly be obtained from activation enthalpy data.

5.2 Surfactants

5.2.1 Static permittivity $\varepsilon_S$

The results for $C_{12}E_4$, $C_{12}E_6$ and $C_{12}E_8$ given in Figure 29 reveal a progressive increase in $\varepsilon_S$ as the length of the polar ethylene oxide chain is increased. However, the change in $\varepsilon_S$ between $C_{12}E_4$ and $C_{12}E_8$ at a given temperature is small, indicating the substantial depolarising effect of the dodecyl ether chain. On the basis of permittivity values, Brij 30 is much closer to $C_{12}E_6$ than to $C_{12}E_4$. This effect is doubtless due to contributions from longer ethylene oxide chain components present in the surfactant. Since polarisation is related to the square of the dipole moment, it is to be expected that, although the average ethylene oxide chain length $\bar{E}_n$
is 4, the measured permittivity will be slightly higher than that of C12E14 as was observed.

The almost identical temperature dependences of the static permittivity \( \Delta \varepsilon_s / \Delta T \) indicate that for all the surfactants studied, very similar structural changes occur when the temperature is varied. The negative temperature dependence of \( \varepsilon_g \) for all the surfactants is in accord with predictions given by the homogeneous mixture equations [2•Q and [2•*0 if it is assumed that the gyz term is constant over the temperature range studied.

5.2.2 Relaxation behaviour of Brij 30

Although the observed time domain relaxation was considered to be too rapid for precise determination of a relaxation time, the value of \( x \) is within the range 50 to 100 ps which is much longer than that of pure water and is approximately a factor of 2.5 faster than the value of 197 ps obtained by Davies et al (192) for tetraethylene glycol (E^) at 20° C. These authors suggested that the dielectric relaxation was due to movement of the whole molecule during reorientation.

Viscosities (n) of Brij 30 and compared using an Ostwald viscometer at the temperature of 34.0° C, show Brij 30 to be a factor of 19.7 higher than that of E^.

Using the Debye expression for the molecular relaxation time \( x = 4\pi n a^3 \) where \( a \) is the radius of the molecule
with the assumption that \( \tau^* = \tau \), putting \( \tau_E = 2.5 \) \( \tau_{\text{Brij 30}} \) gives the result \( a_{\text{Brij 30}} \approx 0.3 a_{E_4} \). The lower value of 'a' correlates with the shorter relaxation time of Brij 30. It is therefore considered that the relaxation of Brij 30 is also due to movement of the whole molecule. The higher \( \tau \) value for \( E_4 \) would also be expected due to the more extensive H-bonding in polyethylene glycols. This is indicated in the high g-value of 2.7 at 20\(^\circ\)C for ethylene glycol (40). The presence of the alkyl ether chains in Brij 30 will result in reduced association analogous to the behaviour of H-bonded molecules diluted in non-polar solvents, and thus give a lower value for \( \tau \).

5.3 Tetra ethylene glycol (E\(_4\))-water mixtures

The experimental values together with those given by the ideal mixing equation [2.5] are given in Table 63 and Figure 38. In order to obtain the appropriate volume fraction, the density was measured in this laboratory using a standard 25 ml SG bottle. A value of 1.129.10\(^3\) kg m\(^{-3}\) at the measurement temperature was obtained.
Table 63

Static permittivity of tetra ethylene glycol-water mixtures.

<table>
<thead>
<tr>
<th>Mass fraction of E₄</th>
<th>Temperature °C</th>
<th>Experimental Value</th>
<th>Ideal Mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>25.0</td>
<td>74.2</td>
<td>73.1</td>
</tr>
<tr>
<td>0.200</td>
<td>25.0</td>
<td>69.6</td>
<td>67.7</td>
</tr>
<tr>
<td>0.300</td>
<td>25.0</td>
<td>65.3</td>
<td>62.2</td>
</tr>
<tr>
<td>0.400</td>
<td>25.0</td>
<td>60.3</td>
<td>56.7</td>
</tr>
<tr>
<td>0.500</td>
<td>25.0</td>
<td>55.3</td>
<td>50.9</td>
</tr>
<tr>
<td>0.600</td>
<td>25.0</td>
<td>49.5</td>
<td>45.1</td>
</tr>
<tr>
<td>0.700</td>
<td>25.0</td>
<td>43.4</td>
<td>39.0</td>
</tr>
<tr>
<td>0.800</td>
<td>25.0</td>
<td>36.7</td>
<td>32.9</td>
</tr>
<tr>
<td>0.900</td>
<td>25.0</td>
<td>28.8</td>
<td>26.6</td>
</tr>
</tbody>
</table>

In these mixtures, the permittivity values are higher than those given by the ideal mixing equation. This behaviour is attributed to co-operative molecular association between the E₄ and water causing an enhanced dipole moment as occurs in alcohols. Deviations from the ideal mixing equation have been observed for many mixtures of associated liquids, the extensive studies of Decroocq (56) being worthy of note. In aqueous
solutions, permittivity values higher than those given by the ideal mixing equation are exhibited by methanol (56), ethylene glycol (55) and polyethylene glycol $E_n$ \{n = 91\} (192). Davies et al (192) made the comment that the observed permittivity behaviour in $E_n$ \{n = 91\} "is surprising and is not understood".

5.4 Surfactant-water binary mixtures

The regions in which isotropic solutions occur in aqueous mixtures of $C_{12}E_4$ and Brij 30 are indicated on the phase diagrams given in Figure 44 (page 250). Comparison of the two diagrams reveals similarity in the surfactant-rich section but in the water-rich section, there is the important difference that $C_{12}E_4$ has two separate clear regions whereas Brij 30 has only one.

The phase diagram for aqueous mixtures of $C_{12}E_6$ given in Figure 45 reveals that isotropic solutions are formed (p 263) in water-rich mixtures over a much larger temperature range than in the $C_{12}E_4$ case. This is due to the longer oxyethylene chain giving greater solubility. This aspect is emphasised in the phase diagram for aqueous
Phase diagrams for binary mixtures of surfactant with water

Temperature/°C

a) C₁₂E₄

- WATER + L₂
- WATER + L₃
- LIQUID (L₃)
- L₃ + LAM
- WATER + LAM
- LIQUID (L₁)
- WATER + L₁
- LIQUID (L₁)

%C₁₂E₄ (by mass)

(b) Brij 30

Temperature/°C

- WATER + L₂
- LIQUID (L₂)
- WATER + LAM
- LAMellar

%Brij 30 (by mass)
mixtures of \( \text{C}_{12}\text{E}_{8} \) (Figure 45) which reveal the presence of isotropic solutions over a wide temperature range for an even wider range of compositions than in the \( \text{C}_{12}\text{E}_{6} \) case. In order to explain the observed dielectric behaviour of the binary mixtures, a number of mixture equations have been tested. In the first instance, spherical micelles have been assumed and the ideal mixing [2.5], Rayleigh [2.14], Bruggeman [2.16], Looyenga [2.17], Böttcher [2.19], Hanai O/W [2.29] and Hanai W/O [2.31] equations have been applied. The permittivity of water at the measurement temperature was obtained using the precise relation given by Malmberg and Maryott (43) and that of the surfactants from the data obtained in this work. The volume fraction of the component liquids was obtained from the known mass fraction values together with the appropriate density values at the measurement temperature. The temperature dependence of the density was assumed to be the same for all the surfactants and the value of \( 7.5 \times 10^{-4} \, \text{kgm}^{-3} \, ^{\circ}\text{C}^{-1} \) obtained for \( \text{C}_{12}\text{E}_{4} \) was used. The densities of water were obtained from Kaye and Laby (193).

5.4.1 \( \text{C}_{12}\text{E}_{4} \)- and Brij 30-water mixtures

The permittivity values given by the mixture equations together with the experimental values for (i) the \( \text{C}_{12}\text{E}_{4} \)-water mixtures are given in Table 64 and Figure 32 and (ii) the Brij 30-water mixtures are given in Table 65 and
Table 64
Comparison of experimental static permittivity values
with values given by mixture equations.

<table>
<thead>
<tr>
<th>C12E4-water mixtures</th>
<th>0.00%</th>
<th>0.09%</th>
<th>0.18%</th>
<th>0.27%</th>
<th>0.36%</th>
<th>0.45%</th>
<th>0.54%</th>
<th>0.63%</th>
<th>0.72%</th>
</tr>
</thead>
<tbody>
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<td>9.6</td>
<td>6.9</td>
<td>10.8</td>
<td>14.0</td>
<td>17.2</td>
<td>20.4</td>
<td>23.6</td>
<td>26.8</td>
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</tr>
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<td>19.9</td>
<td>23.1</td>
<td>26.3</td>
<td>29.4</td>
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<td>19.2</td>
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<td>25.5</td>
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<td>11.8</td>
<td>14.9</td>
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<td>11.6</td>
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* The mixture for p = 0.60 would not turn fully transparent.

Figure 33: (NB Since the Bruggeman equation gives almost identical values to the Hamai equation when the dispersion is O/W, only the Hamai equation has been used for such dispersions.)
Table 65

Brij 30–water mixtures

Comparison of experimental static permittivity values with values given by mixture equations

<table>
<thead>
<tr>
<th>Mass fraction</th>
<th>Brij</th>
<th>Water</th>
<th>Rayleigh</th>
<th>Bruggeman</th>
<th>Börrnai–Hani</th>
<th>Rayleigh</th>
<th>Bruggeman</th>
<th>Börrnai–Hani</th>
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<tr>
<td>P/C</td>
<td>57.1</td>
<td>54.5</td>
<td>61.1</td>
<td>58.6</td>
<td>58.7</td>
<td>56.3</td>
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<td>0.101</td>
<td>0.202</td>
<td>0.300</td>
<td>0.400</td>
<td>0.500</td>
<td>0.600</td>
<td>0.700</td>
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</table>
Comparison of the permittivity values given by the various mixture equations with the experimental values reveals that at the measurement temperatures, none of the equations gives \( \varepsilon \) values close to the experimental ones over the whole composition range. However, for both the \( \text{C}_{12}\text{E}_4^- \) and Brij 30-water mixtures, a number of conclusions can be drawn.

(a) the ideal mixture equation is clearly unsuitable over the whole composition range in giving much too high values for the permittivity.

(b) substantially better agreement with the experimental data is given by both the Rayleigh O/W and Hanai O/W equations than with either the Böttcher O/W or the Looyenga equations.

(c) for \( p > 0.3 \), the Rayleigh and Hanai equations for O/W dispersions give much better agreement with experimental values than for W/O dispersions; the Hanai O/W equation gives closest agreement.

(d) for \( p < 0.4 \), the experimental values for the low temperature mixtures of \( \text{C}_{12}\text{E}_4^- \) are in good agreement with values given by the Hanai O/W equation but both the high temperature experimental values for \( \text{C}_{12}\text{E}_4^- \) and those for the Brij 30 mixtures are significantly lower than the values given by the Hanai O/W equation.

Since the permittivity values given by the Hanai O/W equation give the closest agreement with experimental values over the range \( p = 0.6 \) to \( 0.9 \), it is considered
that at the measurement temperatures, these micellar mixtures of the surfactants \( \text{C}_{12}\text{E}_4 \) and Brij 30 are water continuous over the \( p = 0.6 \) to 0.9 range of surfactant concentration and that the dielectric behaviour is best described by a heterogeneous mixture model. Since the low surfactant concentration mixtures give good agreement with the Hanai O/W equations at low temperatures, it is considered that the low surfactant concentration mixtures are also water continuous.

In the low surfactant concentration mixtures of both Brij 30 and \( \text{C}_{12}\text{E}_4 \) at the higher temperature, the temperature range for transparency was typically only about \( 1^\circ \text{C} \). Thus these studies were of necessity performed at a temperature only just below the cloud point. Since it is well established that very rapid micellar growth occurs at the cloud point (80), it was considered that the anomalous dielectric behaviour of these mixtures could be related to the presence of large micelles. This is supported by the appearance of a marked blue opalescence in these mixtures which was particularly evident at the lowest concentrations. In order to account for the marked deviations between the experimental data and the Hanai O/W values in these high temperature solutions, two approaches have been considered, these are (i) deviation from spherical shape causing a reduction in the measured permittivity value and (ii) secondary aggregation effects causing an increase in the effective volume of the dispersed oil phase.
(i) It has been shown by Tanford et al (74) that non-ionic surfactants form oblate spheroidal rather than spherical micelles at low surfactant concentrations. In order to determine the effect of such a spheroidal shape on the permittivity, the extended form of the Bruggeman equation derived in this work (equation [2.64]) has been used to calculate the shape factor $A_a$ required to attain agreement between calculated values and the higher temperature experimental data. The required $A_a$ values together with the axial ratios $b/a$ given by equation [2.40] to obtain agreement with the experimental values for the $C_{12}E_4$-water mixtures at low concentration are given in Table 66.

**Table 66**

Micelle shape factors for $C_{12}E_4$-water mixtures

<table>
<thead>
<tr>
<th>Mass Fraction of Surfactant, $p$</th>
<th>Shape Factor $A_a$</th>
<th>Axial Ratio $b/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.099</td>
<td>0.68</td>
<td>3.6</td>
</tr>
<tr>
<td>0.198</td>
<td>0.60</td>
<td>2.6</td>
</tr>
<tr>
<td>0.301</td>
<td>0.54</td>
<td>2.1</td>
</tr>
<tr>
<td>0.400</td>
<td>0.48</td>
<td>1.7</td>
</tr>
<tr>
<td>0.500</td>
<td>0.39</td>
<td>1.2</td>
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</table>

For all compositions $A_a > \frac{1}{3}$, indicating an oblate rather than prolate spheroidal shape which agrees with the proposals of Tanford et al (74). The results also indicate a steadily decreasing eccentricity towards
spherical shape as the proportion of surfactant is increased. The values of $A_a$ required to obtain agreement with the experimental values for Brij 30-water mixtures at low concentration are given in Table 67.

Table 67
Micelle shape factors for Brij 30-water mixtures

<table>
<thead>
<tr>
<th>Mass fraction of Surfactant, $p$</th>
<th>Shape Factor $A_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.101</td>
<td>0.60</td>
</tr>
<tr>
<td>0.202</td>
<td>0.53</td>
</tr>
<tr>
<td>0.300</td>
<td>0.48</td>
</tr>
<tr>
<td>0.400</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Comparison of these $A_a$ values with those for the $C_{12}E_4$ mixtures given in Table 66 reveals a slightly lower value of $A_a$ at the lowest concentration of surfactant corresponding to an axial ratio $(b/a)$ of 2.6:1.

The $(b/a)$ values for both surfactants are similar to those reported by Tanford et al (74) for micelles in aqueous solutions of $C_{12}E_8$ where values in the range 2.5:1 to 1.9:1 were reported. The rather higher figure of 3.5:1 for the $C_{12}E_4$ mixtures at the lowest concentration is to be expected because, as reported by Tanford et al (74, 194), reduction in the length of the oxyethylene chain produces a reduction in the repulsive forces between the surfactant headgroups which leads to an
increase in the aggregation number and thus micelle size. These authors pointed out that large size can only be achieved by a change from spherical to spheroidal shape due to a limitation that one dimension of the hydrocarbon core of the micelle cannot exceed the length of two fully extended alkyl chains. Thus increased aggregation number must be accompanied by a more spheroidal shape which is in agreement with the higher \((b/a)\) values obtained in this work.

The lower \((b/a)\) value obtained for the Brij 30 mixtures at any given surfactant concentration is probably due to contributions by the lower aggregation number \(E_n\) \((n > 4)\) components present in this surfactant.

It is considered that neither the Böttcher \([2.19]\) nor the Looyenga \([2.17]\) equations are suitable for describing the above dielectric behaviour even when they are used in the generalised forms of Polder and van Santen \([2.49]\) for the Böttcher equation and equation \([2.78]\) derived in this work for the Looyenga equation. Both equations \([2.49]\) and \([2.78]\) give similar results to those of the generalised Hanai-Bruggeman equations derived in this work, in that for oblate spheroids the permittivity is reduced and for prolates it is increased. However application of \([2.49]\) and \([2.78]\) to this data would required postulation of a much wider range of the shape factor \(A_a\) to account for the fact that at some
compositions, the spheroids are oblate and at others prolate in shape.

Another point that should be noted is that the equations of Grosse and Greffe ([2.46] to [2.48]) are considered to be unsuitable for application to the experimental data in this work because, although their equations give an increased permittivity for the prolate spheroidal shape, for an oblate shape the permittivity change is negligibly small.

(ii) Interpretation of the higher temperature dielectric behaviour of these surfactant water mixtures based on secondary aggregation poses difficulties because there is uncertainty as to whether or not such aggregation involves association of the oxyethylene chains between different micelles. If the proposed secondary aggregation does involve such association, as suggested by Tanford et al (74), it is quite possible that the dielectric properties will be affected. However Staples and Tiddy (80) have suggested that this association is unlikely because, calculations using cloud point data showed the average distance between micelles to be too large. If it is assumed that this association does not occur, but that the primary micelles form clusters and act as rigid spheres, for a close-packed structure they will only be able to occupy a maximum of 74% of the total volume of the aggregated micellar clusters. The
26% interstitial volume between the micelles can be considered as effectively increasing the total volume of the dispersed oil phase and would thus give a reduction in the measured permittivity. However, inspection of the results given in Figure 32 reveals that for the p = 0.099 mixture, the required mass fraction to achieve agreement between the Hanai O/W value and the experimental value is approximately 0.2. This doubling of the effective mass fraction of the dispersed phase cannot be justified on the basis of the increase in volume arising from close-packing considerations. However, such an increase could be accounted for by a more loosely-packed structure.

An alternative suggestion based on secondary aggregation is that the 26% interstitial volume between the aggregated micelles is filled with unassociated water. This would similarly produce a reduction in permittivity because the volume fraction of the continuous aqueous phase would have been reduced due to some of the water being used to fill the interstitial volume. However, the required volume fraction correction is still too large and a more loosely-packed structure would again be required.

It is concluded that the C_{12}E_{4}− and Brij 30-water mixtures contain normal micelles over the whole composition range. For mass fractions of surfactant above 0.5, the static permittivity values are in good agreement with those given by the Hanai-Bruggeman mixture equation for
spherical dispersions. At lower surfactant concentrations, the permittivity values of the C₁₂E₄ mixtures at the lower temperature give similarly good agreement with the predictions of the above equation but deviations occur in both the C₁₂E₄ mixtures at the higher temperature and the Brij 30 mixtures.

The deviations can be accounted for by proposing oblate spheroidal micelle shape with an axial ratio of 3.6:1 in C₁₂E₄ and 2.6:1 in Brij 30 at the lowest concentration studied, which with increase of surfactant concentration, progressively changes towards spherical shape.

An alternative interpretation to account for the deviations between theory and experiment at low surfactant concentration is based on secondary aggregation involving loose-packing of the primary micelles.

5.4.2 C₁₂E₄-water mixtures
Since the Looyenga [2.17] and Böttcher [2.19] equations have already been found to be unsuitable for the C₁₂E₄ and Brij 30 mixtures, only the ideal mixing [2.5], Rayleigh O/W [2.14] and Hanai O/W [2.29] equations have been applied here. The permittivity values given by these equations together with the experimental values are given in Table 68 and in Figure 34.
Table 68  
C\textsubscript{12}E\textsubscript{6}-water mixtures  
Comparison of experimental static permittivity values with values given by mixture equations.

<table>
<thead>
<tr>
<th>Mass fraction of Surfactant, p</th>
<th>Temperature /°C</th>
<th>Experimental Value</th>
<th>Ideal Mixing</th>
<th>Rayleigh O/W</th>
<th>Hanai O/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.097</td>
<td>25.4</td>
<td>69.1</td>
<td>71.0</td>
<td>68.2</td>
<td>68.1</td>
</tr>
<tr>
<td>0.201</td>
<td>24.8</td>
<td>60.8</td>
<td>63.5</td>
<td>58.7</td>
<td>58.1</td>
</tr>
<tr>
<td>0.300</td>
<td>35.2</td>
<td>49.5</td>
<td>53.7</td>
<td>48.0</td>
<td>47.0</td>
</tr>
<tr>
<td>0.400</td>
<td>43.3</td>
<td>39.7</td>
<td>45.2</td>
<td>39.2</td>
<td>37.8</td>
</tr>
<tr>
<td>0.500</td>
<td>44.7</td>
<td>32.8</td>
<td>38.3</td>
<td>32.4</td>
<td>30.6</td>
</tr>
<tr>
<td>0.600</td>
<td>66.6</td>
<td>23.5</td>
<td>28.8</td>
<td>23.9</td>
<td>22.3</td>
</tr>
<tr>
<td>0.699</td>
<td>66.6</td>
<td>18.7</td>
<td>23.0</td>
<td>18.9</td>
<td>17.4</td>
</tr>
<tr>
<td>0.798</td>
<td>51.2</td>
<td>15.3</td>
<td>18.4</td>
<td>15.1</td>
<td>14.0</td>
</tr>
<tr>
<td>0.880</td>
<td>51.2</td>
<td>12.4</td>
<td>13.3</td>
<td>11.2</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Even though the micellar mixtures are again considered to be water continuous, they exhibit significantly different behaviour from that of the C\textsubscript{12}E\textsubscript{4} and Brij 30 mixtures. Of the equations used, the Rayleigh O/W gives in general closest agreement with the experimental data, the agreement for p between 0.4 and 0.8 being very good. However for p ≤ 0.3 and p = 0.9, significant deviations are evident and for both low and high values of p, the ideal mixing equation is almost as good as the Rayleigh O/W.
Phase diagrams for binary mixtures of surfactant and water

(a) $C_{12}E_8$

(b) $C_{12}E_6$
If a prolate spheroidal shape is proposed, the Hanai O/W values can be made to agree with the experimental values by using the appropriate $A_a$ value in equations [2.64] or [2.72]. There is some justification for proposing micelles of this shape because the phase diagrams for aqueous mixtures of $C_{12}E_6$ and $C_{12}E_8$ (Figure 45) reveal the presence of a hexagonal liquid crystalline phase containing cylindrical micelles at surfactant concentrations within the range 40 to 60% whereas in $C_{12}E_4$ and Brij 30 (Figure 44) only a lamellar phase occurs. It is quite possible that over the concentration range at which the hexagonal phase occurs, when the temperature is raised so that an isotropic solution is formed, this solution contains prolate spheroidal micelles. However such a proposal cannot be maintained at concentrations of 60% and above because a lamellar liquid crystalline phase forms at lower temperatures at these concentrations. Since the agreement with the Rayleigh equation is good over the range $p = 0.4$ to 0.8, it is considered that a prolate spheroidal shape interpretation is inadequate.

As the aggregation number in these mixtures is lower than that in both the $C_{12}E_4$ and Brij 30 solutions (74), the micelle sizes will be smaller and thus effects due to deviation from spherical shape and secondary aggregation are less likely. It is suggested that the better agreement with the Rayleigh rather than the Hanai equation is related to the micelles in these mixtures being of
smaller size. The deviation at high surfactant concentration could be due to limitations of the Rayleigh equation at these concentrations but this will not be the case for the p ≤ 0.3 mixtures which have unexpectedly high permittivity values. These higher values could be due to deviation from spherical to prolate spheroidal shape at very low surfactant concentrations, because deviation from spherical shape is most likely at these concentrations.

5.4.3 $\text{C}_{12}\text{E}_8$-water mixtures

As in the $\text{C}_{12}\text{E}_6$-water mixtures, only the ideal mixing \[2.5\], Rayleigh O/W \[2.14\] and Hanai O/W \[2.29\] equations have been applied here.

The permittivity values given by these equations together with the experimental values are given in Table 69 and Figure 35.

Table 69

$\text{C}_{12}\text{E}_8$-water mixtures

Comparison of experimental static permittivities with values given by mixture equations.

<table>
<thead>
<tr>
<th>Mass fraction of Surfactant, p</th>
<th>Temperature $^\circ$C</th>
<th>Experimental Value</th>
<th>Ideal Mixing</th>
<th>Rayleigh O/W</th>
<th>Hanai O/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>25.0</td>
<td>57.6</td>
<td>59.0</td>
<td>56.8</td>
<td>56.7</td>
</tr>
<tr>
<td>0.200</td>
<td>25.0</td>
<td>50.6</td>
<td>53.0</td>
<td>49.2</td>
<td>48.8</td>
</tr>
<tr>
<td>0.300</td>
<td>25.0</td>
<td>44.2</td>
<td>47.1</td>
<td>42.3</td>
<td>41.5</td>
</tr>
<tr>
<td>0.400</td>
<td>25.0</td>
<td>38.1</td>
<td>41.2</td>
<td>35.9</td>
<td>34.7</td>
</tr>
<tr>
<td>0.500</td>
<td>25.0</td>
<td>32.3</td>
<td>35.2</td>
<td>29.9</td>
<td>28.4</td>
</tr>
</tbody>
</table>
Table 69 (Continued)

<table>
<thead>
<tr>
<th>Mass fraction of Surfactant</th>
<th>Temperature °C</th>
<th>Experimental Values</th>
<th>Ideal Mixing</th>
<th>Rayleigh O/W</th>
<th>Hanai O/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.600</td>
<td>25.0</td>
<td>26.5</td>
<td>29.2</td>
<td>24.5</td>
<td>22.8</td>
</tr>
<tr>
<td>0.699</td>
<td>25.0</td>
<td>21.1</td>
<td>23.5</td>
<td>19.3</td>
<td>17.9</td>
</tr>
<tr>
<td>0.801</td>
<td>25.0</td>
<td>15.5</td>
<td>17.5</td>
<td>14.4</td>
<td>13.6</td>
</tr>
<tr>
<td>0.901</td>
<td>25.0</td>
<td>9.5</td>
<td>11.6</td>
<td>10.0</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Again as in the C₁₂E₆-water mixtures, the Rayleigh O/W gives closest agreement with the experimental values but in this case, the agreement is only marginally better than that given by the ideal mixing equation. These results confirm the trend of increasing permittivity at any given concentration of surfactant with increase in oxyethylene chain length, and in these mixtures there is almost equal justification for using the ideal mixing equation as for using the heterogeneous mixture equation of Rayleigh.

On the basis of an interpretation in which deviation from the ideal mixing equation is related to micelle size, it would appear that the micelles in C₁₂E₈-water mixtures are even smaller than those in the C₁₂E₆ mixtures. This conclusion gives further support to the proposal of Tanford et al (74) that for a given length of alkyl ether chain (C₁₂ in this case), increasing oxyethylene chain length leads to a progressive reduction in micelle aggregation number and thus micelle size. In addition
to smaller size, prolate spheroidal shape is also more probable in these mixtures because the \( C_{12}E_8 \) phase diagram reveals a hexagonal phase over a larger concentration range than in \( C_{12}E_6 \) and the lamellar phase is absent. As the prolate spheroidal shape gives a higher permittivity than a sphere, there could be a contribution by this shape to the permittivity.

Interpretation of the dielectric behaviour is made more complicated by the contribution due to association between the surfactant headgroups and water, which as observed in the tetra ethylene glycol-water mixture studies leads to an enhanced permittivity value. As the length of the surfactant oxyethylene chain increases, the contribution by this effect will become progressively more significant.

5.4.4 Temperature dependence of permittivity of surfactant-water binary mixtures

5.4.4.1 Mass fraction of surfactant, \( p = 0.9 \)

The results for the \( C_{12}E_4 \) and \( C_{12}E_8 \) surfactants given in Figure 36a display a monotonous fall in permittivity with increasing temperature for this concentration. Such behaviour is to be expected on the basis of both homogeneous and heterogeneous models. In the homogeneous case, increase of temperature leads to a reduction in permittivity provided that the \( g_{\mu}^2 \) term is unchanged (see eg equation \([2.3]\)). For the heterogeneous
mixture model, a fall in permittivity is expected because of the negative temperature dependence of the permittivity of both components of the mixture.

The rather smaller temperature dependence for the C_{12}E_4 mixture compared with that obtained for the C_{12}E_8 is probably due to H-bonding differences. It is possible that the behaviour is due to more pronounced micellar growth with increasing temperature in the C_{12}E_8 mixture. Since increase of micelle size has already been suggested as giving a lower permittivity value, the higher temperature dependence in the C_{12}E_8 mixture could be related to more rapid micellar growth. Alternatively if the micelles are non-spherical, the behaviour could be due to more pronounced shape changes in the C_{12}E_8.

5.4.4.2 Mass fraction of surfactant, p = 0.1

The temperature dependences of ε_s for the C_{12}E_6- and C_{12}E_8-water mixtures at p = 0.1 given in Figure 36b are identical indicating similar structural changes as the temperature is increased. It is worthy of note that there is no deviation from linearity even at the highest temperatures where more pronounced micellar growth effects might have been expected. Since in both mixtures the highest temperature was at least 10° C below the cloud point, the results are consistent with the proposal that effects such as rapid micelle growth and secondary aggregation only occur at temperatures close to the cloud point (80).
5.5 Surfactant-n-alkane binary mixtures

In order to explain the observed dielectric behaviour of the binary mixtures of Brij 30 with n-heptane, the ideal mixing [2.5], Rayleigh [2.14] for both W/O and O/W, Hanai W/O [2.31] and O/W [2.29] and Bruggeman W/O [2.16] equations have been applied taking Brij 30 as the 'water' component. The permittivity of heptane was obtained from literature data (195) and that of Brij 30, at the measurement temperature, from this work. The density of heptane at the measurement temperature was obtained from literature data (193,196).

The permittivity values given by the mixture equations together with the experimental values are given in Table 70 and Figure 39.

Table 70

Brij 30-n-heptane mixtures

Comparison of experimental static permittivity values with values given by mixture equations.
<table>
<thead>
<tr>
<th>Mass fraction of Surfactant (p)</th>
<th>Temperature /°C</th>
<th>Experimental Value</th>
<th>Ideal Mixing</th>
<th>Rayleigh W/O</th>
<th>Rayleigh O/W</th>
<th>Hanai O/W</th>
<th>Hanai W/O</th>
<th>Bruggeman W/O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>56.3</td>
<td>2.32</td>
<td>2.48</td>
<td>2.28</td>
<td>2.38</td>
<td>3.16</td>
<td>3.04</td>
<td>2.29</td>
</tr>
<tr>
<td>0.40</td>
<td>56.3</td>
<td>2.80</td>
<td>3.13</td>
<td>2.77</td>
<td>2.94</td>
<td>6.33</td>
<td>3.39</td>
<td>2.80</td>
</tr>
<tr>
<td>0.60</td>
<td>56.3</td>
<td>3.65</td>
<td>3.84</td>
<td>3.39</td>
<td>3.61</td>
<td>17.36</td>
<td>3.90</td>
<td>3.45</td>
</tr>
<tr>
<td>0.80</td>
<td>56.3</td>
<td>4.53</td>
<td>4.66</td>
<td>4.27</td>
<td>4.48</td>
<td>113.1</td>
<td>4.63</td>
<td>4.38</td>
</tr>
</tbody>
</table>

(NB Hanai O/W = Bruggeman O/W)
The agreement given by both the Rayleigh W/O and Bruggeman W/O values with the experimental data for \( p = 0.20 \) and 0.40 is very close and significantly better than that given by the ideal mixing equation. Similarly the agreement between the Rayleigh O/W and the Bruggeman O/W equations and the experimental data for high \( p \) values is also very close, with the ideal mixing equation being again less satisfactory. The Hanai W/O equation is unsatisfactory at all compositions.

The agreement of the experimental data with a W/O value at low \( p \) and an O/W value at higher \( p \) values is consistent with an interpretation in which the micellar structure is inverted (W/O) at low surfactant concentration and normal (O/W) at high concentration. It would thus appear that in the limit of \( p = 1 \) corresponding to the surfactant alone, the micelle structure is likely to be O/W. This is in agreement with the proposals of Bostock et al (81) that the surfactant is aggregated into normal micelles.

On the basis of proposals given earlier in which permittivity is dependent on micelle size, the better agreement given with the Rayleigh rather than the Hanai equations could be due to smaller sized micelles in these mixtures when compared with the binary mixtures of this surfactant with water.
Isotropic liquid regions in ternary mixtures of $C_{12}E_4$ with water and n-heptane

$T = 4^\circ C$  $I\phi \equiv$ Isotropic liquid

$T = 0^\circ C$
Isotropic liquid regions in ternary mixtures of $\text{C}_{12}\text{E}_4$ with water and n-heptane
Isotropic liquid regions in ternary mixtures of $\text{C}_{12}\text{E}_4$ with water and n-heptane
Isotropic liquid regions in n-alkane and water systems with increasing concentration of $C_{12}E_4$.

$I\phi$ = isotropic liquid

$40\%$ n-hexadecane + $60\%$ H$_2$O

$40\%$ n-decane + $60\%$ H$_2$O

$40\%$ n-heptane + $60\%$ H$_2$O
Conductivity changes with temperature in n-alkane and aqueous 0.01 M NaCl + C_{12}E_4 systems

(a) 40.3% n-heptane + 49.7% aqueous 0.01 M NaCl + 10.0% C_{12}E_4

(b) 35.9% n-decane + 54.3% aqueous 0.01 M NaCl + 9.8% C_{12}E_4

(c) 34.3% n-hexadecane + 51.7% aqueous 0.01 M NaCl + 14.0% C_{12}E_4

(d) 32.8% n-hexadecane + 49.1% aqueous 0.01 M NaCl + 18.0% C_{12}E_4
Isotropic liquid regions in ternary mixtures of Brij 30 with water and n-heptane

at 27°C

Iφ = isotropic liquid

at 20°C
FIGURE 52

Isotropic liquid regions in ternary mixtures of Brij 30 with water and n-heptane

Temperature

$40^\circ$ C

$I\phi \equiv$ isotropic liquid
5.6 **Surfactant-water-n-alkane ternary mixtures**

The isotropic liquid regions in ternary mixtures of the surfactants C\textsubscript{12}E\textsubscript{4} and Brij 30 with water and heptane are given in Figures 46 to 48, 51 and 52. Similar behaviour of the surfactants appears in the regions of low water content, but differences are evident in the regions of low surfactant content where isotropic solutions are formed with C\textsubscript{12}E\textsubscript{4} but not with Brij 30. As there is currently particular interest in ternary mixtures containing low proportions of surfactant (microemulsions), detailed attention will be given to such mixtures. The isotropic liquid regions of C\textsubscript{12}E\textsubscript{4} in n-alkane + water systems with increasing concentration of C\textsubscript{12}E\textsubscript{4} for the n-alkanes hexadecane, decane and heptane are given in Figure 49 (p 275). For all three n-alkanes there are two separate regions in which isotropic liquids appear at about 15% by mass of C\textsubscript{12}E\textsubscript{4}. However, at lower surfactant concentration, the hexadecane system displays markedly different behaviour from the other two in that below 12% by mass of C\textsubscript{12}E\textsubscript{4} no clear region occurs and between 12% and 14% of C\textsubscript{12}E\textsubscript{4} the upper and lower isotropic regions appear to merge.

The dielectric properties of the ternary systems can best be discussed by considering separately the behaviour within and outside the temperature ranges in which the mixtures form isotropic liquids.
5.6.1 Dielectric properties outside the temperature limits for isotropic liquids

The results given in Tables 59 to 62 and Figure 42 (p 230) show dielectric dispersion behaviour in the RF range as the temperature is lowered beyond the limit for isotropic liquids. The absence of dielectric dispersion at temperatures just above the cloud point is consistent with proposals that separation into two phases occurs at a temperature which is somewhat higher than the cloud point (11). At temperatures just above the cloud point, the mixture may still be regarded as a single phase system but with larger micelles. Since dielectric dispersion was not observed over the temperature range in which isotropic liquids are formed, similar behaviour would be expected just above the cloud point.

In contrast, at temperatures just below the lower limit for isotropic liquids very considerable structural changes occur for a very small temperature change, with separation into a two phase emulsion ((a), (b) and (c) in Figure 42) or formation of a liquid crystalline phase ((d) in Figure 42) depending on the composition of the mixture, occurring rapidly.

The observation of Cole-Cole arc type dispersion at these temperatures (Figure 42) is worthy of note, and it does appear that when dielectric dispersion occurs in emulsions, this type of dispersion is the norm. However,
it is considered incorrect to attribute observed Cole-Cole arc type dispersion to the presence of a heterogeneous structure as suggested by Peyrelasse et al (106) because there are a number of examples of simple liquids which also exhibit such dispersion, eg chlorinated diphenyls (135).

5.6.2 Dielectric properties of ternary mixtures within temperature range for isotropic liquids

In order to attempt to explain the dielectric behaviour of the ternary mixtures in the isotropic liquid region, two approaches based on spherical dispersions have been applied. In the first approach, it has been assumed that the dielectric properties of the mixtures are due to the water and n-alkane only and the permittivity values for spherical dispersions have been calculated using the equations of Rayleigh [2.14] for both W/O and O/W, Hanai for W/O [2.31] and O/W [2.29] and Bruggeman [2.16] for W/O.

In the second approach, the observed dielectric properties have been considered to be due to contributions from all three components of the mixture and the permittivity values have been calculated using (i) the ideal mixing equation [2.5] and (ii) spherical dispersions with shells equations of Maxwell [2.55] and [2.56] for both W/O and O/W dispersions.
The permittivities of the hydrocarbons heptane and decane at each measurement temperature were obtained from literature data (195). As the permittivity of hexadecane was not given, a value of 2.04 was adopted based on extrapolation of the literature values in reference 195 for the C_5 to C_{12} n-alkanes. The permittivity of water at each measurement temperature was calculated from the relation given by Malmberg and Maryott (43). The densities of the hydrocarbons were obtained from literature data (196). The densities of the hydrocarbons were all assumed to have the same temperature dependence and a value for this based on literature data for pentane (193) was used. The permittivities of the surfactants at each measurement temperature were obtained from the values given in this work.

The permittivity values given by the various mixture equations together with the experimental values for the C_{12}E_4 ternary mixtures are given in Table 71 and 72 and the Brij 30 ternary mixtures in Table 73.
5.6.2.1 Ternary mixtures of n-alkane-water-C_{12}E_{8}

5.6.2.1.1 Microemulsion region

Table 71

Comparison of experimental static permittivity values with values given by mixture equations.

<table>
<thead>
<tr>
<th>Mass fraction fraction of water</th>
<th>Mass fraction fraction of n-alkane</th>
<th>Temperature (°C)</th>
<th>Experimental value</th>
<th>Rayleigh W/O</th>
<th>Rayleigh W/O Ideal</th>
<th>Maxwell 3</th>
<th>Maxwell Ideal</th>
<th>Mixing 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
<td>(6)</td>
<td>(7)</td>
<td>(8)</td>
<td>(9)</td>
</tr>
<tr>
<td>0.40</td>
<td>0.40</td>
<td>0.34</td>
<td>0.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>0.35</td>
<td>0.35</td>
<td>0.33</td>
<td>0.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
<td>0.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Hexa-decane

Decane

Heptane
In order to interpret the permittivity values of these compositions, the results for the three n-alkanes studied will be considered separately in the following subsections.

(i) **n-heptane**

Comparison between values given by the Hanai equations for the mixture containing 40% by mass of water, 50% heptane and 10% surfactant reveals very close agreement with the Hanai equation for a spherical O/W dispersion at the lower temperature and good agreement with the Hanai equation for a spherical W/O dispersion at the higher temperature. It is therefore suggested that in this micellar mixture which can be termed a microemulsion as the surfactant concentration was low, micellar inversion from a normal (O/W) to an inverted (W/O) micelle has take place between 4.2° and 13.0° C. Support for such micellar inversion is given in the conductivity data of Bostock (83), given in Figure 50, page 276.

On the basis of proposals made earlier, the agreement with Hanai equation values suggests that the micellar dimensions in this microemulsion are large and comparable to those in dilute aqueous solutions of C_{12}E_{4} which is in agreement with the proposals on globule size in microemulsions given by various authors (89, 90, 91).

There is evidence that deviation from spherical shape occurs in these mixtures at intermediate temperatures.
because the upper clear region appears at 10.8° C but the conductivity value does not fall to a value appropriate to that of an oil continuous phase until the temperature reaches 12° C as shown in Figure 50. In addition, the mixture exhibits streaming birefringence within the above temperature range. These observations led Bostock et al (197) to conclude that in the temperature range 10.2° to approximately 12° C the micellar aggregates have a basically lamellar structure. In view of this lamellar interpretation between 10° and 12° C, the possibility of non-spherical aggregates at the measurement temperature of 13.0° C in the dielectric studies cannot be excluded. As dielectric dispersion was not observed, it is possible that the appropriate permittivity value is given by \( \epsilon \), rather than \( \epsilon' \), which with the Hanai equations is the same as the Bruggeman mixture equation value.

Use of the experimental permittivity value in the generalised Bruggeman equation derived in this work (equation \( \text{[2.64]} \)) gives a shape factor \( A_a = 0.27 \) which corresponds to prolate spheroids of axial ratio \( b/a = 1.2 \) when equation \( [2.39] \) is used.

Alternatively, since deviations from the Hanai O/W equation were reported by Clausse et al (131) for O/W microemulsions with mass fractions of surfactant above about 10%, which were attributed by these authors to a
contribution by the surfactant to the dielectric properties; it is possible that the Maxwell three component equation may be more appropriate, even though it is considered to be limited to relatively low volume fractions of dispersed phase, as discussed in Chapter 2.

In order to determine the effect of spheroidal shape on the permittivity of a three component mixture, equations [2.55] and [2.56] have been modified by using the Rayleigh equation [2.14] which is the basis of [2.55] and [2.56] in the generalised form given by van Beek (equation [2.36]). Application of this procedure gives the following for the three component equations generalised to spheroidal shape:

\[
\varepsilon_1 = \varepsilon_{sh} \frac{\varepsilon_{sh} + \frac{A_a(1 - \phi) + \phi}{\varepsilon_{sh} + A_a(1 - \phi)\varepsilon_2 - \varepsilon_{sh}}}{\varepsilon_{sh} + \frac{A_a(1 - \phi)\varepsilon_2 - \varepsilon_{sh}}{\varepsilon_{sh} + A_a(1 - \phi)\varepsilon_2 - \varepsilon_{sh}}} \quad [5.1]
\]

and \[
\varepsilon = \varepsilon_1 \frac{\varepsilon_1 + \frac{A_a(1 - \phi) + \phi}{\varepsilon_1 + A_a(1 - \phi)(\varepsilon_2 - \varepsilon_1)}}{\varepsilon_1 + \frac{A_a(1 - \phi)(\varepsilon_2 - \varepsilon_1)}{\varepsilon_1 + A_a(1 - \phi)(\varepsilon_2 - \varepsilon_1)}} \quad [5.2]
\]

Application of these two equations to a W/O dispersion of shape factor \( A_a = 0.18 \), which corresponds to prolate spheroids of axial ratio \( a/b = 2.0 \), gives a permittivity value of 7.2 which agrees satisfactorily with the experimental value of 7.3. Since small deviations from spherical shape are not expected to be revealed by streaming birefringence studies, prolate spheroids of axial ratio of 1.2:1 given by the generalised Bruggeman equation are considered to be as equally compatible with
the experimental data as a spherical shape on which the Hanai equation \[ \text{[2.31]} \] is based. Although the axial ratio of 2:1 given by the three component equation is more likely to be revealed in streaming birefringence studies, this is not certain to be so and it is therefore considered that in this composition, the dielectric behaviour at the higher temperature may be satisfactorily described by the Hanai, generalised Bruggeman and generalised three component equations. The lower temperature data is satisfactorily accounted by all three equations without the requirement of significant deviation from spherical shape.

In order to account for the conductivity behaviour of this mixture, Bostock et al (197) have proposed a model for phase inversion, in which at temperatures just below the inversion temperature the normal micellar aggregates have a lamellar shape. They proposed that under the critical interfacial energy conditions close to phase inversion, collision between two or more aggregates leads to the formation of semi-circular and eventually annular structures enclosing water. The phase inversion was suggested as arising from coalescence between these annular structures, eventually leading to the observed clear phase containing inverted micelles. The proposal of lamellar type structure formation as phase inversion is approached is supported by the predictions given by the conductivity equation \[ \text{[2.71]} \] derived in the present
work because such a structure will arise from distortion from a spherical to oblate spheroidal shape which will cause the shape factor to increase giving a lower conductivity. However, difficulty is encountered in justifying phase inversion on the basis of coalescence of annular structures because it would seem more probable that in coalescing the inverted micelles so formed would have an oblate spheroidal shape, which with rise of temperature, becomes spherical. This is counter to the predictions of equation [2.75] which gives an increase in conductivity as the shape factor $A^*$ reduces to the value of 3 for spheres. In order to be compatible with equation [2.75] a prolate rather than oblate spheroidal shaped inverted micelle is required.

A revised form of the proposals of Bostock et al (197) is proposed as follows. At the lower temperature, the oblate spheroidal micelles are envisaged as being distorted towards a more elongated structure. When coalescence occurs due to collision, it is suggested that as in the Bostock et al model, because the changes in curvature occur principally at the edges of these elongated spheroids, the coalescence will occur between the edges of two (or more) such spheroidal aggregates. However, because the effective collision cross-section will be greater along the 'long' side of these aggregates, it is considered more probable that this
(a) Coalescence of oblate spheroidal normal micelles (shape distorted to show effect)

(b) Coalescence of cylindrical W/O aggregates to form prolate spheroidal inverted micelle.
will lead to cylindrical rather than annular structures surrounding water. Coalescence between these cylindrical aggregates would lead to an inverted micellar structure of extended prolate spheroidal shape which with increasing temperature changes to a prolate spheroid and then a sphere. The proposed coalescence is sketched in Figure 53. The above behaviour will then be entirely compatible with predictions given by the conductivity equations [2.71] and [2.75]. These proposals are also in accord with predictions given by the permittivity equations [2.72] and [2.76] as a continuous fall in permittivity between 4.2° and 13° C was observed.

(ii) n-decane

The ternary mixture with the n-alkane decane contained a small proportion of surfactant (15% by mass) and can thus be termed a microemulsion. The mixture exhibits a marked permittivity fall between 7.5° and 19.0° which suggests that inversion from normal to inverted micelles has occurred between the two temperatures. However the Hanai O/W equation gives a permittivity value at 7.5° C which is too high and the Hanai W/O equation also gives too high a permittivity value at 19° C.

The conductivity data of Bostock (83) for this mixture (Figure 50) suggests the presence of normal micelles at the lower temperature but at the higher temperature the conductivity value is too high to justify an inter-
pretation based on inversion from normal to inverted micelles.

The lower temperature dielectric data is very satisfactorily accounted for by the three component O/W equation \[2.55\] and \[2.56\] and the higher temperature data is intermediate between values given by the Hanai W/O and Bruggeman W/O equations.

Since the surfactant concentration in the decane mixture is higher than that in the heptane one considered in (i), it is likely that effects due to the contribution of the surfactant layer to the dielectric properties will be more significant in the decane mixture. The close agreement between the three component O/W values and the lower temperature data clearly gives support to this proposal. The poor agreement between the spherical three component equation for W/O and the higher temperature data could be due to incomplete micellar inversion and be related to the presence of non-spherical micellar aggregates. Application of the generalised three component equations to the higher temperature data for an O/W dispersion of shape factor \(A_a = 0.78\), which corresponds to oblate spheroids of axial ratio \(b/a = 5.5\) when equation \[2.40\] is used, gives a permittivity value of 15.6. Alternatively for a W/O dispersion of shape factor \(A_a = 0.1\), which corresponds to prolate spheroids of axial ratio \(a/b = 3\) when equation \[2.39\] is used,
gives a permittivity value of 15.6. Both values are the same as the experimental value.

It is thus possible to account for the dielectric behaviour at the higher temperature on the basis of either oblate spheroidal normal or prolate spheroidal inverted micelles.

Tanford (194) has calculated aggregation numbers for spheroidal micelles and his results show that for $C_{12}$ surfactants an oblate spheroidal structure of axial ratio 1.25 has the same aggregation number as that of a prolate spheroidal structure of axial ratio 1.5. Assuming the micelle aggregation number is unchanged during inversion, it is proposed that when an oblate spheroidal micelle is inverted, the prolate spheroidal micelle so formed will have an axial ratio $(1.5/1.25)$ higher than the oblate type. Thus in order to decide whether a micellar aggregate is normal or inverted, the criterion adopted will be that the axial ratio for the prolate spheroid must be less than $6/5$ times that for the oblate spheroid in order that the former be selected.

Since the axial ratio in the decane mixture at the higher temperature is lower for a prolate spheroidal shape, it is suggested that the aggregates are prolate spheroidal inverted micelles.
Although the two component equations are considered to be of more limited use in this mixture due to neglect of the contribution of surfactant layer, it is of interest to compare conductivity values given by the equations for spheroidal dispersions with those given for spherical dispersions. For oblate spheroidal normal micelles of shape factor $A_a = 0.78$ as given above, the conductivity of this mixture given by equation $[2.71]$ is a factor of 7 lower than that for spherical normal micelles. For prolate spheroidal inverted micelles of shape factor $A_a = 0.1$ the conductivity of this mixture given by equation $[2.75]$ is a factor of 170 higher than that given for spherical inverted micelles. The data of Bostock reveals that the conductivity at the higher temperature is (i) about a factor of 70 lower than that at the lower temperature and (ii) it is about a factor of 1,500 higher than the value obtained for the heptane mixture in the upper clear region when inversion is complete. As the discrepancies between the conductivity values given by both the oblate spheroidal O/W and the prolate spheroidal W/O equations and the experimental data are similar, both the oblate and prolate spheroidal shapes are about equally probable on the basis of conductivity values. However, as these comments are based on two component equations which are considered to be less adequate, the prolate spheroidal shape is preferred due to its lower axial ratio as given by the three
component permittivity equations.

(iii) *n*-hexadecane
In the ternary mixture with hexadecane containing 18% by mass of surfactant, the dielectric data at the lower temperature is consistent with a normal micellar interpretation where, as in the decane mixture, since the surfactant concentration is higher than the 10% used in the heptane mixture, the contribution by the surfactant layer to the dielectric behaviour is expected to be more significant. This is revealed by the more satisfactory agreement with the three component O/W equation than with the Hanai O/W equation. At the higher temperature however, agreement with the Hanai W/O equation is good which would suggest the presence of spherical inverted micelles. Such behaviour is contrary to the proposals of Bostock who has suggested that, on the basis of conductivity data given in Figure 50, normal micelles are present in the lower temperature clear region whereas in the higher temperature clear region, the conductivity is much too high to justify an interpretation based on micellar inversion.

Since a micellar inversion proposal cannot be maintained, it is considered that this agreement with the Hanai W/O is entirely fortuitous and further emphasises the limitations of the Hanai equations in applications to microemulsions of nonionic surfactants at higher
surfactant concentrations. As the three component equation is the most appropriate in describing the lower temperature behaviour, it is considered to be also the most appropriate for the higher temperature behaviour. The deviation between the spherical three component equation and the experimental data is again attributed to deviation from spherical shape, and as in the decane mixture, there are two possibilities (a) oblate spheroidal normal or (b) prolate spheroidal inverted micelles. The generalised three component equation for O/W with a shape factor $A_a = 0.65$, which corresponds to oblate spheroids of axial ratio $b/a = 3.3$, gives a permittivity of 19.2; whereas for W/O with a shape factor $A_a = 0.07$, which corresponds to prolate spheroids with an axial ratio $a/b = 4.2$, the equation gives a permittivity of 18.8. Both permittivity values compare satisfactorily with the experimental values of 19.2.

In this case, the axial ratio for the prolate shape is a factor of $4/3$ higher than the oblate shape. Since this is higher than the $6/5$ figure discussed earlier, it is considered that the aggregates at the higher temperature are more likely to be oblate spheroidal normal micelles.

In the hexadecane mixture containing 13% by mass of surfactant, the permittivity at $28.4^\circ C$ is too low to be accounted for by any of the spherical O/W equations.
and at 31.4° C is too high to be accounted for by any of the spherical W/O equations. At the lower temperature, the three layer O/W equation gives the closest agreement and at the higher temperature the Hanai W/O equation gives closest agreement.

The data of Bostock for this composition (Figure 50) reveals a progressive fall of conductivity as the temperature is increased with no evidence of phase inversion behaviour. Since the conductivity at 28.4° C is approximately 5% lower than the value at the lower limit of the clear region (25° C), it is quite possible that the micelles at 28.4° C are normal but of an oblate spheroidal rather than spherical shape as equation [2.71] gives a lower conductivity for the oblate spheroidal shape. Such a shape would account for the measured permittivity being lower than that given by any of the O/W equations. Since the three component equation is considered to be the most suitable for describing the dielectric behaviour at surfactant concentrations higher than about 10% by mass, it is presumed that this equation is the most suitable one for describing the behaviour of this mixture.

At the lower temperature for an O/W dispersion of shape factor \( A_a = 0.5 \), which corresponds to oblate spheroids of axial ratio \( b/a = 1.9 \), a permittivity value of 26.0 is obtained. This is satisfactorily close to the
experimental value of 26.3.

At the higher temperature, it is possible that the aggregates are either oblate spheroidal normal or prolate spheroidal inverted micelles. For an O/W dispersion of shape factor $A^\wedge = 0.6$, which corresponds to oblate spheroids of axial ratio $b/a = 2.5$, a permittivity value of 22.5 is obtained. For a W/O dispersion of shape factor $A^\wedge = 0.05$, which corresponds to prolate spheroids of axial ratio $a/b = 5$, a permittivity value of 22.6 is obtained. The permittivity values given for both types of micellar aggregate compare satisfactorily with the experimental value of 23.1.

It is thus again possible to account for the experimental value at the higher temperature by either normal oblate or inverted prolate micelles. However, as the axial ratio for an oblate spheroidal shape is much less than that for the prolate shape, the oblate shape is favoured.

Whilst it is not possible to be unequivocal about the micellar structure, it could be that the micellar inversion process may be due to an increasingly oblate spheroidal shape becoming less favoured than a prolate shape and then inversion occurs when the axial ratio for a prolate spheroidal inverted micelle becomes lower than that required for an oblate spheroidal normal micelle subject to the $6/5$ condition already discussed.
With the above interpretation, micelle inversion as the temperature is raised is envisaged as a continuous process involving change from spherical to oblate spheroidal to prolate spheroidal and back to spherical shape. A well-defined boundary between the transition from oblate spheroidal normal to prolate spheroidal inverted micelles would not be expected and this is in agreement with the phase diagram, conductivity and permittivity behaviour.

(iv) **Summary of microemulsion behaviour**

The observed dielectric behaviour of the microemulsions formed with the n-alkanes heptane, decane and hexadecane can be satisfactorily accounted for on a model for phase inversion involving micelle shape changes: spherical normal → oblate spheroidal normal → prolate spheroidal inverted → spherical inverted. In the heptane mixture inversion is complete, ie all four changes occur, whereas with the longer alkanes the above process cannot be completed. In the decane mixture, the prolate spheroidal inverted micelle is formed but in the hexadecane mixtures, two phases are formed when the micelle is still an oblate spheroidal normal micelle.

These observations are consistent with the proposals of other workers. Particular attention has been given to the so-called "surfactant phase" observed at temperatures close to that for inversion in microemulsions of $C_{12}E_4$.
with the n-alkane hexadecane (82, 84, 86, 87). Shinoda et al (84, 87) suggested that this phase has a basically lamellar shape. Friberg et al (86) showed that a regular layer structure having constant spacing was ruled out by the results of low angle X-ray diffraction and favoured an interpretation based on closed structures in which the mixture involved a rather complex mixing of spherical aggregates together with planar structures. These authors also suggested that deviation from spherical shape was revealed in anomalous hydrocarbon solubilisation behaviour. The model of phase inversion given in this work, which is a modification of that of Bostock et al (197) is much more detailed and more satisfactory in that deviation from spherical shape is accounted for without the requirement of postulating the complex "mix" of Friberg et al (86) or the basically lamellar structure of Shinoda et al (84, 87). The observation of streaming birefringence behaviour indicates that the phase inversion model of Robbins (198) which is based on spherical micelles in unsatisfactory, whereas the spheroidal shapes proposed in this work are consistent with such birefringent behaviour.

Although the O/W microemulsion studies of Mackay and Agarwal (199) were on the rather different system of the commercial nonionic surfactant Tween with water, an oil and n pentanol; their conductivity data, which
exhibited significant deviations from the Hanai-Bruggeman equation, is of interest. These authors favoured an interpretation of their data based on increase in the size of the dispersed oil globules as oil was added causing the microemulsion to become polydisperse. It is not clear why polydispersity should cause the observed conductivity behaviour.

These authors did not discuss micelle shape. If an oblate spheroidal rather than spherical shape is adopted, the observed conductivity behaviour can be accounted for by using equation \[ 2.7 \] derived in this work because with a shape factor \( A_a = 0.6 \), which corresponds to oblate spheroids of axial ratio \( b/a = 2.5 \), the observed conductivity behaviour is accurately described. Such micelle dimensions are comparable values given both in this work and by Tanford et al (74).
### Other ternary mixtures

| Composition | Maxwell | Ideal | 3-component | Brugg | Hand | W/O | W/O | W/O | W/O | Value | Rayleigh | Experiment | Temperature |
|-------------|---------|-------|-------------|-------|-------|-----|-----|-----|-----|-------|-----------|------------|-------------|-------------|
|             | 41.0    | 54.4  | 47.4        | 47.4  | 54.4  | 41.0| 60.9| 32.2| 22.9| 17.8| 0.10     | 0.10       | 0.00        | 0.00        |
|             | 3.3     | 9.5   | 6.2         | 6.2   | 9.5   | 3.3 | 7.6| 4.9 | 3.0 | 7.2 | 0.70     | 0.70       | 0.10        | 0.10        |
|             | 4.7     | 13.2  | 4.2         | 4.2   | 13.2  | 4.7 | 7.9| 3.8 | 3.0 | 7.2 | 0.50     | 0.50       | 0.00        | 0.00        |
|             | 2.9     | 10.2  | 2.5         | 2.5   | 10.2  | 2.9 | 7.4| 4.9 | 4.0 | 7.2 | 0.30     | 0.30       | 0.00        | 0.00        |
|             | 3.2     | 7.5   | 2.5         | 2.5   | 7.5   | 3.2 | 6.9| 2.5 | 2.5 | 6.9 | 0.20     | 0.20       | 0.00        | 0.00        |

Table 72: Comparison of experimental static permittivity values with values given by mixture equations.
The experimental data given in Table 72 for the set of mixtures containing 10% by mass of water are more accurately described by W/O equations for high hydrocarbon concentration with the three component equation giving closest agreement, but the measured permittivity values are higher than those given by any of the W/O equations. This discrepancy between the W/O equation values and experiment increases with increasing surfactant concentration and at 70% by mass of surfactant (20% heptane), the three component O/W equation gives the best fit.

It is suggested that the dielectric behaviour of these micellar solutions is consistent with a structure in which there are inverted micelles at high hydrocarbon concentration and normal micelles at low hydrocarbon concentration. Inverted micelles would be more likely at high hydrocarbon concentration and, since it has been proposed that binary mixtures of C₁₂E₄ and water contain normal micelles over the whole composition range, normal micelles would also be expected at low hydrocarbon concentration. The discrepancies between the experimental data and the three component equation values are attributed to inadequacies in this equation at higher volume fractions of the shell component.

The temperature dependence of the permittivity dεₛ/dT, of the 10% water mixtures changes from \(-9.9 \times 10^{-2} \, °C^{-1}\) at the highest heptane concentration (70% by mass) to an almost concentration-independent value of \(-3.2 \times 10^{-2} \, °C^{-1}\).
when the heptane concentration is 40% and below. The more pronounced temperature dependence at high heptane concentration would not be expected on the basis of the various mixture equations because the surfactant has a higher temperature coefficient than the heptane. The higher $d\varepsilon_s/dT$ value for the 70% heptane mixture could be due to micellar reorganisation.

The data of Bostock (83) for the 10% water mixture containing 70% heptane reveals a rapid fall in conductivity over a very small temperature range, to account for which the possibility of inversion from normal to inverted micelles has been proposed. It is suggested that the anomalously high $d\varepsilon_s/dT$ value for this mixture is due to micellar inversion behaviour.

In this mixture, it is considered that the micelles will be rather smaller than in the microemulsions and are thus less likely to deviate from spherical shape. Hence a mechanism of inversion based on change of micelle shape as proposed by Bostock et al (197) and this author for microemulsions cannot be applied here.

A tentative explanation of inversion in these mixtures may be given in terms of the dynamic equilibrium of the micelle. Winsor (200) has pointed out that micelles must be considered as structures capable of rapid breakdown and, due to the short half-life of micellar breakdown, rapid re-formation. At lower temperatures
the interfacial energies will be such that normal micelles are continuously broken and reformed. Using the formalism of Winsor (200) where the term $R$, defined by

$$R = \frac{\text{tendency of surfactant to become convex to oil}}{\text{tendency of surfactant to become convex to water}},$$

is used, normal micelles have $R < 1$. At higher temperatures, the micelles are inverted ($R > 1$), and these inverted micelles are similarly continuously broken and reformed. At the temperature corresponding to phase inversion $R = 1$ and in principle there is equal probability of formation of either normal or inverted micelles. It is suggested that the so called breakdown of micelles under both the $R < 1$ and $R > 1$ conditions does not involve complete micellar dissociation but rather only a number of the molecules contained in a micelle. At low temperatures where $R$ is less than unity, the effect of increase of temperature can be regarded as causing an increase in the number of molecules being involved in the micellar breakdown process. At a critical temperature, $T_c$, corresponding to $R = 1$, there will be complete micellar dissociation and as a normal micelle dissociates it will reform as either a normal or inverted micelle depending on whether, due to local thermal fluctuations, the temperature is above or below $T_c$ when the micelle is reformed.
As the temperature is raised fractionally above the
R = 1 temperature, the micelles will be inverted and
the number of molecules involved in the 'breakdown'
will then steadily fall as the temperature is raised
further above the R = 1 condition. With this inter­
pretation, there will be no deviation from spherical
symmetry which is consistent with the absence of
streaming birefringence effects in this 10% by mass of
water mixture (83). On the other hand, the above
interpretation is not applicable to the microemulsions
because at all compositions studied, streaming bire­
fringence behaviour is observed at temperatures close
to that for inversion (83) indicating the presence of
non-spherical aggregates.

The experimental value of 7.0 for the C₁₂E₄ ternary
mixture containing 30% by mass of water and 50% heptane
is not accounted for by any of the mixture equations.
As the permittivity is rather closer to values given by
W/O rather than the O/W equations, it is considered
probable that the micelles are inverted. This proposal
is consistent with the phase diagram given in Figure 47
(p 273) because at 17° C the isotropic liquid region
shows continuity to the alkane corner. In addition, the
measurement temperature is rather higher than the
temperature at which inversion occurred in the micro­
emulsion containing n-heptane.
As the surfactant concentration was 20%, the three component equation is considered the most appropriate. The discrepancy between theoretical and experimental values could be due to inadequacies in this mixture equation when the volume fraction of the surfactant shell is comparable with that of the water core, as is the case for inverted micelles in this mixture. Alternatively, because the surfactant concentration is only marginally higher than that used in the microemulsions, the discrepancy could be due to prolate spheroidal rather than spherical micelle shape as proposed for the microemulsions above the inversion temperature. If the micelles are assumed to have a prolate spheroidal shape of axial ratio $a/b \approx 2$, there is good agreement between theory and experiment.

The experimental value of 32.3 for the $C_{12}E_4$ ternary mixture containing 70% by mass of water and 10% heptane is not accounted for by any of the mixture equations. Since the hydrocarbon concentration of 10% is very low, it is likely that the micellar structure will be very similar to that of the binary mixtures of the surfactant with water for which normal micelles are favoured. This interpretation is supported by the fairly similar permittivity values given by the binary aqueous mixtures at approximately similar proportions of surfactant and water. The poor agreement between the three component O/W equation and the experimental data is
probably due to inadequacies in the equation because for normal micelles the volume fraction of the surfactant shell is greater than that of the hydrocarbon core. Alternatively there could be a contribution due to deviation from spherical to oblate spheroidal shape, as proposed for the binary mixtures of C12EH with water at low surfactant concentration.

5.6.2.2 Brij 30 ternary mixtures

The isotropic liquid regions are shown in Figures 51 and 52 p 277, 278.
Table 73

Comparison of experimental values with values given by mixture equations.
As the binary mixture studies of surfactant and water revealed considerable differences between the dielectric behaviour of the surfactants $C_{12}E_4$, $C_{12}E_6$ and $C_{12}E_8$, the uncertain polydispersity of Brij 30 precludes detailed interpretation of the dielectric behaviour.

The mixtures containing 10% by mass of water are considered to be satisfactorily accounted for by proposing inverted micelles at high hydrocarbon concentration and normal micelles at low concentration. As in the $C_{12}E_4$ mixtures of similar composition the measured permittivities are not satisfactorily accounted for by the mixture equations. This is again attributed to inadequacies in the equations at higher surfactant concentrations.

The conductivity data of Bostock (83) is consistent with an interpretation based on inverted micelles at the higher hydrocarbon concentrations and normal micelles at the lower concentrations. As in the $C_{12}E_4$ mixtures, since the surfactant itself is considered to contain normal micellar aggregates, normal micelles are to be expected at low hydrocarbon concentrations.

The mixtures at 20% by mass of water are also considered to contain inverted micelles at the higher hydrocarbon concentrations and normal micelles at lower concentrations.
However, the agreement between calculated values and the experimental data at low hydrocarbon content is unsatisfactory, possibly due to polydispersity in the surfactant. At 30% by mass of water, there is encouraging agreement with the Hanai W/O values for two of the compositions, indicating that the micelles are inverted and of large size. The 35% water mixture gives similarly good agreement with the Hanai W/O equation. At 40% by mass of water, the situation is less satisfactory. A mean of the Bruggeman W/O (ie Hanai equation for $\varepsilon_\infty$) and that of the Hanai W/O is required for the 20% Brij 30 mixture, whereas at 30% Brij 30 the Bruggeman W/O is the best. It is suggested that these mixtures contain inverted micelles.

Conductivity data of Bostock (83) is again consistent with an interpretation of the 20% water data on the basis of inverted micelles at higher hydrocarbon concentrations and normal micelles at lower concentrations. The conductivity data for the mixtures with water concentrations in the range 30 to 40% by mass at the measurement temperatures of the dielectric studies is consistent with an interpretation based on inverted micelles (83). Inverted micelles for these 35% and 40% water mixtures are considered likely on the basis of inversion temperatures because the $C_{12}E_4$ microemulsions with n-heptane exhibited inversion between 4.2°C and 13.0°C. As the measurement temperatures in these Brij 30 ternary
mixtures were above 20° C, inverted micelles are to be expected.

5.7 Conclusions

5.7.1 Surfactant-water binary mixtures

For all compositions studied the micelles are normal (O/W) over the whole composition range in the temperature regions in which clear phases occur. For the shortest oxyethylene chain length surfactants, C₁₂E₄ and Brij 30, the static permittivity values at higher concentrations are lower than the ideal mixing equation values, and are satisfactorily described by the Hanai-Bruggeman equation for spherical dispersions. Deviations at low surfactant concentration are attributed to either oblate spheroidal micelle shape or secondary aggregation of micelles. Using equations derived in this work for concentrated dispersions of spheroidal globules, the oblate spheroidal interpretation requires an axial ratio of 3.5:1 in C₁₂E₄ and 2.6:1 in Brij 30 at the lowest concentrations.

The permittivity values of C₁₂E₆-water mixtures over most of the concentration range are satisfactorily described by the Rayleigh equation. None of the mixture equations describes the permittivity behaviour of C₁₂E₈-water mixtures. The dielectric behaviour of the C₁₂E₆ and C₁₂E₈ mixtures is attributed to progressively smaller micelle sizes for a given alkyl chain length as
the length of the oxyethylene chain is increased. This leads to an increasing contribution by co-operative molecular association between the ethylene oxide groups and water which gives an enhanced permittivity value. There is a basis for believing that there might be a contribution due to prolate spheroidal micelles in the C12Eb-water mixtures at the lowest concentration and in the C12Ea mixtures over the whole concentration range. However in the C12E8 mixtures, this latter effect is considered to be of only secondary importance.

5.7.2 Surfactant-n-alkane binary mixtures
The dielectric behaviour of binary mixtures of Brij 30 with heptane is attributed to the presence of inverted micelles at low surfactant concentration and normal micelles at high concentrations. The permittivity values are satisfactorily described by heterogeneous mixture equations, with the Rayleigh equation being the most suitable.

5.7.3 Surfactant-water-n-alkane ternary single phase mixtures
The dielectric behaviour of the microemulsion of C12E8 with water and n-heptane is satisfactorily described in terms of a structure in which there are spherical normal micelles at the lower temperature and spherical inverted micelles at the higher temperature. On the basis of equations for both the permittivity and conductivity of a spheroidal dispersion given in this work, the
inversion behaviour can be described in terms of micelle shape changes. With increase of temperature the spherical normal micelle changes to an oblate spheroidal shape and then by coalescence of extended oblate-spheroidal aggregates, a prolate spheroidal inverted micelle is formed, which with increase of temperature, becomes spherical.

The rather different behaviour of microemulsions with the n-alkanes decane and hexadecane is attributed to the greater length of the alkyl chain causing the system to form two phases before the above inversion process can be completed. With decane this occurs when the prolate spheroidal inverted micelle has formed, whereas with hexadecane, it occurs when the aggregates are oblate spheroidal normal micelles.

The behaviour of ternary mixtures containing 10% by mass of water is considered to be satisfactorily accounted for by inverted micelles at high hydrocarbon concentration and normal micelles at low concentration. In the mixture containing 10% water, 70% heptane and 20% C_{12}E_4, micelle inversion has been proposed which has been interpreted in terms of the dynamic equilibrium of the micelle. Deviations between theory and experiment are attributed primarily to limitations of the mixture equations at higher surfactant concentrations.

The dielectric behaviour of Brij 30 ternary mixtures
at high water concentration is interpreted in terms of inverted micelles. At low water concentrations there are similarities with the C_{12}E_4 system in that the micelles are again inverted at high hydrocarbon concentrations and normal at low concentrations. The polydispersity of this surfactant precludes detailed interpretation.

5.8 Further Work

It is suggested that dielectric studies of the compositions reported in this work be performed at higher frequencies in order to determine whether or not the dielectric dispersion predicted by the generalised Hanai equations derived in this work occurs in these systems. Such studies will give more information on the applicability or otherwise of the equations to spheroidal micellar systems.

In order to gain support for proposals given in this work, it is desirable to investigate the dielectric behaviour of both binary and ternary micellar solutions of other members of the polyoxyethylene-alkyl ether series surfactants. The C_{12}E_3 -water system should be of value because it has a phase diagram similar to that of the C_{12}E_4 system (187) but the shorter oxyethylene chain will result in even larger micelles than in C_{12}E_4. Thus effects due to oblate spheroidal shape should be more pronounced and should enable the proposals given in
this work concerning micelle shape to be further evaluated.

The C\textsubscript{i6}E\textsubscript{lz} - and C\textsubscript{10}E\textsubscript{b}-water systems should also be of value because their phase diagrams show similarity to the C\textsubscript{lz}E\textsubscript{a} system in that a hexagonal liquid crystalline phase is the dominant feature at lower temperatures (187). As in C\textsubscript{i2}E\textsubscript{8} this will result in prolate spheroidal micelles being more probable. The relative balance between the alkyl chain and the polar headgroup for these two systems will be different from that for C\textsubscript{i2}E\textsubscript{8}, hence the relative contributions to measured permittivity values of prolate spheroidal shape and association between headgroups and water will be different.

It would also be of interest to study the dielectric properties of microemulsions of other polyoxyethylene alkyl ether surfactants to obtain confirmation of the structural proposals given in this work.
REFERENCES

1. Pimentel G C and McClellan A L - The Hydrogen Bond
   W H Freeman and Company, San Francisco and
   London 1960
2. Vinogradov S N and Linnell R H - Hydrogen Bonding
   Van Nostrand Reinhold Company, New York 1971
3. Bordewijk P, Gransch F and Böttcher C J F
   Trans Far Soc 1970, 66, 293
4. Fletcher A N
   J Phys Chem 1972, 76, 2562
5. Dannhauser W and Flueckinger A F
   Phys Chem Liq 1970, 2, 37
6. Brink G, Campbell C and Glasser L
7. Brown A C and Ives D J G
   J Chem Soc 1962, 1608
8. Lawrence A S C, McDonald M P and Stevens J V
   Trans Far Soc 1969, 65, 3231
   and macromolecular systems
10. Shinoda K, Nakagawa T, Tamamushi B-I and Isemura T
    Colloidal Surfactants
    M J Edward Arnold Publishers (Ltd), London, 1967

- 316 -
12. O'Connell J P and Brugman R J - Improved Oil Recovery by Surfactant and Polymer Flooding
   Eds Shah D O and Schechter R S - Academic Press
   New York and London 1977

13. Debye P - Polar Molecules
   Chemical Catalog Co, New York, 1929

14. Onsager L
   J Am Chem Soc, 1936, 58, 1486

15. Kirkwood J G
   J Chem Phys 1939, 7, 911

16. Dannhauser W and Cole R H
   J Chem Phys 1955, 23, 1762

17. Liszi J and Naray M
   Acta Chem (Budapest) 1974, 81, 11

18. Dannhauser W and Bahe L W
   J Chem Phys 1964, 40, 3058

19. Garg S K and Smyth C P

20. Garg S K and Smyth C P
   J Chem Phys, 1967, 46, 373

21. Hassion F X and Cole R H
   J Chem Phys 1955, 23, 1756

22. Johari G P and Dannhauser W
   J Phys Chem 1968, 72, 3273

23. Oster G and Kirkwood J G
   J Chem Phys 1943, 11, 175

24. Bordewijk P, Kunst M and Rip A
25. Malecki J and Jadzyn J
   J Phys Chem 1974, 78, 1203
26. Campbell C, Brink G and Glasser L
27. Jakusek E and Sobczyk L - Dielectric and Related
    Molecular Processes - Vol 3
    Chemical Society, London 1977
28. Crossley J
29. Glasser L, Crossley J and Smyth C P
    J Chem Phys 1972, 57, 3977
30. Chekalin N V
    Zh Fiz Khim, 1971, 45, 452
31. Kauzmann W
    Rev Mod Phys, 1942, 14, 12
32. Bauer E
    Cahiers Phys, 1944, 20, 1
33. Brot C and Magat M
    J Chem Phys, 1963, 39, 841
34. Campbell C, Crossley J and Glasser L
    Adv Mol Relax Proc, 1976, 9, 63
35. Sagal M W
    J Chem Phys, 1962, 36, 2437
36. Hanna F F and Hakim I K
    Z Naturforsch, 1971, 26A, 1194 and 1972, 27A, 1363
37. Van den Berg J F, Michielson J C F and Ketelsar J A A
    Rec Trav Chim Pays Bas, 1974, 93, 104
38. Komooka H
   Bull Chem Soc Jap, 1972, 45, 1696
39. Koshii T, Arie E, Nakamura M, Takahashi H and Higasi K
   Bull Chem Soc Jap, 1974, 47, 618
40. Hasted J B - Dielectric and Molecular Processes
    Vol 1
    The Chemical Society, London, 1972
41. Hasted J B - Aqueous Dielectrics
42. Grant E H, Sheppard R J and South G P - Dielectric
    Behaviour of Biological Molecules in Solution
43. Malmberg C G and Maryott A A
    J Res Nat Bur Standards, 1956, 56, 1
44. Hill N E
    Trans Far Soc, 1963, 59, 344
45. Zafar M S, Hasted J B and Chamberlain J
46. Afsar M N and Hasted J B
47. Bernal J D and Fowler R H
    J Chem Phys, 1933, 1, 515
48. Pople J A
    Proc Roy Soc, 1951, A205, 163
49. Bernal J D
50. Haggis G H, Hasted J B and Buchanan T J
   J Chem Phys, 1952, 20, 1452
51. Eisenberg D and Kauzmann W - The Structure and
    Properties of Water
    Oxford University Press 1969
52. Pauling L - Nature of the Chemical Bond
    Cornell University Press, Ithaca, New York, 1948
53. Rahman A and Stillinger F H
54. Grant E H and Sheppard R J
    J Chem Phys, 1974, 60, 1792
55. Akerlof G
    J Am Chem Soc, 1932, 54, 4125
56. Decroocq D
    Buli Soc Chim F, 1964, 127
57. D'Aprano A
    J Phys Chem, 1974, 78, 652
58. Lippold B C and Adel B C
    Arch Pharmaz 1972, 305, 417
59. Tjia T H - Thesis
    University of Leiden, 1974
60. Hill N E, Vaughan W E, Price A H and Davies M -
    Dielectric Properties and Molecular Behaviour
61. Schallamach A
    Trans Far Soc 1946, 42A, 180
62. Daumezon P and Heitz R
    J Chem Phys, 1971, 55, 5704

- 320 -
63. Denney D J and Cole R H
   J Chem Phys, 1955, 23, 1767
64. Chekalin N V and Shakhparonov M I
   Russ J Phy Chem, 1971, 45, 250
65. Chekalin N V and Shakhparonov M I
   Fiz Fiz Khim Zhidk, 1972, 1, 151
66. Peyrelasse J
   CR Acad Sci Ser B, 1977, 284, 185
67. Sarojini V
   Trans Far Soc, 1961, 57, 1534
68. Buck D E - PhD Thesis
   M I T 1965
69. Davies M
   Acta Phys (Pol), 1976, A50, 241
70. Shinoda K and Kunieda H
   J Colloid Interface Sci, 1973, 42, 381
71. Nakagawa T - Non-ionic Surfactants
   Ed Schick M J, Edward Arnold Publishers Ltd
   London 1967
72. Mysels K J - Introduction to Colloid Chemistry
   Wiley, New York, 1959
73. Elworthy P H, Florence A T and Macfarlane C B -
   Solubilisation by Surface Active Agents and its
   Applications in Chemistry and the Biological Sciences
   Chapman and Hall, London 1968
74. Tanford C, Nozak Y and Rohde M F
   J Phys Chem, 1977, 81, 1555
75. Tanford C
   J Phys Chem, 1974, 78, 2469

76. Elworthy P H and Macfarlane C B
   J Chem Soc 1963, 907

77. Attwood D
   J Phys Chem, 1968, 72, 339

78. Ottewill R H, Storer C C and Walker T
   Trans Far Soc, 1967, 63, 2796

79. Corkill J M and Walker T
   J Colloid Interface Sci, 1972, 39, 621

80. Staples E J and Tiddy G J T

81. Bostock T A, McDonald M P and Tiddy G J T, Discussion of
   Colloid and Interface Sci. Group of Far Div of Chemical
   Society, Hull September 1978

82. Brown J B, Lapczynska I and Friberg S
   Proc Int Conf Colloid Surf Sci
   Ed Wolfram (Kiado, Budapest) Vol 1, 1975

83. Bostock T A
   (Private Communication)

84. Shinoda K and Friberg S
   Adv Coll Interface Sci, 1975, 4, 281

85. Friberg S and Lapczynska I
   Progr Coll and Polymer Sci, 1975, 56, 16

86. Friberg S, Lapczynska I and Gillberg G
   J Colloid Interface Sci, 1976, 56, 19

87. Shinoda K and Kunieda H - Microemulsions Theory and
   Practice
   Ed Prince L M, Academic Press, New York and
   London, 1977
88. Schulman J H, Stoeckenius W and Prince L M
   J Phys Chem, 1959, 63, 167
89. Shah D O, Bansal V K, Chan K and Hsieh W C -
   Improved Oil Recovery by Surfactant and Polymer
   Flooding
   Eds Shah D O and Schechter R S, p 293
90. Friberg S - Microemulsions
   and London, 1977
91. Prince L M
   Ibid p 1
92. Kitchener J A and Mussell White P R - Emulsion
   Science
   York, 1968
93. Gerbacia W, Rosano H L and Whittam J H
   Colloid and Interface Science, Ed Kerker M,
94. Prince L M
   J Colloid Interface Sci, 1975, 52, 182
95. Eicke H F
   J Colloid Interface Sci, 1977, 59, 308
96. Ruckenstein E and Chi J C
   J Chem Soc, Far Trans 2, 1975, 71, 1690
97. Crooks J E
   J Colloid Interface Sci, 1978, 66, 355
98. Shinoda K and Sagitani H
   Ibid, 1978, 64, 68

99. Shinoda K
   Ibid, 1967, 24, 4

100. Shinoda K and Ogawa T
   Ibid, 1967, 24, 56

101. Shinoda K
   Ibid, 1970, 34, 278

102. Saito H and Shinoda K
   Ibid, 1971, 35, 359

103. Kaatze U, Limberg C H and Pottel R
   Ber Bunsenges Phys Chem, 1974, 78, 561

104. Eicke H F and Shepherd J C W
   Helv Chim Acta, 1974, 57, 1951

105. Beard R B, McMaster T F and Takashima S
   J Colloid Interface Sci, 1974, 48, 92


107. Cavell E A S
   J Colloid Interface Sci, 1977, 62, 495

108. O'Konski C T
   J Phys Chem, 1960, 64, 605


110. Kaatze U
   Ber Bunsenges Phys Chem, 1978, 82, 690
111. Tartar H V  
   J Colloid Interface Sci, 1959, 14, 115
112. Anacker E W  
   J Phys Chem, 1964, 68, 81
113. Schwarz G  
   J Phys Chem, 1962, 66, 2636
114. Tartar H V  
   J Phys Chem 1955, 59, 1195
115. Grant E H  
   J Mol Biol 1966, 19, 133
116. Pennock B E and Schwan H P  
   J Phys Chem 1969, 73, 2600
117. Eicke H F and Christen H  
   J Colloid Interface Sci 1974, 48, 281
118. Eicke H F, Hopmann R F W and Christen H  
   Ber Bunsenges Phys Chem 1975, 79, 667
119. Clausse M, Sheppard R J, Boned C and Essex C G  
   Colloid and Interface Science, Vol 2, ed Kerker M  
120. Hanai T  
   London 1968
121. Hanai T  
   Kolloid Z 1961, 177, 57
122. Hanai T, Koizumi N and Gotoh R  
   Kolloid Z 1962, 184, 143
123. Hanai T and Koizumi N
124. Clausse M
    C R Acad Sci 1972, 274B, 887
125. Lafargue C, Clausse M and Lachaise J
    C R Acad Sci 1972, 274B, 540
126. Clausse M
    C R Acad Sci 1973, 277B, 261
127. Clausse M
    Colloid and Polymer Sci 1977, 255, 40
128. Sjöblom E and Friberg S
    J Colloid Interface Sci 1978, 67, 16
129. Senatra D and Guibilaro G
    J Colloid Interface Sci 1978, 67, 448
130. Senatra D and Guibilaro G
    ibid 1978, 67, 457
131. Clausse M, Sherman P and Sheppard R J
    J Colloid Interface Sci 1976, 56, 123
132. Peyrelasse J, Boned C, Xans P and Clausse M
    C R Acad Sci 1977, 284B, 235
133. Fröhlich H - Theory of Dielectrics
    Oxford University Press, London 1949
134. Oster G
    J Am Chem Soc 1946, 68, 2036
135. Cole K S and Cole R H
    J Chem Phys 1949, 9, 341
136. Davidson D W and Cole R H
    J Chem Phys 1951, 18, 1417
137. Powles J G
    J Chem Phys 1953, 21, 633
138. Glarum S H
    J Chem Phys 1960, 33, 1371
139. O'Dwyer J J and Sack R A
    Aust J Sci Res 1952, A5, 647
140. van Beek K L H - Progress in Dielectrics
    7, 71, Heywood, London 1967
141. Rayleigh J W
    Phil Mag 1892, 34, 481
142. Wiener O
    Abh sächs Akad Wiss Math-Phys K1 1912, 32, 509
143. Runge I
    Z Tech Phys 1925, 6, 61
144. Meredith R E and Tobias C W J
    J Appl Phys 1960, 31, 1270
145. Bruggeman D A G
    Ann Phys Lpz 1935, 24, 636
146. Looyenga H
    Physica 1965, 31, 401
147. Landau L D and Lifshitz - Electrodynamics of
    Continuous Media
    Pergamon Press, London 1960
148. Kraszewski A, Kulinski S and Matuszewski M
    J Appl Phys 1976, 47, 1275
149. Böttcher C J F - Theory of Electric Polarisation
    Elsevier, Amsterdam 1952
150. Hanai T, Koizumi N, Sugano T and Gotoh R
    Kolloid Z 1960, 171, 20
151. Naiki T, Fujita K and Matsumara S
    Mem Fac ind Arts Kyoto Univ 1959, 8, 1
152. Mandel M
    Physica 1961, 27, 827
153. Maxwell J C
    Electricity and Magnetism Vol 1, Clarendon
    Press, Oxford, 1892
154. Wagner K W
    Arch Elektrotech 1914, 2, 371
155. Hanai T and Koizumi N
    Bull Inst Chem Kyoto Univ 1976, 54, 248
156. Sillars R W
    J Inst Elec Eng 1937, 80, 378
157. Stratton J A
    Electromagnetic Theory, McGraw-Hill, New York 1941
158. Grosse C and Greffe J L
    C R Acad Sci Ser C 1976, 283, 95
159. Polder D and Van Santen J H
    Physica 1946, 12, 257
160. De Loor G P - Thesis
    University of Leiden 1956
161. De Loor G P
    J Microwave Power 1968, 3, 67
162. Pauly H and Schwan H P
    Z Naturf 1959, 14b, 125
163. Kraszewski A

J Microwave Power 1977, 12, 216

164. Dryden J S and Meakins R J

Proc Phys Soc 1957, 70B, 427

165. Chapman I D

J Phys Chem 1968, 72, 33

166. Le Petit J P, Delbos G, Bottreau A M, Dutuit Y

Marzat C and Cabanas R - J Microwave Power 1977, 12, 335

167. Reynolds J A - Thesis

University of London 1955

168. Pradhan B P and Gupta R C

Dielectrics 1964, 1, 195

169. Fellner-Feldegg H

J Phys Chem 1969, 73, 616

170. Whittingham T A

J Phys Chem 1970, 74, 1824

171. Suggett A, Mackness P A, Tait M J, Loeb H W and Young G M

Nature, 1970, 228, 456

172. Loeb H W, Young G M Quickenden P A and Suggett A

Ber Bunsenges Phys Chem 1971, 75, 1155

173. Van Gemert M J C, De Loor G P, Bordewyk P and Suggett A

Adv Mol Relaxation Proc 1973, 5, 301

174. Fellner-Feldegg H

J Phys Chem 1972, 76, 2116

175. Van Gemert M J C,

Philips Res Dept 1973, 28, 530

- 329 -
176. Suggett A - New techniques in Biophysics and Cell Biology
Ed B H Pain and B Smith, J Wiley and Sons
London and New York 1975

177. Clark A H, Quickenden P A and Suggett A
J Chem Soc Far Trans II 1974, 70, 1847

178. Clarkson T S, Glasser L, Tuxworth R W and Williams G
Adv Mol Relax Interact Proc 1977, 10, 173

179. Giese K and Tiemann R
Adv Mol Relaxation Proc 1975, 7, 45

180. Fellner-Feldegg H and Barnett E F

181. Brehm G A and Stockmayer W H
J Phys Chem 1973, 77, 1348

182. Shannon C
Proc I R E 1949, 37, 10

183. Samulon H A
Proc I R E 1951, 39, 175

184. Clarkson T S and Williams G
Chem Phys Lett 1975, 34, 461

185. Stevens J V - PhD Thesis
University of Sheffield 1970

Trans Far Soc 1967, 63, 2839

187. Tiddy G J T - Private Communication
188. Sato H, Koshii T and Takahasi H
    Chem Lett 1974, 579

189. Arnoult R, Lebrun A and Boullet C
    Arch Sci phys et nat (spec) 1956, 9, 44

190. Lebrun A,
    Cahiers Phys, 1955, 60^, 11

191. Mulley B A
    Nonionic Surfactants Ed Schick M J
    Edward Arnold Publishers (Ltd), London, 1967

192. Davies M, Williams G and Loveluck G D
    Z Elektrochem, 1960, 56, 576

193. Kaye G W C and Laby T H
    Tables of Physical & Chemical Constants

194. Tanford C
    The Hydrophobic Effect : Formation of
    Micelles and Biological Membranes

195. Maryott A A and Smith E R
    Table of Dielectric Constants of Pure Liquids
    Nat Bur Standards Circular 514, 1951

196. Handbook of Chemistry and Physics, 49th Edition
    The Chemical Rubber Company, Cleveland,
    Ohio, 1968
197. Bostock T A, McDonald M P, Tiddy G J T and Waring L

SCI Chemical Society Symposium on Surface Active Agents, Nottingham, September 1979
(Preprint)

198. Robbins M L

ACS 48th Nat Coll Symp, Austin, 1974
Preprints p 174

199. Mackay R A and Agarwal R

J Colloid Interface Sci 1978, 65, 225

200. Winsor P A

Chem Rev 1968, 68, 1
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APPENDIX

COMPUTER PROGRAM FOR FOURIER TRANSFORM (FORTRAN IV G1)

```fortran
DIMENSION TITLE (20)
INTEGER Z (99)
READ (5,1) TITLE

FORMAT(20A4)
DIMENSION A(25), B(250), WIG(99), W(99), TC(25), TS(250)
R(99), C(250), D(250), UC(250), US(250), ALPHA(99), S(99), T(99)
EO(99), ET(99), P(250), E(250), THETA(99), PHI(99), EK(99)
GO(250), G(250), V(250), VC(250), VS(250), GAM(99), Y(250), RT(250)
DEL(250), EOR(250), ETR(250), PR(250), ER(250), OGR(250), PHIR(99)
WRITE(6,2) TITLE

WRITE(6,3)

JJ=1
KK=1
READ(5,10) N, X

FORMAT(I2, F6.3)
WRITE(6,12) N, X

FORMAT(32X, 'N=', I2, 3X, 'X/100PS=', F6.3)
X=X/1.E10
DO251 I=1, N
READ(5,20) Z(I)

FORMAT(I4)
WIG(I)=Z(I)*6.2832
W(I)=WIG(I)*1.E06
CONTINUE

READ(5,30) K, A(1)

FORMAT(I3, F5.2)
WRITE(6,33) K

FORMAT(33X, 'K=', I3)
DO37 I=2, K
READ(5,35) A(I)
CONTINUE

READ(5,40) M, C(1)

FORMAT(I3, F5.2)
DO44 I=2, M
READ(5,42) C(I)
CONTINUE

READ(5,45) LL, MM, KL, ML

FORMAT(I2, I2, I2, I3, 1X, I3)
B(JJ)=A(JJ)
JJ=JJ+1
DO50 I=JJ, K
B(I)=A(I)-A(I-1)
CONTINUE

D(KK)=C(KK)
KK=KK+1
DO60 I=KK, M
```

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\[ D(I) = C(I) - C(I-1) \]

CONTINUE

\[ JJ = JJ - 1 \]

DO75I = 1, N

CUM = 0
SUM = 0
L = 1

DO70J = JJ, K

\[
TC(J) = B(J) \times (\cos((L-0.5)W(I)X)) \\
TS(J) = B(J) \times (\sin((L-0.5)W(I)X)) \\
CUM = CUM + TC(J) \\
SUM = SUM + TS(J) \\
L = L + 1
\]

CONTINUE

\[ \text{THETA}(I) = \text{ATAN}(CUM/SUM) \]

\[ R(I) = \sqrt{((CUM^2 + SUM^2)^2 + 2\times \sin(W(I)X/2)^2)^2} \]

CONTINUE

\[ \text{KK} = KK - 1 \]

DO85I = 1, N

DUM = 0
TUM = 0
L = 1

DO80J = KK, M

\[
UC(J) = D(J) \times (\cos((L-0.5)W(I)X)) \\
US(J) = D(J) \times (\sin((L-0.5)W(I)X)) \\
DUM = DUM + UC(J) \\
TUM = TUM + US(J) \\
L = L + 1
\]

CONTINUE

TUM = ABS(TUM)

\[ \text{ALPHA}(I) = \text{ATAN}(DUM/TUM) \]

\[ S(I) = \sqrt{((DUM^2 + TUM^2)^2 + 2\times \sin(W(I)X/2)^2)^2} \]

CONTINUE

DO100I = 1, N

\[
T(I) = (-R(I)/S(I)) \\
PHI(I) = (((\text{THETA}(I)) - (\text{ALPHA}(I))) \\
EO(I) = (((1 - T(I)*T(I)) - (1 - T(I)*T(I))) - 4 \times T(I)*T(I)*SIN \times (PHI(I)))^2 \\
ET(I) = ((4 \times (1 - T(I)*T(I)) \times T(I)*T(I)*SIN(PHI(I)))^2) \\
\]

WRITE(6, 90) EO(I), ET(I), Z(I), THETA(I), ALPHA(I), R(I), S(I), T(I), PHI(I)

FORMAT(33X, 'K=', I3, 4X, 'M=', I3)

IF(K.GE.LL) GO TO47

READ(5, 150, END=400) JJ, KK

FORMAT(11, 11)

IF(JJ.EQ.O) GO TO400
WRITE(6,160) JJ, KK
160 FORMAT(34X,'JJ=',I1,3X,'KK',I1)
K=KL
M=ML
GO TO 46
400 READ(5,420) ES
420 FORMAT(F5.2)
WRITE(6,422) ES
422 FORMAT(34X,'ES=',F5.2)
WRITE(6,425)
425 FORMAT(10X,'REFCO',7X,'PERMIT',6X,'LOG(ES-E)')
K=KL
DO 440 I=1,K
P(I)=A(I)/C(I)
E(I)=((1+P(I))**2)/((1-P(I))**2)
IF(ES.GT.E(O)) OG(I)=ALOG(ES-E(I))
WRITE(6,430) P(I), E(I), OG(I), A(I), C(I)
430 FORMAT(10X,F6.4,4X,F8.3,4X,F7.4,4X,F5.2,3X,F5.2)
440 CONTINUE
500 CALL EXIT
END