"A DIELECTRIC AND SPECTROSCOPIC STUDY OF MOLECULAR ASSOCIATION IN SOLUTIONS OF ALCOHOLS"

by

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Corrigenda

Page 5, line 5: ε_o is the limiting permittivity at low frequency and ε is the permittivity of free space.

Page 81, line 1: replace sentence starting "Then applying........" to end of that paragraph as follows.

The frequency response of a sample may be expressed as the Fourier transformation, F, where

$$F\ (\text{sample}) = S(f).R(\omega)e^{-2\gamma l} . \frac{1+R_s(\omega)}{1-R(\omega).R_s(\omega)e^{-2\gamma l}}$$

and S (f) is the spectrum of the incident wave-form. A similar expression describes the spectrum of a short and since $R(\omega) = -1$ for a short, one obtains

$$F\ (\text{short}) = S(f).(-1).e^{-2\gamma l} . \frac{1+R_s(\omega)}{1-(-1).R_s(\omega)e^{-2\gamma l}}$$

Then applying

$$\frac{F\ (\text{sample})}{F\ (\text{short})} = \text{Rapp}\ (\omega) = \frac{R(\omega).[1+R_s(\omega).e^{-2\gamma l}]}{-[1-R(\omega).R_s(\omega)e^{-2\gamma l}]} \quad , 2.\text{xvii}$$

where Rapp (ω) is the experimentally measured reflection coefficient, R (ω) is that of the sample under investigation and $R_s(\omega)$ is that of the sampler obtained as described above, one obtains improved frequency domain information for the sample.

ACKNOWLEDGEMENTS

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ABSTRACT

This study is concerned with the association characteristics of solutions of alcohols in some non-polar solvents. The permittivities at 2 MHz and 25°C for solutions of the straight chain octanols in cyclohexane, carbon tetrachloride and benzene have been examined over the entire solute concentration range, with particular attention being paid to the range below 0.1 mol ℓ^{-1}. By applying the Kirkwood-Fröhlich equation to these data, the apparent dipole moments of the alcohols as a function of concentration have been evaluated. These concentration dependencies have been correlated with infrared absorption results on the same systems to provide information on the sizes and configurations of the proposed hydrogen bonded multimers. It is concluded that, at very low solute concentrations, the alcohol molecules exist as monomers; but with increasing concentration, two types of hydrogen bonded multimers are formed, the first (at low concentrations) being of high dipole moment and the second (at higher concentrations) being of low dipole moment. At high concentrations, the molecules associate to form a three-dimensional network.

Attempts have been made to determine equilibrium parameters for molecular models which are consistent with the qualitative understanding of the association behaviour. These parameters were obtained by applying least-squares,curve-fitting techniques to the low concentration permittivity data.

A similar investigation has been conducted on solutions of 2,3,4-trimethyl-3-pentanol in the same solvents. The steric hindrance around the hydroxyl group of this alcohol modifies the association behaviour so that a three-dimensional network does not

form at high solute concentrations. Proton magnetic resonance chemical shifts for the hydroxyl proton of this alcohol in carbon tetrachloride solutions have been measured. Attempts have also been made to determine equilibrium parameters which describe formation of the hydrogen bonded multimers.

To extend this study to include solutes other than octanols, similar experiments have been conducted on solutions of t-butanol in hexadecane, a system which has recently been investigated by other workers using different experimental techniques. The association behaviour of this system is qualitatively similar to that of the straight-chain octanols.

The combination of permittivity and infrared measurements, although proving extremely powerful in interpreting the association characteristics of dilute alcohol solutions, is less adequate at high solute concentrations. Attention was therefore directed towards dielectric relaxation and viscosity studies to investigate concentrated solutions. The relaxation times at 20°C of the low frequency dispersion have been measured for solutions of 1-propanol, 1-butanol, 1-hexanol, 1-octanol and 1-decanol in cyclohexane using time domain reflectometry techniques. Similar measurements have also been made on solutions of 1-butanol and 1-octanol in carbon tetrachloride and in benzene. The concentration dependence of the viscosities of certain of these systems has also been examined in an independent study.

The ratio of the dielectric relaxation time to the viscosity, the "reduced relaxation time", is qualitatively similar for each system studied. This similarity leads to an explanation of the molecular process responsible for the low frequency dispersion in terms of the proximity of the hydroxyl groups in concentrated alcohol solutions and the fraction of the groups which are not involved in hydrogen bonding.

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INTRODUCTION

Hydrogen bonded liquid systems are of interest to the physical chemist because, in such systems, the general, non-specific van der Waals interactions are relatively small. Consequently, attention may be focussed on the specific molecular interactions involved in hydrogen bonding which are, however, sufficiently weak to display interesting dynamic properties. An understanding of the characteristics of hydrogen bonding is desirable in view of its ubiquity in biochemical systems and of its effect on the physical properties of solutions, typically melting point, boiling point and vapour pressure.

An understanding of the behaviour of solutions requires a detailed knowledge of the molecular interactions involved. The aliphatic alcohols constitute a particularly suitable and interesting class of compounds for study. They readily form hydrogen bonds (which are their only significant interaction) giving rise to associated species of different size and configuration. Many different alcohols (including geometrical isomers and enantiomers of particular alcohols) are commercially available; this allows for a systematic study of the influence, on the solution properties, of changes in the microscopic environment around the hydroxyl group. For these reasons, much effort has been devoted towards gaining an understanding of the association properties of alcohols and their solutions in non-polar solvents.

Many physical techniques have been used to study intermolecular behaviour in solution; however, no single method gives a complete understanding of the nature of these interactions. In particular, infrared and NMR spectroscopies, which are commonly used, give little information concerning the alignment of neighbouring molecules. Such information is vital for a full understanding of the physical properties of solutions since, although it is accepted that hydrogen bonded multimers of varying sizes are formed, little is known about their sizes and configurations. On the other hand, the determination of dipole moments of solutions can give information on the alignment of molecular dipoles within associated species, from which an understanding of the configurations of such species may be obtained. These measurements can be used in conjunction with infrared spectroscopic measurements to provide qualitative and possibly quantitative information on the equilibria among the associated species.

An even more detailed description of the physical characteristics of the associated solutions requires a knowledge of the dynamics of the molecular motions of the species present. Such information can be obtained from relaxation experiments conducted over many decades of frequency.

This study is concerned essentially with the static permittivities and relaxation characteristics of solutions of alcohols in non-polar solvents. The relaxation experiments were conducted in the microwave region, up to 5GHz, using the relatively new technique of time domain spectroscopy. Infrared and NMR spectroscopies were used to facilitate the interpretation of the dielectric results.

The experiments were conducted principally on selected octanol isomers but were extended to include other alcohols. The permittivities of pure octanol isomers vary from 9.8 to less than 3 at 25°C, indicating a wide range of bonding situations in the pure liquid. However, it was anticipated that in dilute solution the association behaviours might be very similar. Carbon tetrachloride, cyclohexane and benzene were chosen as representative, non-polar solvents.

CHAPTER 1

ASSOCIATION IN ALCOHOLS AND THEIR SOLUTIONS

Section 1.1. Association and Static Dielectric Permittivity

1.1.1. Development of Current Theories

In the nineteenth century, workers investigated the behaviour of materials under the influence of an externally applied electric field. A particularly important development of the period was the concept of the internal field, suggested by Lorentz (1880): this is the average field experienced by individual microscopic particles in a macroscopic dielectric medium. This concept was incorporated into equations expressing the dielectric permittivity, ε, in terms of the electric polarisability and of the volume of the microscopic particles. These equations were developed by Mosotti (1847) and later, independently, by Clausius (1879). Lorentz (1880), simultaneously with Clausius, presented a similar relationship in terms of the square of the refractive index, n^2. Following Maxwell's relation, $\varepsilon = n^2$, these equations are identical at a given frequency.

The resulting Clausius - Mosotti and Lorentz - Lorenz equations were found to have a very limited range of applicability : they failed to describe, even in the gaseous phase, the behaviour of a class of compounds described as "associating". Various ideas were proposed to explain the lack of agreement of which the most successful was Debye's suggestion (1912) of a permanent electric dipole moment, μ, for each molecule. He presented a relationship incorporating this concept with the more usual dipolar polarisability, assuming that the force couple which tends to orient a dipolar molecule in a polarised medium is proportional to the internal field described by Lorentz. The equation thus obtained is called the Debye equation:

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = 4\pi N \cdot \frac{(\alpha + \mu^2/3kT)}{3\varepsilon} , \qquad 1.i$$

where k and T are Boltzmann's constant and absolute temperature respectively, N is the number of dipoles per unit volume, α is the molecular polarisability, ε_0 is the dielectric permittivity at very high frequency and ε is the measured permittivity. This equation, which was increasingly applied to experimental results as the knowledge of molecular geometries became more refined, provided quantitative agreement when gases or dilute solutions of polar compounds in non-polar solvents were examined. However, for other systems, the lack of correlation between experimental and theoretical results was disturbing. Modifications of the Debye equation were developed by several workers (Smyth, 1955), but these did not improve the understanding of the principles until Onsager (1936) recognised the limitations of the Lorentz internal field.

He noted two contributions to the internal field:

a) a cavity field which contributes to the orienting force-couple and is produced in the empty cavity by the externally applied field; and

b) a reaction field which, being parallel to the dipole moment of the molecule, does not contribute to the orienting force couple.

Onsager used the same molecular model as Debye and, with electrostatic arguments, described the permittivity of a solution in terms of the dipole moment:

$$\frac{(\varepsilon_0 - n^2)(2\varepsilon_0 + n^2)}{\varepsilon_0 \, (n^2 + 2)^2} = \frac{4\pi N\mu^2}{9kT\varepsilon} . \qquad 1.ii$$

This equation, known as the Onsager equation, was more successful than the Debye equation since it provided for the enhancement of the dipole moment by the reaction field. However, its description of the behaviour of associated liquids was still inadequate. Attempts to improve the model by allowing for non-spherical molecules met with limited success since a far more serious limitation of the theory was the neglect of short range interactions. Thus, although the theory was a considerable improvement over earlier ones, refinements were necessary to allow for consideration of all classes of compounds.

Kirkwood (1939) developed a modification of Onsager's theory by considering the effect of hindered molecular rotation on the polarisation of liquids. He considered the dipole moment of a single molecule and the total moment, $\bar{\mu}$, of a molecule and its neighbours in the absence of an external field. This eliminated Onsager's most serious defect of a molecular cavity in a continuum of uniform permittivity. By assuming the macroscopic dielectric permittivity to be a fair representation of the dielectric permittivity outside the region containing a molecule and its two nearest neighbours, Kirkwood deduced

$$\mu \cdot \bar{\mu} = \mu^2 \left(1 + 2 < \cos\gamma >_{\mathrm{av.}}\right) , \qquad 1.\mathrm{iii}$$

where γ is the angle between the dipole moments of a pair of neighbouring molecules and the integral defining $< \cos\gamma >_{\mathrm{av.}}$ extends over all relative orientations of the pair. This equation defines the rôle of hindered rotation. The torque hindering the relative rotation of a pair of nearest neighbours may arise from short range intermolecular forces as well as from dipole-dipole interactions.

In its final form, the Kirkwood equation is

$$\frac{(\varepsilon_o -1)(2\varepsilon_o + 1)}{3\varepsilon_o} = \frac{4 \pi N}{\varepsilon} \cdot \frac{\mu.\bar{\mu}}{3kT} \quad . \qquad 1.\text{iv}$$

When the orientation by a molecule of its neighbours (which are considered to form part of a dielectric continuum) occurs only through dipole interactions, $\bar{\mu}$ reduces to μ and the Onsager equation is obtained.

Oster and Kirkwood (1943) introduced a correlation parameter, g, such that

$$\mu.\bar{\mu} = g\mu^2 \quad . \qquad 1.\text{v}$$

The correlation parameter may, in principle, be calculated using statistical mechanics; however, a sufficiently detailed knowledge of liquid structure is usually lacking. It is therefore more usual to measure g experimentally, particularly for solutions in which association occurs. The values of g may provide information on the molecular structure of the solution : a value of $g = 1$ implies random orientation of dipoles in solution; values greater than 1 result from a parallel alignment of the dipoles of neighbouring molecules while values less than 1 are obtained when neighbouring dipoles adopt an anti-parallel alignment. Great caution must be exercised, however, before concluding, from an experimentally measured value of $g = 1$, that no association of molecules takes place : the value 1 may arise when a weighted average of low and high dipole moment species, both present in solution, combine to produce a situation in which no correlation seems to exist.

Using a molecular model similar to that of Debye, Fröhlich (1948) invoked classical statistical mechanical arguments to obtain a more general expression than that of Kirkwood. He considered all particles inside a spherical region of average dipole moment m* and treated the volume beyond as a continuous dielectric described by the macroscopic permittivity. The dipole moment, m, of a particle in a given configuration in the spherical region differs from m* essentially because of short range interactions. Using the function $< m.m^* >_{av.}$, Fröhlich developed the expression

$$\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} = \frac{4\pi N}{\varepsilon} \cdot \left< \frac{m.m^*}{3kT} \right>_{av.} \cdot \qquad 1.vi$$

If one considers each particle to contain one dipole and that contributions to m* occur by dipolar orientation, then $m = \mu$ and $m^* = \bar{\mu}$, from which it can be shown that

$$< m.m^* >_{av.} = < \mu.\bar{\mu} >_{av.} = \mu.\bar{\mu} \quad . \qquad 1.vii$$

Under these circumstances, the Kirkwood and Fröhlich equations are identical. The Kirkwood-Fröhlich equation may be written as

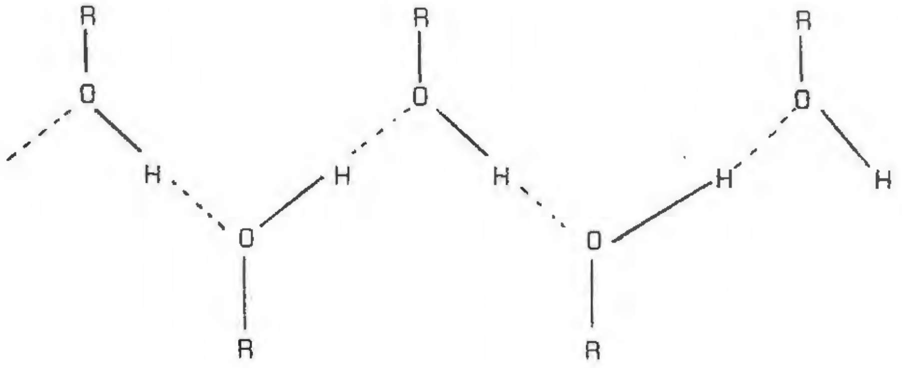
$$\frac{(\varepsilon_o - \varepsilon_\infty)(2\varepsilon_o + \varepsilon_\infty)}{\varepsilon_o(\varepsilon_\infty + 2)^2} = \frac{4\pi L \rho}{9kT \varepsilon M} \cdot g\mu_g^2 \cdot \qquad 1.viii$$

where L, ρ and M are Avogadro's number, density and molecular mass respectively and μ_g is the observed gas phase dipole moment for a molecule, calculated by assuming spherical particles of dipole moment, μ, in a medium of permittivity ε_∞ :

$$\mu_g = \frac{3\mu}{(\varepsilon_\infty + 2)} \quad . \qquad 1.ix$$

1.1.2. Some Early Models of Alcohol Association and Their Limitations

With the development of Kirkwood's and Fröhlich's equations, a more refined understanding of the process of association could be attained. Kirkwood and Oster (1943) applied equation 1.iv in a study of water and some pure, liquid alcohols. They noted X-ray scattering experiments on liquid alcohols which suggested, on the basis of an observed average coordination number of 2, that the alcohol molecules are arranged in linear, hydrogen bonded chains of the type:



Kirkwood and Oster assumed these chains to be infinitely long, with free rotation around the hydrogen bonds. The correlation factor then becomes

$$g = 1 + 2 \sum_{n=1}^{\infty} < \cos\gamma_n >_{av.} \quad , \qquad 1.x$$

where γ_n is the angle between the dipole moments of two molecules separated by n bonds in the chain. Making assumptions about the environment around an alcohol molecule, they calculated a value for g of 2.57. (This value was subsequently modified to 2.39 by Dannhauser and Cole (1955) who used improved values for the partial moments of the alcohol molecules.) This theoretical value was in fair agreement with the experimentally determined values considering the general assumptions invoked. However, Kirkwood and Oster's model failed to predict or allow for the temperature dependence of g, later established by Dannhauser and Cole (1955).

These workers improved on the above model by considering a distribution among alcohol chains of varying length, characterised by an equilibrium constant, K, which was independent of the size of the aggregate formed; thus

$$\mathrm{ROH} + (\mathrm{ROH})_{n-1} \overset{K}{\rightleftharpoons} (\mathrm{ROH})_n \quad ,$$

where K is independent of n. Kempter and Mecke (1940) had previously made this assumption in their infrared spectroscopic studies of association in phenol solutions

This concept provided for a limiting high temperature value for g of 1 and a limiting low temperature value of 2.39. However, Dannhauser and Cole observed higher limiting values than 2.39 at low temperatures in a study of the temperature dependence of g for the butanol isomers.

The difference between the experimental and theoretical results of the above study was not unrealistic in view of the qualitative nature of the model. A factor recognised as being important, but not allowed for, was the influence, on the association behaviour, of steric hindrance around the hydroxyl group of the alcohol : the low value of g observed for t-butanol was understood to result from a reduction of the length of the associated chains because of steric interference.

However, a more serious limitation of this model and that of Kirkwood and Oster was that neither could explain an observed correlation factor less than 1. Such values of g had already been observed by Smyth and Stoops(1929a) in their investigation of twenty-two isomeric octanols and, subsequently, by Oster (1946) who found that the g values observed for solutions of ethanol in hexane and in heptane exhibited a minimum at low alcohol concentrations. Oster recognised this behaviour as resulting from the presence in solution of associated species of low dipole moment.

1.1.3. Influence of Temperature and Pressure on g

Following the study of Smyth and Stoops, Dannhauser and co-workers undertook a comprehensive set of measurements on a series of pure alcohols. By examining alcohols with systematically altered features, they attempted to clarify the function of the microscopic -OH environment in determining the association behaviour. This was achieved by measuring the temperature and pressure dependencies of ε for selected alcohols and subsequent application of these data to the Kirkwood-Fröhlich equation to obtain the liquid-structure related g factor.

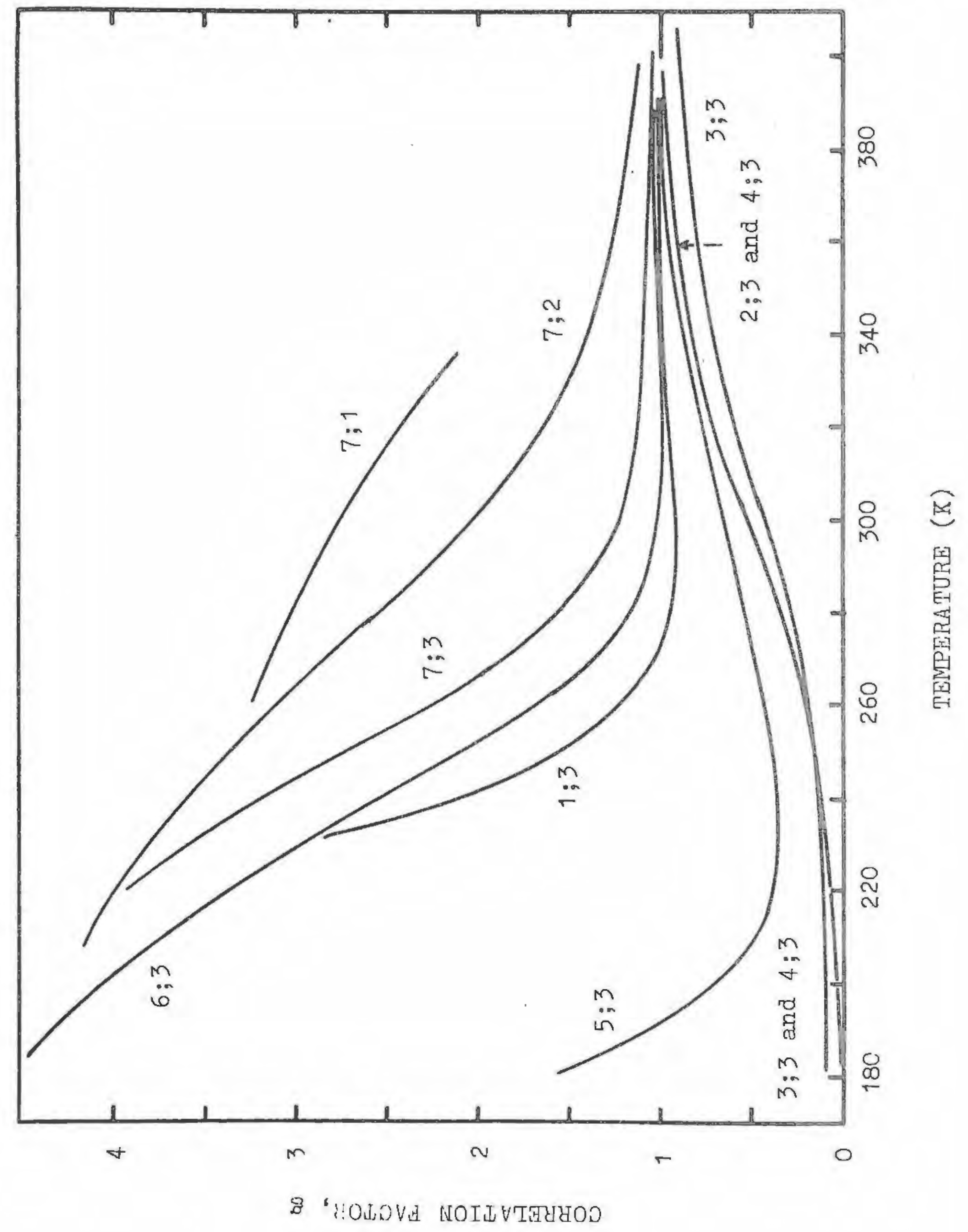
In a study of the temperature dependencies of g for the eight lowest aliphatic alcohols, Dannhauser and Bahe (1964) observed g to decrease and tend to a limiting value of 1 with rising temperature, in accordance with Kirkwood's theory. This decrease was assumed to result from depolymerisation of the linear chains whose large negative entropies of formation were considered to make them unstable at high temperatures. The model used to quantify the data did not allow for the presence of cyclic species and, therefore, its conclusions must be treated with caution. However, the data and the qualitative aspects of the study remain valuable. Dannhauser again noted that, at the lower limit of temperature, g approached a value significantly larger than 2.39. This was, as before (Dannhauser and Cole, 1955), considered to result from partial hindrance of rotation in the associated chains.

A similar set of measurements was obtained from a series of neo-alcohols (Dannhauser, Bahe, Lin and Flueckinger, 1965) for which there was not expected to be large changes in the association parameters obtained since the microscopic environments around the hydroxyl groups are identical. However, the results were found to be very sensitive to the length of the hydrocarbon side chain. Difficulties in obtaining results over a sufficiently wide temperature range restricted quantisation of the data, but the general trends established by Dannhauser and Bahe (1964) were again evident. The interesting observation was made that α-substitution is most effective in limiting chain formation; β-and γ-substitutions are surprisingly ineffective. Dannhauser, Guerin and Flueckinger (1970) later noted that changes in the hybridisation of the β-carbon caused little change in the association behaviour.

Extending his investigations to the temperature dependence of g for a series of octanols, Dannhauser (1968a) found that the shapes of the curves representing the temperature dependence of g over the whole concentration range were sensitive to the steric environment of the hydroxyl group. This behaviour is depicted in Figure 1.1. For certain alcohols, the data were significantly different to those obtained from studies of the same alcohols by Smyth and Stoops (1929a). Dannhauser considered impurities in their samples to be responsible. To explain the observed minima, Dannhauser now allowed for equilibria

FIGURE 1.1

Correlation factor as a function of temperature for some octanols (reprinted from Dannhauser (1968a)). The nomenclature is based on a two digit code for monomethyl-substituted heptanols, the first number describing the position of the methyl substituent and the second that of the hydroxyl group. The latter number is the smallest possible e.g. 5;3 is 5-methyl-3-heptanol.



among cyclic and chain associated species in his model, but unfortunately considered the cyclic species to be a dimer. This assignment neglected the studies of Ibbitson and Moore (1967a,b) and Raczy, Constant and Lebrun (1967) which showed that the first associated species, probably a dimer, is linear and that cyclic species are probably trimers or tetramers. (These, and other, related studies, will be discussed more fully in sub-section 1.1.5.) To some degree, this limitation was not important since only trends in the calculated thermodynamic parameters were examined, small differences being regarded as unmeaningful. The results showed ΔH^{o} for hydrogen bond formation to be insensitive to the alcohol studied; but ΔS^{o} for hydrogen bond formation was extremely sensitive to the environment of the -OH group (although later studies (Dannhauser and Johari, 1968a) suggested a limiting value of ΔS^{o} may be achieved with α- or β- monosubstitution)

Johari and Dannhauser(1968b) conducted experiments to measure the pressure dependence of g for some of the octanols examined in the above study. They found that $d\ln\varepsilon/d\ln p$, an expression used to examine the pressure dependence of permittivity (Jacobs and Lawson, 1952), varied in entirely different ways for the octanols studied. From this they concluded that the effect of pressure was to change the position of the ring-chain equilibrium controlling the liquid structure rather than the dipole moment of the molecules. Using Dannhauser's model of a ring-chain equilibrium, Johari and Dannhauser confirmed earlier findings (Dannhauser, 1968a) that changes in the equilibrium position result from changes in the entropy of the association process : the major effect of pressure changes was seen in the ΔS^{o} values, ΔH^{o} being more-or-less independent of pressure.

1.1.4. Influence of Concentration on g.

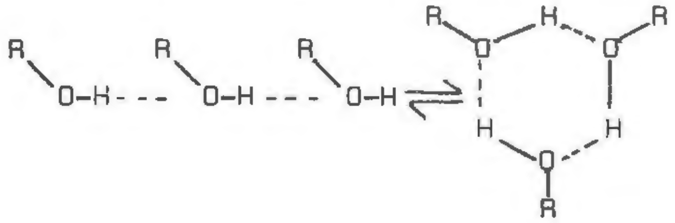
Dannhauser restricted his studies, which have contributed in large measure to the present understanding of association in alcohols, to pure alcohols and did not examine the concentration dependence of g for alcohol solutions. While the influence of concentration parallels those of pressure and temperature, investigation of concentration dependent changes in g gives insight into the specific interactions involved in the liquid state. One can arrange for subtle changes in the microscopic environment around alcohol molecules by changing the basicity, viscosity and electronic properties of the solvent. Further, solution data at normal temperatures and pressures are more amenable to correlation with data obtained using a variety of experimental techniques.

Huyskens and co-workers have made extensive investigations of the effect of concentration on the association behaviour of alcohol solutions. With Cracco (1960), he presented an equation, derived from that of Onsager, which was adapted to studies of solutions. They assumed additivity of the dipole moment contributions from induced dipoles of the solvent together with permanent and induced dipoles of the solute to yield the expression

$$\mu^2 = \frac{9kT}{4\pi L} \cdot \frac{(2\varepsilon_o + \varepsilon_\infty)^2 . \varepsilon}{X(\varepsilon_\infty + 2)^2 (2\varepsilon_o + 1)} \left[\phi\left(\frac{\varepsilon_o - 1}{\varepsilon_o}\right) - \frac{3(1 - X)(\varepsilon_1 - 1)}{2\varepsilon_o + \varepsilon_1} \cdot \phi_1 - 3(\phi - \phi_1 + X\phi_1)\left(\frac{\varepsilon_\infty - 1}{2\varepsilon_o + \varepsilon_\infty}\right) \right] , \qquad 1.xi$$

where ε_1 is the permittivity of the solvent, X is the mole fraction of solute, ϕ is the observed molar volume and ϕ_1 and ϕ_2 are the molar volumes of the solvent and solute respectively. This equation differs from that of Onsager in not assuming additivity of the molar volumes, an assumption which is invalid for associating solutes.

Huyskens and co-workers subsequently used this equation in investigations of the association of alcohol solutions. With Henry and Gillerot (Huyskens, Henry and Gillerot, 1962), he examined the influence of non-polar solvents on the association of isomeric butanols and, for each solvent, found similar solution behaviours : a minimum in the square of the observed dipole moment, μ^2_{app}, (which is equivalent to the correlation factor) was observed at low concentration. As suggested by Oster (1946), the minimum was considered to result from the presence in solution of cyclic, low dipole moment associated species formed in an equilibrium of the type



The minima were noted to be most evident with hydrocarbon solvents such as cyclohexane, but as the proton accepting ability of the solvent increased, the minima became less prominent, indicating a smaller proportion of the cyclic species. This was explained by increased solvent stabilisation of the terminal hydroxyl group of the open species in the above equilibrium which reduces the energy gain on cyclisation. The minima were also found to be sensitive to temperature, decreasing in magnitude as the temperature of the solutions was increased.

The effect of alkyl chain length on the association behaviour was similarly examined for solutions in carbon tetrachloride (Huyskens, Gillerot and Zeegers-Huyskens, 1963) and in cyclohexane (Clerbaux and Zeegers-Huyskens, 1966). In each solvent, qualitatively similar results were obtained, the minimum increasing in importance as the chain length of the alcohol side chain increased. This implies that the increasing length of alcohol side chain hinders the association into the linear chains which predominate in the pure alcohol.

1.1.5. Investigations of Association in Alcohol Solutions of Low Concentration.

The work of Huyskens' group, while providing useful, qualitative information, did little to improve the understanding of the molecular arrangement and size of the associated species formed in solution. To obtain such knowledge, it was necessary to examine alcohol solutions at very low concentrations : here, changes in the mode of association are less likely to be masked by the gross properties of concentrated solutions. Another important factor is that over a limited concentration range, neglect of solution non-ideality is less likely to produce serious errors when attempts are made to quantise the data. In dilute solutions, constants for the formation of associated species can be calculated from experimental data by assuming deviations from the experimental behaviour predicted by the dilute solution laws to result from association. However, over a wide range of concentration, the nature of the medium may change in which case the limiting laws no longer apply. It is then difficult to determine the relative importance of the deviations caused by association and by non-specific solution effects.

Investigations of alcohol association at low concentration had already been conducted by several workers (Smyth and Stoops, 1929b;

Wolf and Herold, 1934; Wolf, Frahm and Harms, 1937 ; Hennings, 1935) but these studies predated the molecular theories of Kirkwood and Fröhlich so that the analyses were necessarily incomplete. Maryott (1941) extended his measurements to such low concentrations that the constant polarisation values indicated the presence of only monomeric alcohol molecules. Later investigations were not sufficiently accurate to render meaningful the small differences in g at low concentrations until two, independent publications (Ibbitson and Moore, 1967a,b; Raczy, Constant and Lebrun, 1967) indicated a rise, the one (Ibbitson and Moore) in solute polarisation and the other (Raczy et al.) in g with increasing alcohol concentration at very low concentrations. The rise in polarisation or g was ascribed by each group to the formation of linear, high dipole moment, dimers and trimers at low concentrations; the subsequent fall was interpreted as resulting from an increasing concentration of a cyclic, low dipole moment species. Ibbitson and Moore identified two rises in polarisation against concentration, but the scatter of their data makes this assignment rather hazardous.

An interesting feature of Ibbitson and Moore's data is the extended linear region in the curve of polarisation against concentration observed for solutions in cyclohexane. Malecki and Jadzyn (1974) criticise explanations of this feature which require simultaneous formation of high and of low dipole moment multimers : they argue that such mutual cancelling of influences is not noted in enthalpy or NMR data. However, the curve obtained from the concentration dependence of any experimentally observed property of an associated solution will be biased according to the weighting attached to each oligomer as appropriate to the technique. While the squares of the dipole moments of the associated species may mutually cancel, there is no reason to expect similar behaviour to occur in other physical properties of the solution. As noted by Malecki and Jadzyn, a change in temperature should destroy the cancelling; however, although they did conduct temperature studies, the scatter of their data precludes a decision on the behaviour.

Bordewijk, Kunst and Rip (1973), in a temperature study of the concentration dependence of the dipole moment for solutions of 1-heptanol in carbon tetrachloride, confirm the rise in μ^2_{app} with concentration. The subsequent fall in μ^2_{app} was also noted and explained as before. The data were quantised, on the assumption that only one type of dimer exists, by fitting mathematical curves using equations which required a mass balance of solute and which expressed the observed dipole moment as a weighted mean of the contributions from each species present. On comparing the results obtained from monomer - linear dimer - cyclic trimer and monomer - linear dimer - cyclic tetramer models, little difference in their standard deviations was found; however, the latter model was preferred because of the systematic trends obtained, with rising temperature, for the calculated equilibrium constants.

The discovery and confirmation of a small, high dipole moment species occurring between the monomer and the cyclic, low dipole moment species is of major importance. Consequently, its presence must be allowed for in the analysis of low concentration data, no matter from which technique the data was obtained. As the alcohol concentration increases, the influence of this species will decrease since the equilibrium behaviour is dominated at low concentrations by the cyclic species and at high concentrations by the linear chains.

1.1.6. Association and the Dielectric Saturation Effect.

While the association behaviour of alcohol solutions is commonly investigated by measuring changes in permittivity, either as a function of temperature,. pressure or concentration, a small group of publications (Böttcher, 1973a) deals with the changes in permittivity induced when a large external field is applied. The field dependence of the permittivity, the dielectric saturation effect, for solutions of three alcohols in non-polar solvents was noted by Malecki (1962) to show a maximum as a function of concentration before decreasing to a minimum value for the pure alcohol. Piekara (1962) subsequently explained this novel behaviour in terms of a dimer, existing in two configurations with an energy separation, ΔU. The dimers in the two configurations have different dipole moments.

Malecki (1965) adopted this model to explain experimental data obtained from 1-hexanol solutions. His results were in reasonable agreement with those of Clerbaux and Zeegers-Huyskens (1966), but this agreement is probably fortuitous in view of the gross approximations made by each author.

In a later, more sophisticated treatment, Malecki and Dopierala (1969a) considered general multimer formation and allowed for alcohol/solvent complexes in an investigation of association in solutions of t-butanol in cyclohexane (1969b) and of 1-dodecanol in cyclohexane, carbon tetrachloride and hexane(1969c). Their model maintained the concept of a dimer existing in two configurations and demanded, as a precondition for solution of the equations describing the system, that the dipole moment of the trimer be zero. Because of the approximations made to simplify the calculations and the difficulty in obtaining acceptable data at low concentrations a quantitive analysis of the results was not justified. Instead, selected values for the equilibrium constants describing the concentrations of the associated species were inserted into the equilibrium equations to evaluate the trends in the data.

The suggestion by Malecki and Piekara that the dimer causes the observed changes in the dielectric saturation effect is open to question since independent studies (Ibbitson and Moore, 1967a,b; Bordewijk et al., 1973) have indicated that dimers exist in significant concentrations only at concentrations considerably below those examined by Malecki and Dopierala. It would therefore seem that more fundamental studies of dielectric saturation effects on alcohol solutions are required before the technique can contribute meaningfully to studies of alcohol association.

1.2 Dielectric Relaxation Studies of Association

1.2.1. Outline of Theories

The dielectric relaxation properties of alcohols have provided intriguing problems to research workers who have attempted to understand both the energetics and kinetics of the molecular processes responsible, as well as the influence of subtle changes of the molecular structure on the observed behaviour.

The initial molecular model and associated equations describing experimental parameters provided by relaxation studies were developed by Debye (1929). His model was based on a description of molecular rotation as a Brownian motion : rotation, in response to an oscillating, applied field, is constantly interrupted by collisions with neighbouring molecules. A molecular friction constant, ζ, relates the resistive torque of the molecular field to the angular velocity of the molecule, from which one may conclude there to be a single relaxation time :

$$\tau = \zeta/2kT \qquad 1.xii$$

To estimate ζ, Stokes's Law was assumed, with spherical molecules of radius a rotating in a continuous viscous fluid of macroscopic viscosity η. Thus

$$\zeta = 8\pi\eta a^3 \quad , \qquad 1.xiii$$

giving

$$\tau = \frac{4\pi\eta a^3}{kT} \quad . \qquad 1.xiv$$

Equation 1.xiv did not satisfactorily describe experimental behaviour, in most cases over-estimating the value of τ. Debye (1934) established that the macroscopic viscosity was an inadequate representation of the microscopic viscosity. However, attempts to improve the model by modifying the description of microscopic viscosity (Hill, 1969a) have met with limited success.

Kauzmann (1942) argued that the description of molecular reorientations by Brownian motion was inappropriate. Using a model derived from Eyring's contention (Glasstone Laidler and Eyring, 1941) that dipole rotation may be treated by analogy with chemical rate processes, he considered molecules to occur in micro-crystalline regions in the fluid and to fluctuate around some equilibrium position. To move from one orientation to another, the molecule must pass through some high energy, intermediate situation characterised by an activation energy, E_a. This use of unimolecular reaction rate theory permits description of the rate process in terms of E_a and an activation entropy S_a:

$$\tau = \frac{h}{kT} \cdot \exp\,(E_a - T.S_a)/RT \quad , \qquad 1.xv$$

where h is the Planck constant.

This description, in terms of discrete energy levels, is in direct contrast to Debye's concept of infinitesimal fluctuations. It has received support because of the reasonable values it predicts for E_a from plots of log τ against $^1/T$.

Kauzmann's model adequately explains the experimentally noted behaviour where a single macroscopic relaxation time or a distribution of times is observed, corresponding to situations in the liquid state where fluctuations occur either very infrequently or frequently compared to other movements. Cole-Cole diagrams (1941) may be used to represent these behaviours. These are complex plane diagrams of the dielectric loss factor, ε'', plotted against the real permittivity, ε'; the quantities ε' and ε'' are the real and imaginary components, respectively, of the complex relative permittivity, $\varepsilon = \varepsilon' - j\varepsilon''$. For a single relaxation time, the Cole-Cole plot is a semi-circle, usually referred to as a Debye semi-circle, but, where there is a distribution of relaxation times, the curve falls inside the Debye semi-circle, giving what is usually referred to as the Cole-Cole arc. Both the Debye semi-circle and the Cole-Cole arc are symmetrical.

However, an asymmetric arc was noted for certain materials, for example glycerol, by Davidson and Cole (1951) and this behaviour cannot be explained in terms of Kauzmann's model. To allow for this behaviour, Glarum (1960) suggested that relaxation occurs in a microcrystalline region by two coexistent mechanisms. Defects may occur in these regions and can facilitate the reorientation of a molecule. This gives rise to a relaxation time, τ, which is independent of the time τ' for rotation in the absence of any defect.

By considering the motion of a defect to be subject to a diffusion law, the three characteristic variations of relaxation phenomena, noted above, can be explained. However, this model has been criticised by Litovitz and McDuffie (1963) who found it did not fully account for dielectric and acoustic relaxation measurements made upon a variety of associated liquids. It was subsequently refined by Anderson and Ullman (1967) who developed an interesting theory based on the description of the relaxation time in terms of an environmental parameter, generally called the free volume. They considered the molecular environment to fluctuate with time, so causing consistent changes in the probability of reorientation. From the magnitude of these fluctuations relative to reorientation, the dielectric relaxation time of the system is determined : if the fluctuations are rapid compared to the reorientation, a single value of τ is found; if they are few, a distribution of τ's is found and in the intermediate situation an asymmetric arc will be obtained.

1.2.2. Features of the Relaxation Behaviour of Alcohol Solutions.

For pure alcohols in which there is no steric hindrance around the hydroxyl group and their concentrated solutions (above 40 mole %) in non-polar solvents, the major portion of the dispersion region is adequately represented by the simple Debye equation, implying that a single species is involved in the relaxation process. The relaxation time characteristic of this region is referred to as τ_1. This simplicity is unexpected in view of the complex association occurring in concentrated alcohol solutions. However, in spite of the relative simplicity of the behaviour, no theory has yet been presented which can adequately account for the various trends observed on changing the alcohol and solvent, and the temperature and pressure at which the experiments are conducted.

Although the initial, low frequency process, hereafter referred to as the τ_1 process, dominates the relaxation behaviour, evidence for two other processes, at higher frequencies, has been found. (Girard and Abadie, 1946; Cole and Davidson, 1952) The relaxation times of these dispersion regions are referred to as τ_2 and τ_3, τ_2 being the region at lower frequency. These processes will be referred to as the τ_2 and τ_3 processes. It is generally found that

$$\tau_1 > \tau_2 > \tau_3 , \qquad 1.xvi$$

and assigning weight factors C_1, C_2 and C_3 which represent the proportion by which processes τ_1, τ_2 and τ_3 contribute to the total dispersion, one notes that

$$C_1 > C_2 > C_3 \quad . \qquad 1.xvii$$

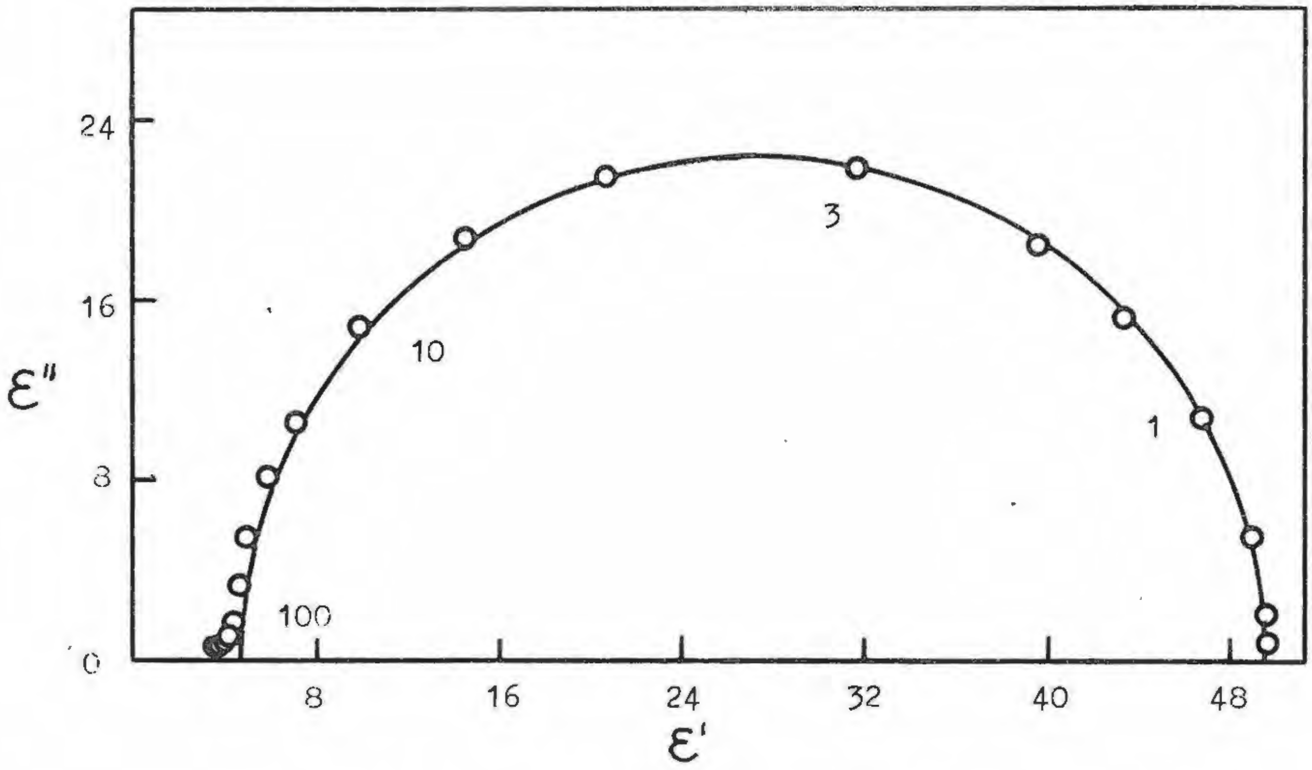
Figure 1.2 illustrates the relative magnitudes of these processes.

1.2.3. Molecular Descriptions of the High Frequency (τ_2 and τ_3) Processes.

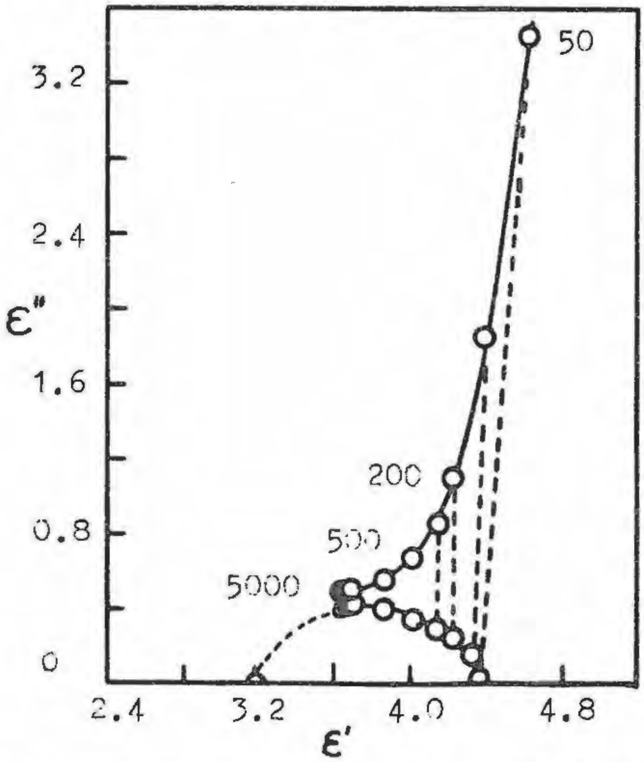
The influence of the solvent, temperature and pressure on the behaviour of each of the three processes for various alcohols has repeatedly been investigated in an attempt to elucidate the liquid structure of alcohol solutions, but with little notable success. Most investigations have attempted to gain an understanding of the mechanism of relaxation in terms of reorientation of molecular species or parts thereof. This has not meaningfully developed the understanding of association in solutions although workers have increasingly studied systems whose association properties are understood to some degree either from investigations using other experimental techniques or by analogy with results from similar systems.

FIGURE 1.2

Cole-Cole plots obtained for 1-butanol at 154K (reprinted from Dannhauser and Cole (1955)). The numbers beside discrete points are frequencies in kHz.



A Major (τ_1) dispersion



B High frequency processes. The dashed lines represent the subtracted contributions of the major dispersion.

Changes in the behaviour of the high frequency (τ_2 and τ_3) absorptions can be studied at low alcohol concentrations without interference from the dominant τ_1 process which is not observed at low concentrations. In contrast to static permittivity studies, the presence of zero (or low) dipole moment species, whose concentrations may be significant at low concentrations, does not affect the relaxation behaviour. Consequently the results must be explained in terms of monomers and the small, high dipole moment species discussed in sub-section 1.1.5.

At very low alcohol concentrations (less than 0.01 mol ℓ^{-1}) where only monomeric alcohol molecules exist, the τ_3 process only is observed and the relaxation time is seemingly independent of molecular size and alcohol concentration (Crossley, 1970). The process has been discussed as arising from reorientation of the alcohol $-CH_2-OH$ group (Leroy and Liebaert, 1963) or of alcohol monomers (Dannhauser, 1968b); however, most studies prefer to consider rotation of the hydroxyl group of the monomer as being responsible, since the relaxation time is similar to that observed for rotation of the -OH group in phenols (Davies and Meakins, 1957; Fong and Smyth, 1963). Crossley (1971) has found the relaxation time for the τ_3 process to be influenced by the solvent and suggests this to be the result of a solvent interaction with the alcohol -OH group.

As the alcohol concentration increases, the dispersion region separates into two distinct regions, the relative weightings of which change with increasing alcohol concentration. The relaxation time for the second (τ_2) process is found to be influenced by the steric environment of the -OH group, the alcohol concentration and the molecular size (Crossley, Glasser and Smyth, 1971). Garg and Smyth (1965) favoured monomer reorientation as the mechanism involved, since the magnitude of the observed relaxation time is similar to that for alkyl bromides (which are unassociated). However, this would require C_2/C_3 to remain independent of concentration; this was not found by Crossley et al. (1971). Glasser, Crossley and Smyth (1972) have suggested that the τ_2 process results from orientation of the terminal -OR group of a hydrogen bonded species. A similar mechanism has been proposed by Hassion and Cole (1955).

Dannhauser (1968b) based his concept of the molecular process responsible for the τ_3 and τ_2 processes on the premise that monomers were the only species with a non-zero dipole moment at low concentrations. (On the basis of his static permittivity studies, he considered a cyclic, low dipole moment dimer to be the first associated species formed.) He thus proposed monomer reorientation to be responsible for the τ_3 process, with the τ_2 process being associated with the long, multimer chains formed at higher alcohol concentrations. The magnitudes of the relaxation times typically observed for the τ_3 process are too small to be identified with monomer reorientation which makes Dannhauser's description of the τ_3 process doubtful. His description of the τ_2 process may also be questioned since Crossley et al. (1971) and Glasser et al. (1972) have identified the τ_2 process for several alcohols, with no evidence of the τ_1 process which is generally recognised as arising from the linear chains (Crossley, 1970). However, Dannhauser's results did show that the high frequency limit of the τ_1 process, $\varepsilon_{\infty,1}$, differed significantly from the low frequency limit of the τ_2 process, $\varepsilon_{0,2}$ which implies that the molecular motions responsible for the τ_1 and τ_2 processes are not independent. Indeed, Davidson and Wheeler (1959), from isotope studies on 1-propanol, concluded that the mechanisms are closely related.

One may postulate that the small, high dipole moment species found at low concentration (Ibbitson and Moore, 1967a,b; Raczy et al., 1967) contributes to the τ_2 process, perhaps by reorientation of the -OR group, as suggested by Glasser et al. or by reorientation of the molecule at the end of the species, as suggested by Johari and Smyth (1969). This argument is supported by noting that for alcohols in which the -OH group is sterically hindered, no τ_1 process is observed (Crossley, 1970). The τ_2 process in such alcohols must then be associated with the small, high dipole moment species, shown to exist in such alcohols by Raczy et al. (1967), since the process has been shown not to result from monomer reorientation (Crossley et al., 1971).

To investigate this argument further, extensive studies of the concentration dependencies of the relaxation time for the τ_2 region and of the correlation factor in the same concentration range will be needed.

1.2.4. Molecular Descriptions of the Low Frequency (τ_1) Process.

A similar uncertainty is found in the interpretation of the molecular behaviour responsible for the dominant, low frequency process. While the results are usually adequately described by the Debye equation, it was recognised that dielectric relaxation in alcohols does not stem from the viscous-damped, Brownian, rotatory diffusion of Debye's original model. Accordingly, a theory was developed by Bauer, Magat and Brot (Bauer, 1944a and b; Bauer and Magat, 1949; Brot, Magat and Reinisch, 1953; Magat, 1957; Brot, 1957; Brot and Magat, 1963) to explain the behaviour in terms of Kauzmann's model. This theory recognises the linear association found in concentrated alcohol solutions and therefore, by implication, the wide distribution of multimers existing. The relaxation process is considered to occur through rotation of a monomeric unit of an associated chain since the rotation of the whole chains themselves, with their distribution of sizes, would be expected to lead to a distribution of relaxation times. The energy required to rupture the hydrogen bond before orientation can take place is considered to be the activation energy for the process.

This theory has been criticised (Middelhoek and Böttcher, 1966; Sagal, 1962; Bordewijk, Gransch and Böttcher, 1969) principally with respect to the assumption of hydrogen bond breaking being the rate determining step. On examining the experimental values, listed in Table 1.1. for the activation energies for a series of alcohols with increasing chain length, one notes a regular increase in E_a with increasing chain length. This implies, following Bauer, Magat and Brot's theory, that the hydrogen bond energy in the linear associated chains is influenced by the chain length of the alcohol which is unexpected, to say the least. Even more disturbing is the need to envisage marked changes in the hydrogen bond strength as a result of changing the position of the -OH group in the alkyl chain : the experiments of Middelhoek and Böttcher (1966) showed a significant change in E_a for the series of straight chain heptanols. Bordewijk _et al_. (1969) measured the dielectric relaxation properties of mixtures of 1- and 4-heptanols in an attempt to finally discredit the theory. They reasoned that for these alcohols whose permittivities are similar (thus avoiding problems in interpretation of the results), hydrogen bonded species formed from molecules of both alcohols must be present in solution. The mixture of hydrogen bonds should give rise to a distribution or superposition of relaxation times if hydrogen bond rupture is indeed the rate determining step. However, for various mixtures of the two alcohols, a principal dispersion region with a

TABLE 1.1

Alcohol	Temperature Range (^{o}C)	E_a (k Cal $mole^{-1}$)	Reference
Methanol	-100 → + 20	3.5	D.W. Davidson (1957)
Ethanol	-5 → + 50	5.0	M.W. Sagal (1962)
1-Propanol	-80 → + 20	5.5	W. Dannhauser & R.H.Cole (1955)
1-Butanol	-70 → 0	6.3	W.Dannhauser & R.H.Cole (1955)
	- 25 → + 35	7.8	L.Reinisch (1954)
	+ 5 → + 50	7.3	M.W.Sagal (1962)
1-Pentanol	0 → + 40	8.8	L.Reinisch (1954)
1-Hexanol	- 40 → + 35	8.2	L.Reinisch (1954)
1-Heptanol	- 35 → + 50	7.9	C.Oppenheim (1951)
	- 30 → + 30	7.9	J.Middelhoek & C.J.F.Böttcher (1966)
1-Octanol	- 15 → + 50	8.9	R.Dalbert (1953)
	+ 20 → + 60	10.0	C.Klages & D.Roth (1959)
1-Decanol	+ 20 → + 60	10.7	C.Klages & D.Roth (1959)
1-Dodecanol	+ 30 → + 60	11.0	C.Klages & D.Roth (1959)
1-Tetradecanol	+ 40 → + 60	11.2	C.Klages & D.Roth (1959)
1-Hexadecanol	+ 50 → + 60	11.5	C.Klages & D.Roth (1959)

single value of τ was observed. Similar results had already been found for a mixture of methanol and 1-propanol in experiments performed by Denney and Cole (1955).

The experiment of Bordewijk warrants further consideration. Schallamach (1946), from his measurements on mixtures of various types of compounds, formulated a general rule for the relaxation behaviour of mixtures of associating and non-associating compounds : he predicted one relaxation region for polar binary mixtures in which both components are associating or both are non-associating; however, when one component is associating and the other non-associating, two relaxation regions are predicted. Such behaviour, which is consistent with the results of Bordewijk *et al.*, has been observed by other workers (Denney, 1959; McDuffie, 1962); however, in all cases noted above, the results were obtained from experiments conducted in the supercooled state. At room temperatures, Garg and Kadaba (1965) and Smyth and co-workers (Forest and Smyth, 1965; Kilp, Garg and Smyth, 1966) observed two dispersion regions for mixtures of two associating or of two non-associating liquids. Baba, Fujimura and Kamiyoshi (1969), by examining the dispersion of a binary mixture of ethanol and cyclohexanol in the supercooled and liquid states, attempted to discriminate between the two situations. They found a single dispersion in the supercooled state which gradually separated into two distinct regions as the temperature was increased.

This result casts some doubt on the validity of the arguments of Bordewijk *et al.* when their reasoning is extended to room temperature results. The duality of behaviour amply illustrates the difficulties, noted by Glasser *et al.* (1972), in extending information gained at low temperatures, where viscosity effects are vital, to room temperature studies, where they are less significant. Such temperature dependent behaviour may account for the unusual trends in the data of Denney and Ring (1963) when compared to data obtained on similar systems by van Gemert, de Loor, Bordewijk, Quickenden and Suggett (1973). The former workers observed, from studies in the supercooled state, that E_a for a mixture of 1-propanol in 2-methyl-pentane is lower than for the pure alcohol whereas van Gemert et al. observed higher activation energies for mixtures of 1-propanol in benzene and hexane. However, the studies of the latter group were conducted at room temperature which may account for the difference in behaviour when compared with Denney and Ring's results.

On the basis of his extensive dielectric and spectroscopic measurements of heptanol isomers over a wide range of temperatures, Bordewijk (1968) introduced a cyclic tetramer as being an important species existing in concentrated alcohol solutions. This tetramer is postulated to have a high dipole moment owing to the spatial arrangement of the RO- groups and can thus account for the observed rise in g with increasing alcohol concentration. Its uniformity will also explain the single relaxation time found for most primary and secondary alcohols, the relaxation process occurring by reorientation of the tetramer. The activation energy of the relaxation process, according to Kauzmann, depends on the area of the microcrystalline region disturbed to allow reorientation. This area will depend on the length and shape of the alkyl side chain which explains why E_a increases from methanol to decanol. The increases from 1- to 4- heptanol can be similarly explained. However, no reason has been put forward to explain why the low dipole moment species, found at low concentration and commonly discussed as a cyclic trimer or tetramer, should change to a similar single species of high dipole moment as the concentration increases.

Another mechanism often discussed is that proposed by Dannhauser and Flueckinger (1970). They assume that hydrogen bond rupture is necessary to allow relaxation but is not the rate determining step for the process. Structural relaxation is considered to be fast compared to dipolar reorientation implying that the surroundings of all molecules are the same on a time average : consequently a single set of relaxation parameters can define the process. Reorientation, which is infrequent compared to hydrogen bond rupture and reforming, occurs as a cooperative process, the rate of which will be influenced by microscopic features of the alcohol molecule : when the alkyl group is small and unbranched as, for example, in methanol, Dannhauser and Flueckinger consider reorientation to be so facile as to make hydrogen bond breaking the rate determining step.

The final point has been criticised by van Gemert et al. (1973) on the basis of their studies of alcohol relaxation in non-polar solvents. They found the activation energies of the relaxation process for solutions of methanol in benzene and carbon tetrachloride to be significantly influenced by the solvent; this is not consistent with Dannhauser and Flueckinger's model. Notwithstanding that criticism, the general principles of Dannhauser and Flueckinger's arguments are sound and subsequent development of their model may prove fruitful.

Other mechanisms have been suggested by Garg and Smyth (1965), Sagal (1962) and Hassion and Cole (1955) to name a few. However, these models have proved less adequate in describing characteristics of the relaxation behaviour than have the models of Bordewijk and of

Dannhauser and Flueckinger.

1.2.5. Influence of Concentration and Solvent on the Relaxation Time for the Low Frequency Relaxation Region.

Investigations directed towards gaining an understanding of the behaviour responsible for the τ_1 process have been more-or-less confined to studies of pure alcohols. Relatively little effort has been directed towards investigating the concentration range of 30-100 mole % alcohol in which range the low frequency τ_1 process dominates the dispersion behaviour of primary and secondary alcohols. In part, this is due to the experimental difficulties of working in the appropriate frequency range at room temperature although the advent of time domain spectroscopy (van Gemert, 1973, Suggett, 1972; Fellner-Feldegg, 1972) has helped to overcome these difficulties.

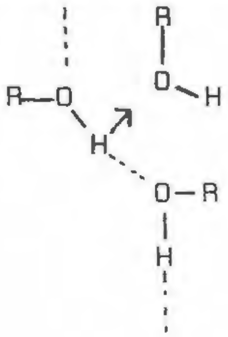
The results that do exist indicate that none of the above theories is capable of fully explaining the observed behaviour for solutions of alcohols in non-polar solvents. In particular, several workers (Sagal, 1962; Hanna and Hakim, 1970; van den Berg, Michielsen and Ketelaar, 1972) have observed maxima in the curves of τ against concentration for solutions of ethanol and of butanol in various solvents. Koshii, Arie, Nakamura, Takahashi and Higasi (1974 a,b) in studies of the concentration dependencies of τ for solutions of both propanols and three butanol isomers in solvents of varying proton accepting ability, observed maxima in the curve of τ against concentration for solutions in the solvents of moderate proton-accepting ability; however, minima were observed as the proton accepting ability of the solvent increased. Such maxima and minima cannot be explained by the existing theories. (The maximum in τ as a function of concentration observed by

Sakellaridis and Hinopoulos (1972) must be discounted since their experimental results were based on measurements at a single frequency which was too high to accurately reflect the locus of the low frequency process only. Consequently their measured τ values have large errors.) This behaviour can be contrasted with that observed by Komooka (1972) : in studies similar to those of Sagal, he found no maximum in τ for cyclohexane solutions of the longer chain alcohols, hexanol and octanol. A third feature is the minimum found by Denney and Ring (1963) in the concentration dependence of τ for solutions of 1-propanol in 2-methyl-pentane although, as has already been noted, the low temperature of this study does not allow a direct comparison to be made with room temperature results on similar systems.

Temperature studies of the concentration dependence of τ for solutions of ethanol in cyclohexane (Sagal , 1962) showed the maximum in the concentration dependence of τ to be influenced by temperature : as the temperature increases the maximum decreases in height. Sagal considered there to be two contributions to the activation energy for the relaxation process which may be described by the equation

$$\nu_c = \nu_c^{o} \exp(-E_a/RT) \qquad 1.xviii$$

where ν_c is the critical frequency and is equivalent to $^1/2\pi\tau$. (The description of ν_c^{o} depends on the model used to describe the relaxation process.) One contribution is thought to come from the energy required to rupture the hydrogen bond of the molecule to allow reorientation to occur and the other from the energy required to overcome the frictional resistance to motion caused by the relatively bulky solvent molecules. As solute is replaced by solvent or as the solute becomes larger, the latter effect becomes increasingly important and, therefore, the activation energy rises. However, replacing solute by solvent breaks up the linear chains, increasing the fraction of monomers and chain ends. These species may lower the energy required for hydrogen bond rupture within the associated chains : if the oxygen atom of such a species is suitably oriented, a molecule of a nearby chain may break its existing hydrogen bond more easily than if the third species was not present and subsequently reorientate to form a new bond with the monomer or molecule at the end of the chain. The accompanying diagram illustrates a possible configuration in which this "switch" might occur.



→ indicates direction of new hydrogen bond

As the fraction of monomers and chain ends increases, the "switching" mechanism will occur more frequently, i.e. ν_c^o increases. Dilution of the alcohol therefore causes two effects which contribute in opposite senses to the observed behaviour. As the relative importance of these effects changes with concentration, the curve of τ against concentration passes through a maximum.

As a consequence of Sagal's theory, the maximum should not be observed when the alkyl group of the alcohol in solution is as large or is larger than the solvent molecule. Such behaviour is qualitatively noted in Komooka's (1972) data which show no maxima, nor do the data of Hanna and Hakim (1972) in their studies of octanol in non-polar solvents. Similarly van Gemert et al. (1973) noted that the activation energies describing the relaxation behaviours for solutions of heptanol in various solvents, in a 1:1 volume ratio, were always less than for the pure alcohol.

In conclusion, it may be stated that while the theories currently available account for many of the features of the relaxation behaviour observed for alcohols and their solutions, the large number of features which are left unexplained emphasises the need for more, systematic investigations of the relaxation properties of alcohol solutions, particularly in the concentration range 40-100 mole % alcohol.

1.3. Infrared Spectroscopic Studies of Association

1.3.1. Infrared Spectroscopic Methods of Studying Hydrogen Bonding

Infrared studies have been described as "the most sensitive, the most characteristic and one of the most informative manifestations of the hydrogen bond". (Hilbert *et al.* quoted by Pimentel and McClellan, 1960a). This statement refers to distinctive changes which appear in the vibrational spectra of compounds which become involved in hydrogen bonding. Freymann (1932) was first to observe the strong concentration and temperature dependencies of the intensity and frequency of the fundamental -OH stretching mode in solutions of alcohols. At very low alcohol concentrations, a single band is observed in the fundamental -OH stretching region and is usually identified as arising from monomeric alcohol molecules. As the concentration increases, various other bands appear, always at lower frequencies than the monomer band, signifying the formation of hydrogen bonded polymeric aggregates of varying size. The decrease in frequency is evidence for the weakening of the -O-H bond, the magnitude of the decrease being regarded as a measure of the strength of the hydrogen bond formed (Badger and Bauer, 1937). As well as being concentration and temperature dependent, the intensities and frequencies of the low frequency bands are sensitive to the interaction between the solute and solvent.

While most workers have confined their efforts to examination of the behaviour of the -OH stretching vibration, either in the fundamental or overtone regions, a small number of workers (Stuart and Sutherland, 1956; Tarte and Deponthière, 1957; Maclou and Henry, 1957) has examined the frequency region in which the deformation vibration of the -OH group occurs. However, such studies have been limited because of difficulties in assigning the bands which occur in a complex region of the spectrum. Overlap from adjacent bands also causes problems in the measurement of intensities. Attempts have also been made to observe hydrogen bonding modes directly by studying hydrogen bonded systems in the far infrared region. Lake and Thompson (1966) studied a homologous series of alcohols in benzene solution and assigned hydrogen bonding modes; they found the intensities of such bands to be proportional to the alcohol concentration. However, such studies involve considerable experimental difficulty and have not been widely applied.

It should be noted that the choice of the fundamental or the overtone infrared region for study may be critical. In the overtone region, one measures larger frequency shifts but lower intensities, relative to the fundamental region, for the absorption bands of -OH groups involved in hydrogen bonding. The first factor reduces the effects of errors which are caused by the overlap of absorption bands : overlap causes problems in determining the intensity of the required band which may receive a contribution from another species absorbing at a frequency very similar to that of the required band. The photometric accuracy of the equipment used in overtone studies is higher and layer thicknesses used are more convenient than in studies of the fundamental region which leads to higher accuracy and reproducibility. However, absorption bands are sometimes difficult to assign in the overtone region because of possible combination bands, while the absorption band associated with the monomer is often intense in the overtone region, although weak in the fundamental region, for concentrated alcohol solutions. Consequently, the overtone region is more suitable for measurements of bands arising from unassociated -OH groups, while the fundamental region is more suitable for studies of bands which are influenced by hydrogen bonding.

1.3.2. Identification of Absorption Bands in the Fundamental Region.

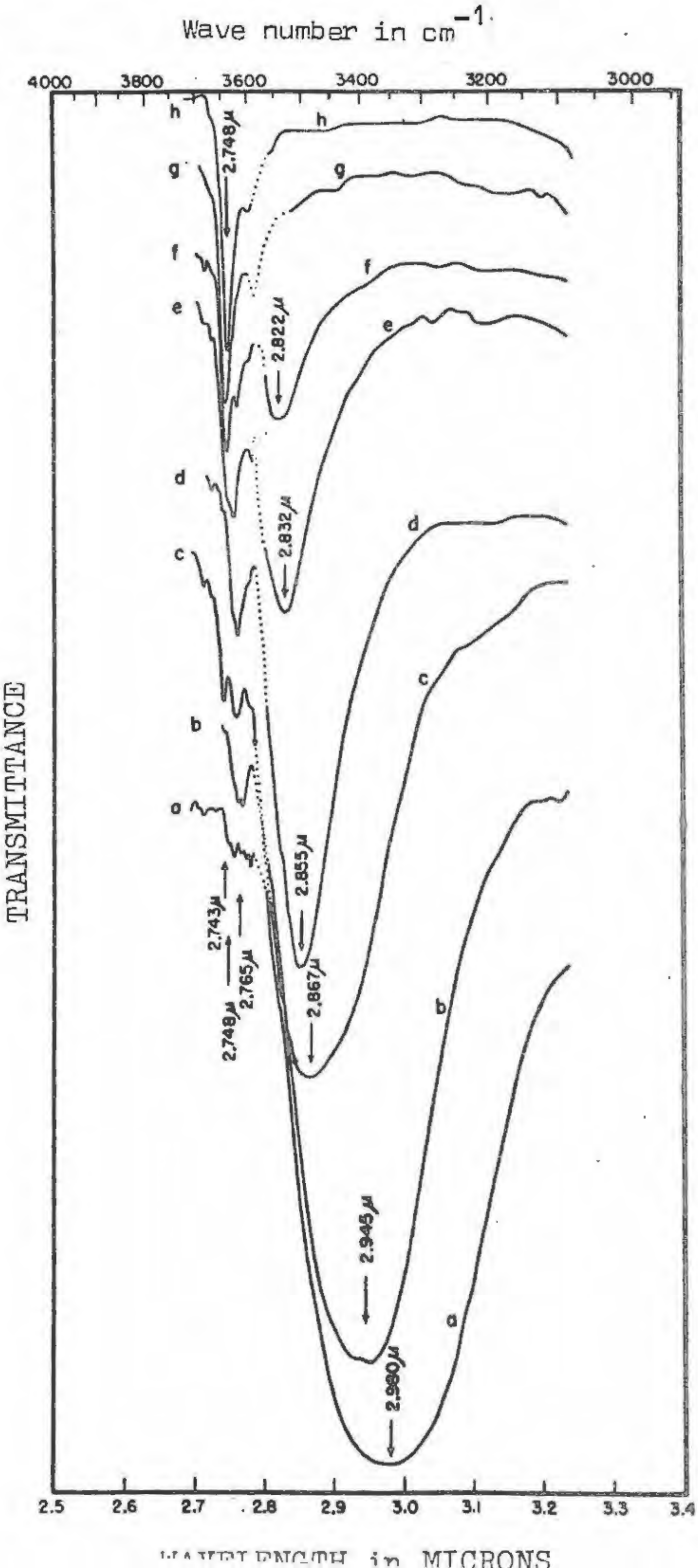
At low concentrations, there appear three absorption bands in the fundamental -OH stretching region for many alcohols, particularly primary and secondary alcohols : the high frequency band, which usually appears at about 3650 cm^{-1}, is associated with alcohol monomers; the second band, which appears at about 3500 cm^{-1},is usually associated with alcohol dimers or trimers (Bellamy and Pace, 1966; Ibbitson and Moore,1967a,b; Tucker and Becker,1973); the third band, around 3350 cm^{-1}, is associated with higher alcohol multimers (Coggeshall and Saier, 1951; Coburn and Grunwald, 1958). Evidence for a fourth band, around 3200 cm^{-1}, has recently been presented (Bourdéron, Péron and Sandorfy, 1972; Duboc, 1974) but no positive assignment of this band has yet been made. Although the frequencies of the band maxima are only weakly, if at all,concentration dependent the band intensities are extremely so and, at high concentration, the 3350 cm^{-1} band dominates the spectrum.

The identification of the associated species responsible for the various bands and particularly the band near 3500 cm^{-1} has been the subject of much research. Smith and Creitz (1951), in concentration studies of several alcohols, inferred the presence of several alcohol multimers in solution, each multimer being characterised by a particular absorption frequency with the absorption intensity reflecting the concentration of each multimer. These studies indicated t-butanol to be less associated than 1-dodecanol, the reason being described as a result of steric hindrance on the hydroxyl group. This result led Smith and Creitz to a study of the effect of steric hindrance on the association behaviour of alcohols. Studying a series of progressively branched alkyl derivatives of 3-pentanol, they noted a systematic shift of the absorption band near 3350 cm^{-1} in 3-pentanol to around 3500 cm^{-1} for 2,4-dimethyl-3-ethyl-3-pentanol until for 2,2,4,4-tetramethyl-3-isopropyl-3-pentanol only one band, ascribed to alcohol monomers, was observed, at 3640 cm^{-1}. This behaviour is illustrated in Figure 1.3. A low frequency shoulder on the peak associated with alcohol monomers is explained as a contribution from the non-bonded -OH group of a linear alcohol dimer. However, concentration studies on various alcohols (Flynn, Werner and Graham, 1959; Geiseler, Fruwert and Stöckell, 1962) have shown that the ratio of the intensities of the peak and its associated shoulder is independent of concentration. This seems to discredit Smith and Creitz' assignment since the ratio would be concentration dependent if the peak and the shoulder were associated with different species existing in solution.

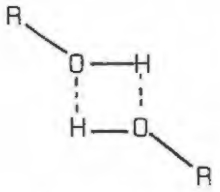
Smith and Creitz consider the peak near 3500 cm^{-1} to be associated with alcohol dimers which are thought to be linear. However, the splitting of the peak at 3502 cm^{-1} for 2,4-dimethyl-3-ethyl-3-pentanol is recognised as suggesting the possibility of an equilibrium between

FIGURE 1.3

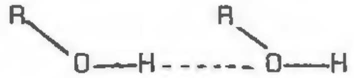
Infrared spectra of alkyl derivatives of 3-pentanol recorded in the fundamental -OH stretching region (reprinted from Smith and Creitz (1951)): a) 3-pentanol; b) 3-methyl-3-pentanol; c) 2,2,4-trimethyl-3-pentanol; d) 2,4-dimethyl-3-ethyl-3-pentanol; e) 2,2,4-trimethyl-3-ethyl-3-pentanol; f) 2,2,4-trimethyl-3-isopropyl-3-pentanol; g) 2,2,4,4-tetramethyl-3-n-propyl-3-pentanol; h) 2,2,4,4-tetramethyl-3-isopropyl-3-pentanol.



linear and cyclic dimers which have the form

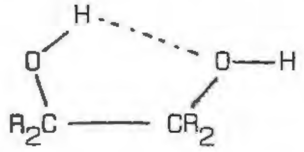


cyclic (or closed) dimer



linear (or open) dimer

Subsequent studies by Kuhn (1952) confirmed that a dimer could be responsible for the peak near 3500 cm^{-1}. Studying 1,2-diols, which, in solution, adopt the form



he noted two absorption bands in the fundamental -OH stretching region. For those diols whose geometry placed no restriction on the -O - - - - H - distance, a band, corresponding to an hydroxyl group whose proton is involved in hydrogen bonding, was found near 3500 cm^{-1}.

1.3.3. Structure of the Alcohol Dimer

While the majority of subsequent publications accepts the assignment of the peak near 3500 cm^{-1} as arising from an alcohol dimer, there has been controversy over whether the dimer is linear or cyclic. Van Theil, Becker and Pimentel (1957), in matrix isolation studies of methanol, found several sharp bands in the fundamental -OH stretching region whose relative intensities changed with the proportion of alcohol in the nitrogen matrix. The band at 3490 cm^{-1} was assigned to a dimer and further bands, at lower frequencies, were assigned to higher polymers. Using a qualitative argument, based on the symmetries of the linear and cyclic dimers, the authors proposed the dimer to be cyclic. However, Barnes and Hallam (1970), from similar studies of methanol and deutero-methanol, favoured linear dimers because of the presence of a strong band in the far infrared region which they assign as a deformation mode of a dimer: such a band is not expected for a cyclic species.

Kuhn and Bowman (1961) extended Kuhn's (1952) earlier measurements and found that the frequency of the intramolecularly bonded -OH in butane -1:4-diol is about the same as that for the intermolecularly bonded -OH of an alcohol dimer, implying a similar type of bond to be formed. Since the geometry of the butane -1:4-diol molecule precludes the formation of a four-membered ring involving two -OH groups, the similarity of the frequency shifts provided strong evidence in favour of the linear dimer. This evidence was further substantiated by their studies of alcohol solutions in diethyl ether in which they observed that the frequency of the band arising from the -OH group of an alcohol molecule bonded (linearly) to an ether molecule is only slightly less than the frequency of the band associated with the intermolecularly bonded -OH of an alcohol dimer. (The slightly lower frequency of the former band is not unexpected in view of ethers being more basic than similar alcohols.) Subsequently Ibbitson and Moore (1967a,b), who correlated infrared spectroscopic and dielectric polarisation measurements, showed that the appearance of the band at 3500 cm^{-1} in the infrared spectra of alcohols in benzene solution is associated with the rise in the concentration dependence of the dielectric polarisation. This indicates formation of a high dipole moment, and therefore linear, multimer.

Subsequently Hammaker et al. (1968) interpreted their infrared measurements on solutions of three alcohols in carbon tetrachloride as providing evidence in favour of the band near 3500 cm^{-1} arising from an alcohol dimer; however, Tucker and Becker (1973) questioned the arguments of Hammaker *et al.* on the basis of an unrealistically large dimer absorptivity calculated from a correlation of the results provided by each group. Instead, Tucker and Becker consider that the band could result from a dimer or a trimer or a mixture of both. However, it is surprising that no bands suggesting simultaneous formation of dimers and trimers have been observed in infrared studies. These differences of opinion emphasise that the assignment of the band near 3500 cm^{-1} remains unresolved.

The strength of the hydrogen bond in the species responsible for the absorption near 3500 cm^{-1} is also of interest. Since the frequency of this band is higher than that of the band associated with higher multimers, the implication is that the hydrogen bond in a dimer (or trimer) is weaker than those in higher multimers. To explain this, Bellamy and Pace (1966) showed that the terminal hydroxyl group of a dimer was more acidic than that of a monomer, making the dimer more susceptible to further hydrogen bonding. Thus, multimer species formed subsequent to dimers have stronger hydrogen bonds because of the enhancement of the proton donor properties of a hydroxyl group already acting as a proton acceptor.

1.3.4. Quantitative Association Models.

Besides the qualitative observations discussed in the previous sub-section, many studies have attempted to represent alcohol association by quantitative models derived from infrared spectroscopic studies.

In an attempt to quantise the association behaviour for solutions of phenol in carbon tetrachloride, Kempter and Mecke (1939 and 1940) studied the second overtone of the hydroxyl vibration and, as discussed in sub-section 1.1.2, considered the formation of all associated species to be governed by a single, stepwise association constant, K. From their assumptions it may be shown that

$$\sqrt{\varepsilon_c} = \sqrt{\varepsilon_o} - \left(\frac{\varepsilon_c c}{\sqrt{\varepsilon_o} K}\right) , \qquad 3.xix$$

where ε_c and ε_o are the extinction coefficients, calculated from Beer's Law, at a concentration, c, and infinite dilution respectively. Plotting $\varepsilon_c.c$ against $\sqrt{\varepsilon_c}$ should therefore produce a straight line. A straight line was observed for solutions of phenol in carbon tetrachloride; however, systematic differences between the experimental and calculated results are noted for almost all alcohol/solvent systems at extremes of concentration. The model is obviously unsatisfactory since it neglects the non-ideal association, over a wide concentration range, of alcohol solutions and also the presence of three bands in the fundamental -OH stretching region at low concentrations. The three bands imply the presence of at least two distinct alcohol multimers (assuming one band to arise from alcohol monomers).

To overcome some of the limitations of the Mecke-Kempter model, Coggeshall and Saier (1951) introduced a discrete association constant for dimerisation in their studies of solutions of several alcohols and phenols in carbon tetrachloride. This conformed with the appearance of the band around 3500 cm^{-1} whose frequency shift, being different to that of the other absorption band, indicated that the multimer responsible had a different energy of formation to that of other multimers. On evaluation, this treatment produced no systematic differences between the calculated and observed results; however, the equilibrium constants describing association of multimers other than dimers were found to be similar for each system studied. This implies that the equilibrium constant is independent of the molecular mass and structure of the alcohol. However, as permittivity studies have shown (sub-sections 1.1.3 and 1.1.4) the formation of the higher polymers is sensitive to the alcohol structure and particularly to the steric environment of the hydroxyl group. Thus, while Coggeshall and Saier's treatment is an improvement over the Mecke-Kempter model, it must still be substantially developed to allow reliable,quantitative results to be obtained.

A study of the association of ethanol in carbon tetrachloride solution was undertaken by Coburn and Grunwald (1958). They considered the alcohol dimer and trimer to be linear species, and the tetramer and next few higher multimers to be cyclic. Following Smith and Creitz (1951), Coburn and Grunwald assigned the three bands which appear in the fundamental -OH stretching region as follows: the band above 3600 cm^{-1} was assigned to the hydroxyl groups of alcohol monomers and the molecules at the end of associated, linear chains; the band around 3500 cm^{-1} was assigned to the hydroxyl group hydrogen bonded at the beginning of a multimer (which is equivalent to the intermolecularly bonded -OH of a dimer); the band around 3350 cm^{-1} was assigned to the internal hydroxyl groups of an associated chain. Then assuming the terminal hydroxyl group of the dimers and trimers to contribute to the monomer band, they calculated the monomer concentration from an analysis of the area of the monomer absorption peak. Coburn and Grunwald considered that the accuracy of their results allowed them to have only two variables; consequently they selected as variables the equilibrium constants for dimer and tetramer formation, K_2 and K_4 respectively, with the trimer association constant, K_3, related to that of the dimer by $K_3 = (^3/2)\ K_2^{\ 2}$. The results thus obtained were in reasonable agreement with those obtained in preliminary studies by Coburn (1954) and also independent studies, on the same system, by Ens and Murray (1957) and Niini (1940). However, the results disagreed markedly with results, again on the same system, presented by Hoffmann (1943). A most important feature of Coburn and Grunwald's model was the concept of the non-hydrogen bonded -OH groups at the end of linear chains contributing to the absorption band above 3600 cm^{-1}.

Further development of the understanding of alcohol association was attempted by Finch and Lippincott (1956 and 1957) who considered changes in a monomer - dimer - multimer equilibrium could not fully account for the temperature dependent changes in intensity and frequency of individual absorption bands. Using a semi-quantitative calculation based on a one-dimensional model of -OH - - - - -O - hydrogen bonding, they attempted to calculate the temperature dependencies of the frequency shifts and band intensities of the fundamental -OH stretching bands observed for various alcohols.

This approach was criticised by Van Thiel et al. (1957) who considered that temperature dependent changes in the association behaviour make the results unreliable. This was discounted by

Finch and Lippincott who argued that no change in the frequency of the hydrogen bonded -OH band was observed on a ten-fold dilution from pure alcohol. Finch and Lippincott's argument is not conclusive however, since the appearance of the band near 3350 cm^{-1} has been shown (Ibbitson and Moore, 1967a,b) to be associated with the appearance of low dipole moment multimers; yet no significant change in frequency occurs when a change to high dipole moment, linearly bonded multimers is found. This shows the frequency of the band near 3350 cm^{-1} is not a sensitive measure of the extent and mode of association.

The approach of Ens and Murray (1957) was rather different to those of other workers since they considered cyclic species as being important for solutions of various alcohols in carbon tetrachloride over the whole concentration range. Determining the monomer concentration using Beer's Law, they obtained the multimer concentration by difference and, hence, the degree of association by a graphical method. They thus found the degree of association to be always less than 4, from which they deduced cyclic tetramers to be the most probable multimeric species. Since the assumptions made by Ens and Murray are, in general, similar to those made by Kempter and Mecke, the method is subject to the same criticism.

Liddel and Becker (1957) restricted their investigation of the temperature and concentration dependencies of the frequency of -OH bands in the fundamental -OH stretching region to dilute alcohol solutions in carbon tetrachloride. Assuming the bands' frequency to be temperature independent over the temperature range studied, they calculated the equilibrium constant for a monomer-dimer equilibrium from the limiting low concentration behaviour of each of three concentration dependent functions of ε_m, the extinction coefficient of the absorption band above 3600 cm^{-1}, and found agreement among the results within the experimental error. The value calculated for ε_m was corrected for absorption from hydroxyl groups at the end of chains. They found the dimer to be a stable species since a plot of monomer concentration against total concentration gave a non-zero intercept : the limiting slope was shown to be proportional to the equilibrium constant for dimerisation.

The results calculated did not agree with those published by Staveley and Taylor (1956) and by Hoffmann (1943) on similar systems. However, Staveley and Taylor's results were considered to extend to an insufficiently low concentration while those of Hoffmann, on recalculation were found to be in agreement with the results of Liddel and Becker. The disagreement among the published results indicated the need for more accurate data.

Although the formation of a dimer is generally accepted, Fletcher, in some recent studies, considers its concentration so insignificant as not to affect the equilibria found at higher concentrations in alcohol solutions. In support of this argument, Fletcher and Heller (1967) who, in a study of the first overtone of the -OH stretching region for 1-octanol solutions in n-decane, show that their data are adequately represented by a monomer - closed tetramer - open tetramer equilibrium over the whole concentration range. In the first stage of their analysis, Fletcher and Heller show that a monomer - tetramer only equilibrium can account for their experimental data over a wide range of temperatures and their subsequent investigation of the temperature dependence of the multimer absorption at two widely separated frequencies confirmed that the absorption is fourth-order with respect to the monomer. The temperature studies showed the multimer absorption to be temperature dependent which implied that two types of tetramer were present and, from the enthalpies of formation of -16.5 kcal mole^{-1} and -20.3 kcal mole^{-1} calculated from a van't Hoff plot, one tetramer was considered linear and the other cyclic.

The development of the monomer - tetramer model is open to question since, at no temperature, did this model provide the best fit of Fletcher and Heller's experimental data. However, Fletcher and Heller (1968) considered that although there were dimer species present in solution, their concentration was too insignificant to affect the material balance of the system. Fletcher was encouraged by the success of the monomer - tetramer model in explaining the infrared data from 1-octanol in n-decane solutions and applied this model to other systems in order to test its validity. In particular, he similarly examined 1-octanol in carbon tetrachloride solutions (Fletcher, 1969). Fletcher considered that carbon tetrachloride formed a weak hydrogen bond to the -OH groups of alcohol monomers and that neglect of this interaction was responsible for mis-interpretation of much experimental data. He found that from his data he could calculate a finite value for the equilibrium constant for a 1:1 alcohol/carbon tetrachloride complex which supported his contention that such a species is important in determining the association behaviour of alcohols in carbon tetrachloride solutions. The decrease in alcohol association in carbon tetrachloride as compared to saturated hydrocarbon solutions was explained as resulting from formation of such a complex which stabilises the -OH groups of alcohol monomers.

By including terms to allow for this complex with the other terms describing his favoured monomer - closed tetramer - open tetramer model, Fletcher was able to adequately describe his infrared measurements on 1-octanol solutions in carbon tetrachloride.

This experiment was criticised by Christian and Tucker (1970) on account of Fletcher's neglect of the solutions' non-ideal behaviour over the whole concentration range; this makes unrealistic the use of a single equilibrium constant to describe the formation of a particular species. However, Fletcher (1970) justified his analysis by emphasising that the use of single-valued equilibrium constants could explain the observed association behaviour.

Fletcher (1972) further extended his studies to include measurements of ethanol-d_1 (CH_3CH_2OD) solutions in n-decane in the first overtone region of the -OD stretching mode. Ethanol-d_1 was selected because its solutions allow higher permittivities and alcohol concentrations than can be obtained in solutions of most other alcohols; this provided a stringent test of his hypotheses. Fletcher again upheld his contention that a tetramer is the most probable species in alcohol solutions over a wide range of concentrations and that alcohol dimers, although present, do not significantly affect the mass balance of the system.

This repeated confirmation of a tetramer along with the dismissal of a dimer, is a most significant feature of Fletcher's work. Although his results have been criticised, his studies warrant consideration because of their systematic development and the consistency of the model derived.

In conclusion one has to question the usefulness of developing association models solely from infrared spectroscopic data. Dunken and Fritzsche (1964) have noted that it is generally possible to find a model with a restricted number of parameters to describe the concentration dependence of infrared spectra of alcohol solutions. Firm conclusions are only possible if a model is consistently adequate over a range of temperatures (as was shown by Fletcher). It is preferable, however, to examine whether the data obtained from investigation of a particular alcohol/solvent system, using a variety of experimental techniques, can satisfy a particular model, as has been done by Tucker and Becker (1973).

1.4. Other Studies of Association

1.4.1. Basic Principles of NMR Studies

Many workers have applied NMR spectroscopic techniques in the investigation of association in alcohol solutions. Changes, as a function of temperature or concentration, in the chemical shift of the alcohol -OH proton are the most useful experimental quantities, although some recent investigations (Rowbotham and Schaefer, 1974) have provided evidence that variations in the nuclear spin-spin coupling constants may provide information on the association behaviour of phenol solutions.

The chemical shift of the alcohol -OH proton is a suitable parameter for study of alcohol association since it undergoes large changes in frequency under the influence of temperature and concentration, and can be very accurately measured. However, NMR studies may be of limited value since the technique gives no measurable quantity directly related to either the concentration or the shape of the discrete,associated species appearing in solution. This presents difficulties in analysis when more than one hydrogen bonded species is considered to be present in solution, as is seen from the equations (presented below) relating the observed chemical shift, δ_{obs}, to the concentration, c. Consequently, certain simplifying assumptions usually have to be made to calculate equilibrium parameters, especially if the data are not analysed in conjunction with information from other experiments.

To allow quantisation of the observed concentration dependence of δ_{obs}, Gutowsky and Saika (1953) developed a relationship to express δ_{obs} in terms of the concentration and chemical shift of each of the associated species present:

$$\delta_{obs} = \frac{\sum_i ic_i\delta_i}{\sum_i ic_i} \quad , \qquad 1.xx$$

where c_i and δ_i are the concentration and chemical shift, respectively, of the i^{th} species. This relationship expresses the observed chemical shift as the weighted mean for all species. If, however, a particular species has two or more protons capable of hydrogen bonding, each with different chemical shifts, δ_{obs} will represent the mean of all these protons. This means that only in the case of a cyclic species will δ_i, the shift for that species, be a true representation of the molecular situation. If we assume ideal association, we can express $c_i = K_i(c_1)^i$, where c_1 is the concentration of monomer and K_i is the equilibrium constant of the i^{th} species; inserting this expression (which will be discussed more fully in Section 4.2.) into equation 1.xx, the Gutowsky-Saika equation may then be written

$$\delta_{obs} = \frac{\Sigma\ i.\delta_i.K_i(c_1)^i}{\Sigma\ i.K_i\ (c_1)^i} \quad . \qquad 1.xxi$$

1.4.2. Association Models for Alcohol Solutions Developed from NMR Concentration Studies

The Gutowsky-Saika equation contains too many variables to allow it to be used conveniently to quantise experimental data; therefore simplifying assumptions are usually made. Saunders and Hyne (1958), who investigated the concentration dependence of the -OH proton chemical shift for solutions of t-butanol, methanol and phenol in carbon tetrachloride, allowed for only one significant associated species throughout the concentration range studied. They also considered that the chemical shift for the single associated species was independent of concentration. These assumptions lead to a simplification of the Gutowsky-Saika equation which can then be expressed:

$$\delta_{obs} = \frac{(\delta_1 c_1 + i\ \delta_i K_i C_1{}^i)}{c_1 + iK_i C_1{}^i} \quad . \qquad 1.xxii$$

where δ_1 is the chemical shift of the monomer. In an elegant treatment, Saunders and Hyne then applied Buckingham's II theorem (Bridgman, 1922): from the theoretical curve of δ_{obs} against concentration, calculated for a particular value of K_i, the curve for any other value of K_i can be calculated by multiplying the concentration axis by an appropriate factor. By using a logarithmic concentration axis, the treatment becomes even simpler since the required adjustment can be made merely by adding the factor to the log c axis. Using the above method, Saunders and Hyne analysed their data in terms of monomer-n-mer equilibria and favoured a monomer-trimer equilibrium for t-butanol and phenol solution but a monomer-tetramer model for methanol solutions. The multimers for both equilibria were considered to be cyclic.

This approach was criticised by Becker (1959) who commented that the use of a logarithmic concentration axis understressed the finite slope at the lower concentration limit of the data.

This finite slope implied the presence of a second associated species, at low alcohol concentrations, which was not allowed for in Saunders and Hyne's analysis. The presence of such a species is also suggested by infrared spectroscopic studies which, as discussed in sub-section 1.3.2., show the appearance of three discrete bands in the fundamental -OH stretching region.) Saunders and Hyne (1959), in turn, accepted the presence of a monomer-dimer equilibrium at low concentrations, but considered that such an equilibrium would not significantly affect the validity of their results. However, Davis, Pitzer and Rao (1960) showed that the inclusion of parameters to allow for a dimer in an equilibrium model produced quite different results to those obtained in the absence of such parameters: allowing for a dimer changed substantially the size of the larger multimer providing the best fit to the experimental data, but, in no case, were they able to obtain results within the experimental errors. Another association model was presented by Littlewood and Wilmott (1966) who assumed the existence of only two types of -OH proton, bonded and non-bonded, each with a characteristic chemical shift. They further assumed the Mecke-Kempter approximation of a single equilibrium constant to describe formation of successive polymers. By this method, Littlewood and Wilmott were able to adequately represent their data on 1-dodecanol solutions in squalene and also certain other data appearing in the literature; but the model was inadequate for other literature data. While their treatment is simple and easily applied, it makes dangerous and invalid assumptions: it requires values for the monomer chemical shift to be estimated and is also subject to the criticisms of the Mecke-Kempter approach.

Much effort has been directed towards evaluating parameters for 1- n-mer models with limited success as witnessed by the lack of consistency among the models favoured (Saunders and Hyne, 1958; Feeney and Walker, 1966; Dixon, 1970). It is therefore attractive to examine systems in which the association behaviour is less complicated than in solutions of primary and secondary alcohols. Simpler association is expected in solutions of alcohols in which there is severe steric hindrance around the -OH group. Accordingly, Davis et al. (Davis and Deb, 1970; ref 44) investigated the association behaviour of carbon tetrachloride solutions of several very hindered alcohols using NMR and infrared spectroscopic data. Davis et al. considered that, for the alcohols studied, ideal monomer-dimer equilibria occur and this was supported by the similarities of the K_2 values calculated from NMR and infrared results. However, extreme care is necessary in such an approach since there is substantial evidence to suggest that two, discrete multimers are present in solutions of hindered alcohols : both Raczy et al. (1967), on the basis of static permittivity studies, and Biais, Lemanceau and Lussan (1967), on the basis of theoretical NMR studies, consider it necessary to allow for two associates, one of high dipole moment and the other of low dipole moment, to explain the solution properties of 2,2,3-trimethyl-3-pentanol.

Another method of simplifying the analysis of the association behaviour of alcohol solutions is to confine one's investigation to low concentration : at low concentration, one need only consider monomer-dimer equilibria. Under these circumstances, δ_{obs} should be a linear function of concentration, any deviations from linearity indicating the formation of higher polymers. From the plot of δ_{obs} against concentration, the equilibrium constant for dimer formation can be obtained (Huggins, Pimentel and Shoolery, 1956) provided a value for δ_2 is available; usually the δ_2 values must be calculated or estimated.

Extending this method, Becker, Liddel and Shoolery (1958) calculated equilibrium constants for dimer formation from the low concentration behaviour of ethanol in carbon tetrachloride solutions. Their results, from NMR studies, were found to agree with results obtained from infrared spectroscopic studies of the same system (Liddel and Becker, 1957). Cohen and Reid (1956) suggested that trimers and tetramers were more favourable than dimers on the basis of their concentration studies of various alcohol/solvent systems. However, Tucker and Becker (1973) showed that the lowest concentration (0.05 mol ℓ^{-1}) examined by Cohen and Reid was not sufficiently dilute so rendering Cohen and Reid's arguments suspect.

The differences between Becker et al.'s and Cohen and Reid's investigation illustrates the major difficulty of the low concentration studies : extreme care must be taken to extend measurements to a sufficiently low concentration to allow a monomer-dimer equilibrium (assuming this equilibrium exists) to adequately represent the association behaviour.

1.4.3. NMR Temperature Studies of Association

Another, not unrelated, field of activity is the investigation, using NMR techniques, of the thermodynamics of alcohol association, particularly the heats of association of the multimers that form in alcohol solutions. The uncertainties in the calculated enthalpy values, ΔH, and equilibrium constants preclude study of the entropy changes observed on multimer formation.

Two methods have been used to calculate thermodynamic quantities from NMR data. The first involves calculation of equilibrium constants at several temperatures for the equilibria under investigation with subsequent application of the van't Hoff equation. The main disadvantage of this method is that it assumes a constant ΔH which may not be valid over a large temperature range for alcohol solutions because of a temperature dependent change in the equilibrium ratio of linear to cyclic multimers present in solution. Such an approach also generally neglects possible temperature dependent changes in the chemical shifts of the protons of the multimers' hydroxyl group : these changes may result from a change in hydrogen bond length with temperature (Muller and Reiter, 1965). A modification of this method is used to evaluate thermodynamic parameters for monomer - dimer equilibria. The value of K_2 cannot normally be determined accurately; therefore one may plot $K_2(\delta_2-\delta_1)$ against $^1/T$ which gives a value for ΔH for dimerisation, assuming δ_2 to be independent of temperature.

Feeney and Walker suggested an alternative approach to the use of the van't Hoff equation to estimate ΔH; this approach avoided the assumption of a constant δ_2. From the equations developed by Saunders and Hyne (1958), they developed the expression

$$-\Delta H = RT \log \frac{(\delta_1 - \delta_{obs})^i}{(\delta_{obs} - \delta_i)^i} + \text{const} , \qquad 1.\text{xxiii}$$

from which a plot of $^1/T$ against $\log \dfrac{(\delta_1 - \delta_{obs})}{(\delta_{obs} - \delta_i)^i}$ allows evaluation of ΔH.

The thermodynamic parameters calculated for various systems (Feeney and Walker, 1966; Davis *et al.*, 1960; Patterson and Hammaker, 1967) are reasonable values for hydrogen bond energies, in spite of the lack of sophistication of the association models applied. This is not unexpected since, as Fletcher and Heller (1967) have noted,

"It would appear that one can fit data to polynomials of the wrong-order models, even though there may be a very poor goodness-of-fit, and yet obtain very reasonable ΔH/bond results.".

It is therefore not justifiable to develop arguments on detailed molecular models solely on the basis of ΔH values calculated from NMR experiments.

1.4.4. Investigation of Association by Non-Spectroscopic Techniques

It can be seen that the non-specificity of the data obtained from NMR experiments renders the analysis of the data difficult. Similar difficulties arise when non-spectroscopic techniques are used since, as for NMR data, the data give no information directly related to either the concentration or shape of the multimers. In spite of this limitation, non-spectroscopic techniques have enjoyed success, as witnessed by the agreement among authors using different experimental techniques, in providing a description of association. Studies of the equilibrium vapour pressure have been particularly important.

In studies of the pressure - volume - temperature (PVT) relationship for alcohol vapours, Kretschmer and Wiebe (1954) found that their experimental results were best described by assuming second and fourth virial coefficients, but no third, implying an equilibrium among monomers, dimers and tetramers in the vapour. A similar model had already been proposed by Weltner and Pitzer (1951) from an interpretation of their heat capacity data for methanol vapour, while Berman (1968), from experiments similar to those of Weltner and Pitzer, on several alcohols, found that a monomer - dimer - tetramer (1-2-4) model was the only one which could fit his data without further assumptions. Similarly this model was found by Inskeep, Kelliher, McMahon and Somers (1958) and by Fletcher (1971) to provide the best fit of a theoretical curve to their infrared spectroscopic measurements on methanol vapour. The agreement on a 1-2-4 model is not confined to gas phase studies: Aveyard, Briscoe and Chapman (1973) investigated, using vapour pressure osmometry and infrared studies, the association of alcohols in n-octane solution and found this model to provide the best description of their data.

While the agreement among the results obtained from various experimental techniques is convincing, it is by no means unanimous. Cheam, Farnham and Christian (1970) investigated the association of methanol in the vapour using a vapour density technique. From their results, Cheam *et al.* concluded that a monomer - trimer model produces the best fit to the experimental curve. However, a most disturbing feature of the experiment was the failure to report results for a 1-2-4 model, which, as has been discussed, had already been shown to adequately describe the association behaviour of alcohol vapour. This omission was dealt with by Fletcher (1971) who showed the 1-2-4 model to provide as good a fit as the monomer - trimer model.

The association of methanol into trimers had already been suggested by Tucker, Farnham and Christian (1969) who investigated the association of methanol in the vapour phase and in n-hexadecane solutions. Their study was initiated by means of vapour pressure measurements. They assumed that the ratio of the molar concentration of monomeric alcohol in solution, $C_A{}^s$, and in the vapour phase, $C_A{}^v$, is represented by a distribution coefficient, K_D, such that

$$K_D = \frac{C_A{}^s}{C_A{}^v} \quad . \qquad 1.xxiv$$

The formal concentration, f_A, of monomeric alcohol in solution is given by

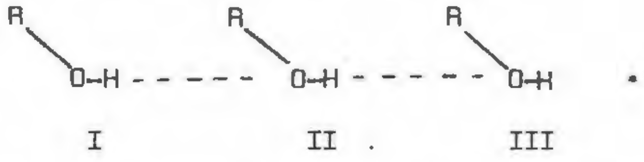
$$f_A = \sum_{i=1}^{\infty} i.K_i \, (K_D C_A{}^v)^i \quad , \qquad 1.xxv$$

assuming an infinite series of associated species. Using equation 1.xxv, a large number of models was applied to the experimental data, and those in which an eighth order term was present consistently provided better fits; in particular, the monomer - trimer - octamer (1-3-8) model was superior at each temperature studied.

A similar analysis on PVT data again led to the 1-3-8 model providing the best fit, with the 1-2-4 system surprisingly yielding a negative K_2 at 15°C.

The 1-3-8 model was then applied to Fletcher and Heller's (1967) infrared data for 1-octanol in n-decane solutions. The relative standard deviations of the 1-3-8 fit were found to be generally larger for the lower temperature data than those for a monomer - tetramer fit. However, the individual deviations of the 1-3-8 fit did not appear to vary systematically with concentration.

To account for the three absorption bands observed in the fundamental -OH stretching regions, it was necessary to postulate three discrete -OH environments in the favoured linear trimer:



The terminal hydroxyl group, III, was considered, from Bellamy and Pace's (1966) studies, to absorb at the frequency associated with the -OH group of alcohol monomers. Group I is in an environment similar to that expected for the intermolecularly bonded -OH of a dimer; therefore it is assigned to the absorption observed near 3500 cm^{-1}. Group II is in an environment similar to that expected for a cyclic multimer and can therefore be assigned to the band near 3350 cm^{-1}. The rapid formation of the cyclic octamer would then explain the rapid increase in intensity with concentration of the low frequency absorption. Using these assignments, the 1-3-8 model was applied to Liddel and Becker's (1957) data and a consistent temperature dependence of the calculated equilibrium constants was observed.

The 1-3-8 model was less satisfactory when applied to published NMR data. However, Tucker and co-workers concluded, from differences in the results calculated from data on identical systems, that discrepancies in the published data may be present.

The investigation was extended by Tucker and Becker (1973) who made extensive vapour pressure, infrared and NMR measurements of t-butanol solutions in hexadecane to ascertain whether the 1-3-8 model could describe the association of an alcohol whose behaviour is modified by steric hindrance around the -OH group. Again equation 1.xxv provided the starting point for analysis of the vapour pressure data. Using this equation, relationships were developed in accordance with three different association descriptions;

the first was Coggeshall and Saier's concept of a discrete equilibrium constant for dimerisation, with subsequent polymers related by a single equilibrium constant; the second description was similar, but had a trimer as the first, discrete, associated species formed. Finally, it was assumed that the equilibrium constant for the reaction

$$A_i + A \rightleftharpoons A_{i+1} \qquad (i \geqslant 3)$$

is related to the limiting equilibrium constant, K_∞, by

$$K_{i,i+1} = \frac{i}{i+1} \cdot K_\infty \, . \qquad 1.\text{xxvi}$$

This implies that the stepwise free energy for multimer formation slowly approaches an approximately constant value.

When applied to experimental data, the monomer - trimer - hexamer (1-3-6) and monomer - trimer - "infinite" multimer (1-3-∞) model developed from the second and third descriptions provided the best fits to the experimental data; no model from the first description was satisfactory.

Tucker and Becker then turned to NMR experiments for which the analysis was based on Lippert's (1963) modification of the Gutowsky-Saika equation. Again the results indicated a trimer to be the most likely species at low concentrations. It was also concluded that only a 1-3-∞ model could satisfy the data from both vapour pressure and NMR experiments.

The equilibrium constants calculated from infrared spectroscopic data were comparable to those obtained from vapour pressure studies. This was further evidence in favour of a 1-3-∞ model.

Tucker and Becker's investigation did not succeed in its original aim of establishing that the 1-3-8 model proposed by

Tucker et al. (1969) was an adequate general description of the association of alcohol solutions in non-polar solvents. Instead the emphasis shifted to confirming the feasibility of a trimer as the multimer first formed in alcohol solutions. However, the correlation of data from several experimental techniques is impressive and indicates a suitable approach for future studies.

The techniques discussed in this Section involve difficult analyses and generally, with the exception of vapour pressure studies, give less valuable information than infrared or static permittivity studies. While the use of a single one of these techniques does not produce a reliable description of association, it is useful to develop such techniques to provide qualitative data which can complement the more descriptive data obtained from infrared and static permittivity studies.

CHAPTER 2

TIME DOMAIN METHODS IN DIELECTRIC SPECTROSCOPY

Section 2.1. Basic Principles

2.1.1. Introduction

In principle, dielectric relaxation phenomena may be investigated by measurement of the response of a system to either a step or a periodic voltage function. Techniques involving the latter method have been more frequently applied although pulse methods have been used in the experimentally difficult low frequency region where periods may extend to tens of seconds. However, the recent development of fast risetime sampling oscilloscope systems, allowing the display of frequency components of waveforms up to about 15 GHz, has led to the introduction and increasing use of transient methods(Fellner-Feldegg, 1972; van Gemert, 1973; Suggett, 1972 and 1973).

These methods are attractive to the physical chemist because of the large frequency range potentially available, the possibility of collecting complete spectral data in a single time-response function, the speed of data capture and the possibility of investigating frequency regions where extreme experimental difficulties have hitherto been experienced.

As these methods have been applied, the initial, superficial technique has become refined leading to more sophisticated experimental and theoretical practices so that the results presently obtained are as accurate as those obtained using the more established frequency domain techniques.

2.1.2. Initial Development

The original application of pulse methods for measuring the reflection properties of transmission lines was in the 1960's when electrical engineers developed a technique called time domain reflectometry (TDR) to ascertain the position of a discontinuity in a coaxial line by propagating a pulse with a short rise time along the line. Any discontinuity is evidenced by a reflection which may be detected by the signal sampling equipment. Subsequently Fellner-Feldegg (1969) recognised the potential in this concept for investigating, quantitatively, the dielectric relaxation properties of a sample in the frequency range 0.01 to 10 GHz by placing it in a coaxial line and studying the responded signal. He first examined a series of aliphatic alcohols but, disappointingly, achieved poor agreement with published frequency domain results. However, Whittingham (1970) noted that Fellner-Feldegg's use of a Laplace transformation to obtain results directly from the time domain was incorrect, while Suggett, Mackness, Tait, Loeb and Young (1970) showed that Fourier transforming the data into the frequency domain produced results of very good quality. Subsequent development of the technique by Loeb, Young, Quickenden and Suggett (1971) has extended the frequency range to higher frequencies while the techniques proposed by de Loor, van Gemert and Gravesteyn (1973), Fellner-Feldegg (1972) and Clark, Quickenden and Suggett (1974) allow the results to be extended to lower frequencies. The frequency range available now encompasses several decades while transmission as well as reflection techniques can be used so that a more appropriate name for the technique is time domain spectroscopy (TDS).

2.1.3. Experimental Approach

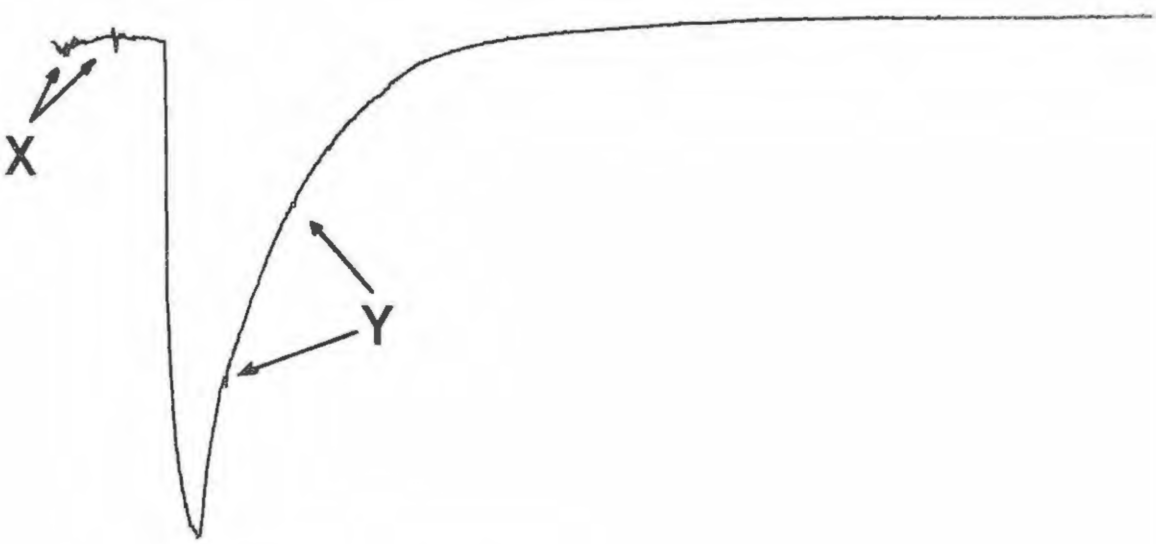
The variety of experimental arrangements which are possible with a single pulse generator and sampler is a very exciting feature of TDS. The single (direct) reflection and transmission from the air/dielectric interface may be examined and analysed either independently or together (Loeb *et al.*, 1971). However, before such techniques can be applied, relaxation must be complete within the time window or truncation occurs, leading to spurious spectral features. If this condition cannot be attained before echo pulses appear, one may examine the response after what may be considered an infinite number of reflections and transmissions of the input signal *i.e.* until a virtually complete decay is obtained. This gives rise to *total reflection* methods of analysis. Figure 2.1. illustrates a typical oscilloscope trace for single and multiple reflection experiments.

Further diversity is possible by use of different sample thicknesses; this may bring a different frequency process into the available time window or simplify the calculations involved (Fellner-Feldegg, 1972), according to the approximations made. Although each method provides information on dielectric relaxation phenomena, the sensitivity, accuracy and reproducibility and frequency limits vary. However, by selection of complementary techniques, a very full dielectric spectral analysis is possible.

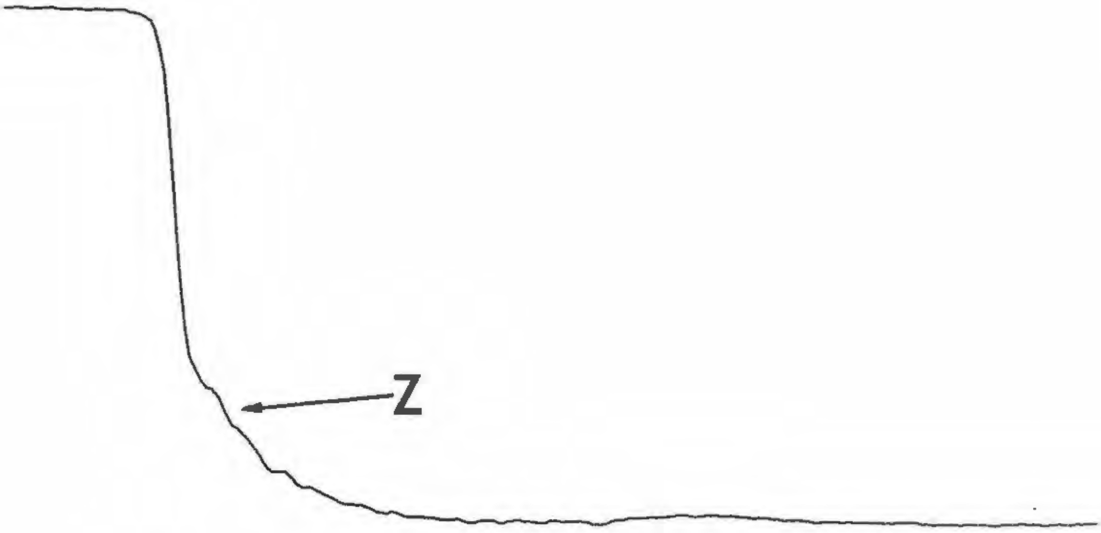
As has been noted, the shape of voltage step-pulse propagated along a coaxial line remains unchanged as long as the propagation properties of the loss-free line remain constant. However, when a dielectric material is inserted in the line, a discontinuity will occur such that the voltage step will be partly reflected and partly transmitted at the interface. The resulting pulse shape will be determined by the nature of the discontinuity and the dielectric properties of the material and it is the analysis of the resultant pulse shape which constitutes the basis of TDS.

FIGURE 2.1

Comparison of typical time domain waveforms for single reflection and total reflection experiments. Aberrations in the waveforms are noted at points X,Y,Z.



A Total reflection



B Single reflection

2.1.4. Some Fundamental Equations

For a coaxial line of negligible resistance filled with a dielectric medium, the characteristic impedance, Z, is given by

$$Z = Z_0/\sqrt{\varepsilon^*(\omega)} \quad , \tag{2.i}$$

where Z_0 is the characteristic impedance of the air-filled line and $\varepsilon^*(\omega)$ is the complex relative permittivity of the sample in the line where

$$\varepsilon^* = \varepsilon' - j\varepsilon'' - {}^{j\sigma}/\omega\varepsilon \quad , \tag{2.ii}$$

σ being the specific electric conductance and ε the permittivity of free space. (For alcohols, the final term in expression 2.ii may usually be neglected). The voltage reflection and transmission coefficients, $\rho(\omega)$ and $\tau(\omega)$, are then given by

$$\rho(\omega) = \frac{Z - Z_0}{Z + Z_0} = \frac{1 - \sqrt{\varepsilon^*(\omega)}}{1 + \sqrt{\varepsilon^*(\omega)}} \tag{2.iii}$$

$$\text{and } \tau(\omega) = \frac{2Z}{Z + Z_0} = \frac{2}{1 + \sqrt{\varepsilon(\omega)}} \quad . \tag{2.iv}$$

The quantities $\rho(\omega)$, $\tau(\omega)$, Z and $\varepsilon^*(\omega)$ are all frequency dependent.

Equations 2.iii and 2.iv describe a single reflection and transmission respectively, from an air/dielectric interface, and are sufficient to evaluate the relaxation parameters for a single reflection or direct transmission experiment. However, when a totally reflected or totally transmitted signal is examined, the relationships are not available in closed form. Here the complex permittivity is expressed in terms of the total reflection or total transmission (or scattering) coefficients, $R(\omega)$ and $T(\omega)$, respectively:

$$R(\omega) = \rho(\omega) \, . \, \frac{1 - \exp(-2\gamma\ell)}{1 - \rho^2(\omega)\exp(-2\gamma\ell)} \tag{2.v}$$

$$\text{and} \quad T(\omega) = \frac{[1 - \rho^2(\omega)] . \exp(-\gamma\ell)}{1 - \rho^2(\omega) . \exp(-2\gamma\ell)} \quad , \tag{2.vi}$$

where ℓ and c represent the sample length and velocity of light, respectively, and $\gamma = (j\omega/c).\varepsilon^{*}(\omega)$.

2.1.5. Application of Fourier Transformation

While the analysis of the frequency domain data is seen to be relatively straight-forward, there remains the difficulty of converting the raw data from the time domain to the more familiar frequency domain. The change is readily achieved by use of the Fourier transform which relates a pulse in the time domain, f(t), to a complex spectrum in the frequency domain F(ω):

$$F(\omega) = \int_{-\infty}^{+\infty} f(t)\,\exp(-\,j\omega t).dt \quad . \qquad 2.vii$$

Hence, in principle, the behaviour of a dielectric in the frequency domain may be evaluated by examining the ratio of the Fourier transforms of a reflected signal and a corresponding incident signal:

$$R(\omega) = F(\omega)/V(\omega) \quad . \qquad 2.viii$$

The latter signal is usually the response of the incident signal to a short at the sample position which establishes the spectrum of the incident signal, with all its imperfections, at the position of the sample. However, since the data are invariably obtained as a set of discrete sampled voltages (or some function thereof), the Fourier transform is not known analytically; hence, a numerical Fourier transform method must be used to effect the transformation. The discrete Fourier transform (DFT) cannot be applied directly since it requires the waveform to be periodic; since the initial and final voltages are different for TDS experiments, the difference would be treated as a step, leading to false information in the transformed data. This source of error may be eliminated by application of the Samulon (1951) modification of the Shannon (1949) sampling theory which relates

$$F(\omega) = \frac{\Delta t}{1 - \exp(-j\omega t)} \sum_{n=-\infty}^{\infty} \big(f(n\Delta t) - f(n\Delta t - \Delta t)\big) \exp(-j\omega n\Delta t), \qquad 2.\text{ix}$$

where Δt is the time interval between any adjacent pair of digitised samples. The subtraction of successive pairs of samples effectively differentiates the waveform and re-integration is provided by the pre-summation factor. While this relation has been successfully applied to several systems, Nicolson (1973) has noted that the subtraction of two, nearly equal, quantised values tends to enhance the noise levels. To avoid this, he proposed that a ramp voltage be subtracted from the step response before applying the discrete Fourier transform which then yields correct values only at frequencies $f = kf_o$ where $k = 1,2,3.....$ and $f_o = {}^{1}/N\Delta t$, N being the total number of digitised samples.

A more efficient method than application of equation 2.ix has been presented by Loeb (1972). He proposed the use of a modified version of the fast Fourier transform (the fast Fourier transform being merely an efficient method of calculating a DFT) from which results may be obtained for a number of frequencies which is small compared to the number of digitised samples.

2.2. Experimental Methods

2.2.1 Single Reflection Experiments

While the general principles describing TDS have now been outlined, it will be valuable to describe, more fully, those techniques which have actually been used : the practical difficulties, the expected results and the limitations of the methods will be briefly discussed.

For single reflection experiments, the experimental arrangement is illustrated in Figure 2.2. A modification of this arrangement was suggested by Suggett et al. (1970) whereby a "matched Tee" was introduced between the pulse generator and sampler. This split the

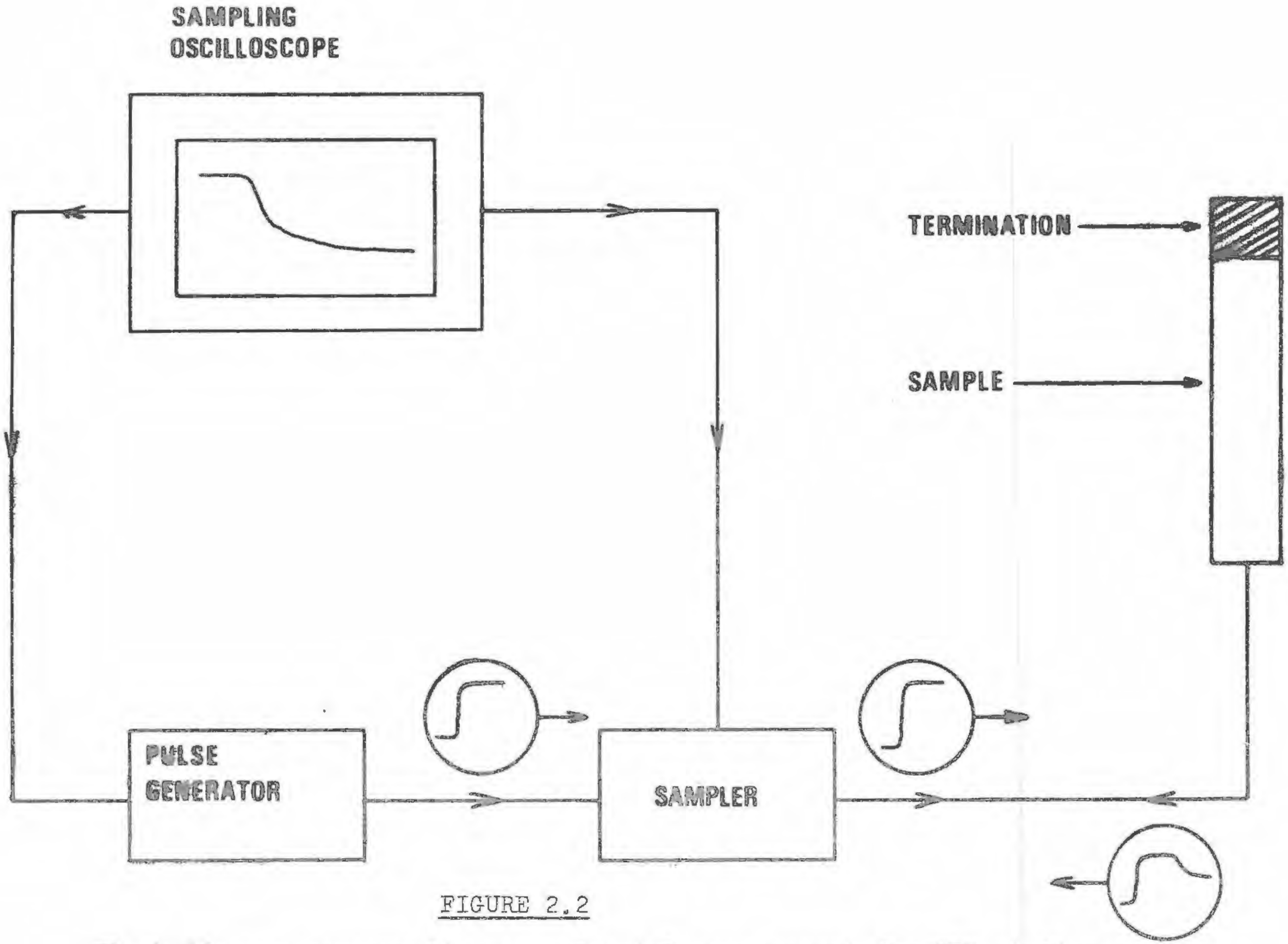


FIGURE 2.2

Block diagram representing experimental arrangement for TDR studies.

incident signal into two, one part being used to provide the pulse which will be reflected at the sample, and the other to provide a time marker pulse. The necessity for a time reference point on the waveform arises since one cannot measure the incident and reflected signals simultaneously; it is therefore necessary to be able to refer the incident and reflected signals, very accurately, to a common point in time.

Another, much simpler, method of time referencing is to calculate the time corresponding to the intersection point between the horizontal and most steeply sloping portion of the time domain waveform. While this method provides a relatively inaccurate reference time, the value is often adequate when only moderate losses are encountered which, coupled with the simplicity of the measurement, explains why it has often been adopted.

The difficulties of time referencing cannot be avoided since all TDS experiments require the ratio of two signals in the analysis. A timing error limits the high frequency information available by giving rise to a phase error which may be significant compared to the expected values.

The phase error Δ , is related to the time uncertainty, Δt, by $\Delta = 0.36\Delta t^{o}$/GHz where Δt is expressed in picoseconds. For a typical time uncertainty of 2 ps, the phase error, at 3 GHz, is about 2^{o} which is very significant for water with its high dielectric loss. For lower loss liquids, such as the aliphatic alcohols, errors in the amplitude seem more significant since

$$\frac{\Delta\varepsilon_0}{\varepsilon_0} = -\frac{\Delta r_\infty}{r_\infty}\cdot\sqrt{\varepsilon_0} \quad \text{for } \varepsilon_0 \gg 1, \tag{2.x}$$

where ε_0 is the low frequency permittivity and r_∞ the response to the

the input signal (the reflection coefficient) after the relaxation is complete (van Gemert, 1973). Thus for a given $(\Delta r_\infty/r_\infty)$, the error in ε_0 is proportional to $\sqrt{\varepsilon_0}$.

The lower frequency limit is dependent upon the sample length used: the relaxation must be complete before echo pulses interfere with the signal reflected from the air/dielectric interface. Thus one could envisage all experiments being conducted by means of single reflection procedures by the use of sufficiently long coaxial cables. In practice, however, restrictions, based on the commercial availability of long coaxial lines (which usually do not exceed 30 cm because of mechanical difficulties) and a desire to conserve sample material, prevent such experiments.

To conduct experiments investigating transmission characteristics of a sample, the only change necessary in the arrangement of Figure 2.2 is that the sample should be inserted between the pulse generator and sampler.

When the equations describing transmission experiments are examined, it can be seen that $\varepsilon^*(\omega)$ cannot be obtained from analytical solutions. Consequently one must resort to the application of numerical methods, such as the Newton-Raphson procedure, to obtain the relaxation parameters. However, Loeb et al. (1971) avoided this problem by using the transmission coefficient ratio (TCR) method which provides an analytical expression for the transmission properties of two samples of length l_1 and l_2:

$$\varepsilon^*(\omega) = \frac{c^2}{\omega^2(l_1-l_2)^2}\,[\phi^2-(\ln S)^2 - 2j\phi\ln S] \;, \qquad 2.xi$$

where T_1/T_2, the TCR, is expressed as $S\exp(j\phi)$, S and ϕ both being frequency dependent quantities. The ω^2 factor in the denominator limits the frequency range available, but, because of the large phase shifts obtained, this method is much less sensitive to timing errors than the single reflection method. Loeb <u>et al</u>. (1971) combined the complementary information from TCR and single reflection experiments to obtain results of very high quality for aqueous solutions.

2.2.2 Total Reflection Methods

With the problems associated with measuring the relaxation parameters in the available time window, it is attractive to think of including the echoes in the analysis of reflected or transmitted signal waveforms. As before, the complex permittivity can be found after Fourier transformation of the time domain data, although, as has been noted, the relationships are not always available in closed form which causes some difficulties in analysis. (However, experience shows these difficulties to be minimal except, perhaps, in real-time analysis.) To overcome these, one may make restrictions upon the sample length or solve the equations by numerical methods.

The former approach, which was adopted by Fellner-Feldegg (1972), requires that the sample length be short enough so that contributions from multiple reflections are contained in a time interval which is short relative to the relaxation time being investigated. Under these circumstances, $2\gamma l \ll 1$ so that $\exp(-2\gamma l) \simeq 1 - 2\gamma l$ and equation 2.v may then be written as

$$R(\omega) = \frac{j\omega l}{2c}\left(1 - \varepsilon^*(\omega)\right) \quad . \qquad 2.xii$$

Assuming a Debye-type dielectric, Fellner-Feldegg was able to obtain results of good quality, in minutes, using computer controlled data acquisition and processing. Recently, van Gemert (1974) presented a more rigorous mathematical analysis of Fellner-Feldegg's thin sample method.

While the speed of analysis makes the thin sample method very attractive, it is limited by the need for a knowledge of the behaviour, in the frequency domain, of the sample; for instance assumption of Debye-type behaviour. No such restriction exists with the direct application of relation 2.v. Clark, Quickenden and Suggett (1974), who applied this equation using a Newton-Raphson iterative procedure to solve for $\varepsilon^*(\omega)$, showed that it could provide information over a wide range of frequencies and, in particular, at frequencies lower than those obtained from single reflection experiments. The spectral information obtained above 0.1 GHz was not superior to that obtained by single reflection methods, but the short sample lengths generally used make this method suitable where a restricted volume of sample is available. The method also lends itself to measurements on conducting solutions.

de Loor, van Gemert and Gravesteyn (1973) used a slightly different experimental arrangement to investigate the low frequency behaviour of $\varepsilon^*(\omega)$: here the sample was terminated by a short in which case the reflection coefficient becomes

$$R(\omega) = \frac{Z/Zo-1}{Z/Zo+1} \quad , \qquad 2.xiii$$

where $Z/Zo = \tanh\left\{j\omega(l/c)\sqrt{\varepsilon^*(\omega)}\right\} / \sqrt{\varepsilon^*(\omega)}$. 2.xiv

The frequency domain information was determined by a graphical method although, as the authors noted, there is no reason to prevent a numerical procedure being used.

Another interesting feature of Fellner-Feldegg's thin cell method was that it was the first example of a direct analysis of the time domain data to produce relaxation parameters. Subsequently, Cole (1974, 1975) presented much less restricted analyses which allow the frequency domain information to be obtained directly, without assumptions as to its form, and for a considerable range of sample thicknesses. Such direct methods are obviously attractive since they avoid the need for Fourier transformations, the calculation of which is often the most time-consuming procedure of the analysis.

2.3. Errors in the Time Domain Signal

2.3.1. Removal of Unwanted Components of Time Domain Signals

To this point, little recognition has been given to the fact that reflections and transmissions occur through imperfect connectors and along imperfect coaxial lines which may have impedance mismatches; mismatches between the pulse generator and sampler may also be present. Further sources of error arise from the use of a short to correct for the non-uniform frequency content of the incident step; the short and associated correctors are not perfect reflectors and may absorb some of the incident voltage. The trace from the short may include echo pulses reflected from the sampler and, finally, the reflection from the short will not exactly represent the incident pulse to the sample since, during the mounting of the sample cell, connectors are disturbed. While many of these unwanted reflections can be displaced from the time window, in the single reflection procedure, by careful distribution of lengths of coaxial line, examination of the sample traces shown in Figure 2.1 shows that the response at the sample can by no means be considered ideal.

Smoothing of the frequency domain data, to reduce errors, has been reported by de Loor <u>et al</u>. (1973) but this is not a satisfactory procedure since information may inadvertently be lost. It is therefore preferable to analyse the raw time domain data in such a way as to remove those parts of the waveform which do not arise from the molecular relaxation process. One may also substract the response from the empty sample cell terminated with a matching impedance. To achieve the former objective, Fellner-Feldegg (1972) suggested using a reference material and two methods have subsequently been presented to allow this; the first, by Giese (1974) for single reflection experiments and the second, which should be generally applicable, by Glasser (1975).

The first method considers the dielectric response for a liquid which is known to exhibit no relaxation behaviour in the frequency region of interest. Any deviations from the expected behaviour, caused by imperfections as discussed above, are considered to occur similarly in all systems examined for the same experimental set-up; the sampler/sample connection is assumed to be ideal and all imperfections are assumed to occur at the sampler. For a sampler connected, by a coaxial line, to an infinitely long sample (i.e. the time trace is recorded for the period before echo pulses influence the waveform), the situation is represented diagrammatically in Figure 2.3.

The total reflection coefficient, $R_{total}(\omega)$, may be expressed as a series:

$$R(\omega)_{total} = -(1+R_s(\omega))[R(\omega)\exp(-2\gamma l)+R_s(\omega)R^2(\omega)\exp(-4\gamma l) \ldots \ldots R_s^{n-1}(\omega)R^n(\omega)\exp(-2\gamma nl)] \quad . \qquad 2.xv$$

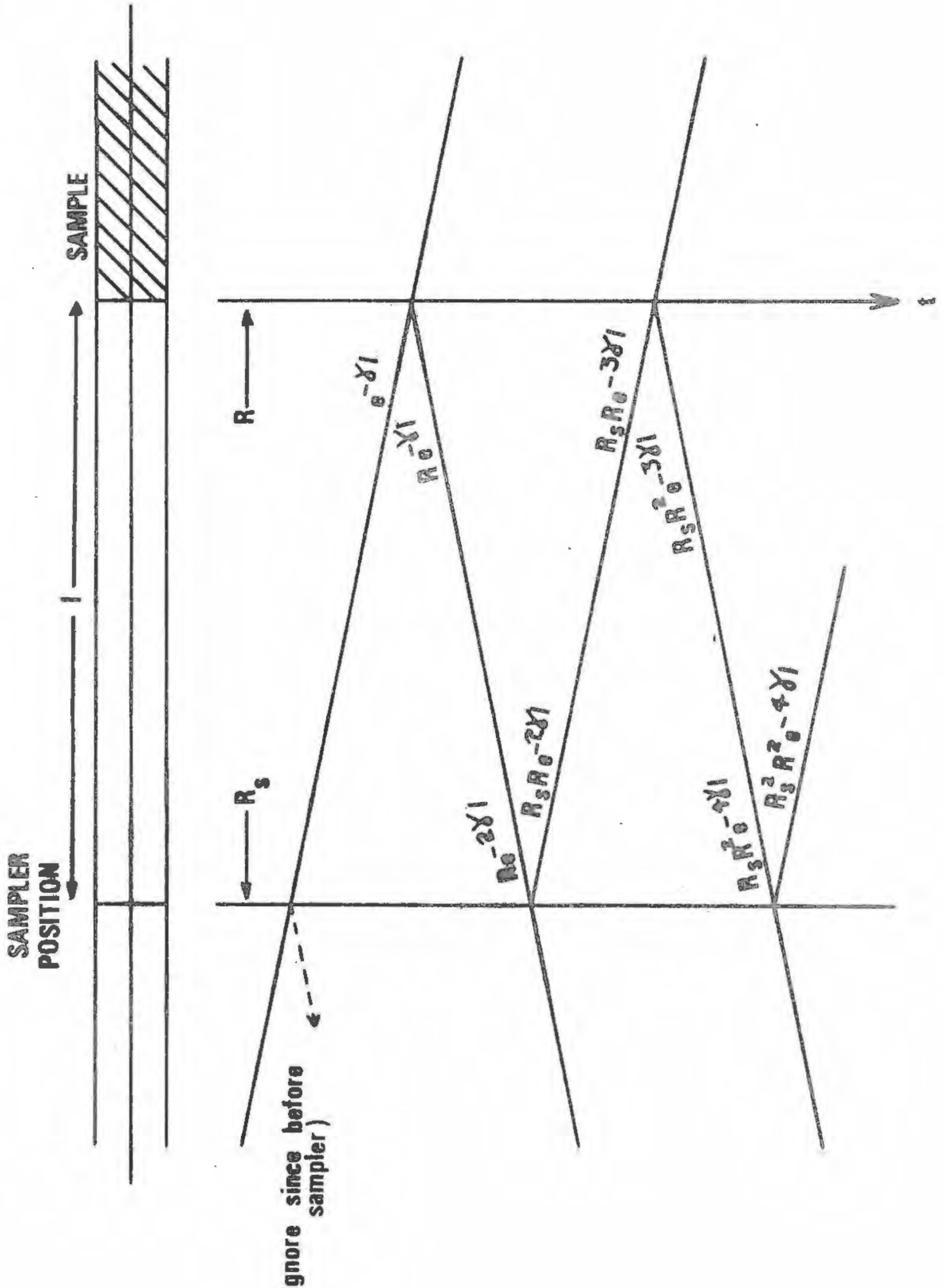
This equation may be expressed as the sum of a geometric progression which has $R(\omega)e^{-2\gamma l}$ as its first term and $R_s(\omega).R(\omega)e^{-2\gamma l}$ as its common ratio. Thus

$$R(\omega)_{total} = -(1+R_s(\omega)).\ \frac{R(\omega)\exp(-2\gamma l)}{1-R_s(\omega)R(\omega)\exp(-2\gamma l)} \quad . \qquad 2.xvi$$

Thus from the reflection properties of the reference liquid, the reflection coefficient of the sampler can be calculated, as a function of frequency, and this is assumed to remain unaltered when the sample

FIGURE 2.3

Diagrammatic representation of multiple reflections from a sampler and from an infinitely long sample, indicating the relative contributions from the various reflections.



under study replaces the liquid. Then applying

$$R(\omega)_{app} = -\frac{R(\omega)(1+R_S(\omega))}{1-R(\omega)R_S(\omega)} , \qquad 2.xvii$$

where $R(\omega)_{app}$ is the apparent, measured reflection coefficient and $R(\omega)$ is the desired reflection coefficient of the sample under investigation ($R(\omega)_{app}$, $R_S(\omega)$ and $R(\omega)$ all being complex, frequency dependent quantities), improved frequency domain information for the sample is obtained.

The second method also involves corrections derived from deviations from the expected behaviour of a reference liquid but, in this case, the reference liquid is chosen to exhibit similar relaxation characteristics to those of the sample. Generalising equation 2.viii, the apparent reflection coefficient may be written as

$$R(\omega) = \frac{F(\omega)}{[V(\omega)/S(\omega)]_{ref}} , \qquad 2.xviii$$

where $S(\omega)_{ref}$, the complex reflection coefficient for the short, is ideally assumed to be -1. When a known sample is used instead of a short, $V(\omega)$ represents the Fourier transform of the time-trace for that sample in the cell and $S(\omega)_{ref}$ is calculated from the known dielectric parameters of the sample (*e.g.* if the sample exhibits a Debye relaxation, $S(\omega)_{ref}$ may be calculated, at various frequencies, if ε_0, ε_∞ and τ are known). The corrections thus obtained for the reference spectrum will be accurate for aberrations occuring in the sample cell, but will not fully allow for non-ideal behaviour in the air-line preceding the sample. However, such errors are unlikely to be significant, and will reduce with samples of low permittivity.

These procedures provide the prospect of extending the frequency range available to the experimental worker and also improving the accuracy of the measured dielectric parameters. In particular, the second method may prove able to overcome the problems experienced in investigating the experimentally difficult (in TDS) frequency range from 0.01 to 0.05 GHz.

Glasser (1975) has also suggested that the construction of a sample cell which allows the sample to be introduced and removed without disturbing the connectors would be useful in helping to overcome the difficulties associated with investigating the above frequency range. He has shown that removal and replacement of the termination (as would be required if the sample liquid were to be changed) between collection of the time domain data for two signals produces significant differences in the frequency domain spectrum calculated from each signal.

2.3.2. Errors Arising from Sampling and Digitisation

While the errors arising from time referencing difficulties and unwanted reflections have been noted, those arising from the sampling and digitisation of the analogue time signal must not be neglected. It is necessary to select a timing interval that will minimise errors caused by aliasing and a long enough time window to avoid truncation of the data. To reduce aliasing errors, the general principle to be satisfied is that sampling must occur frequently enough to prevent loss of information from the signal, which implies that a changing signal must be sampled at a rate much faster than any change that occurs. This is expressed in the sampling theorem which states that

".... if a continuous, bandwith - limited signal contains no frequency components higher than f_c, then the original signal can be completely recovered, without distortion, if it is sampled at a rate of at least 2 f_c samples per second.".

If the sample rate is not sufficient, some of the high frequency components of the signal are "folded" back into the signal waveform as illustrated in Figure 2.4.

The inclusion of high frequency components causes distortion when one tries to recover the original signal. Although a high sampling rate may reduce this effect, it can never be entirely eliminated due to wideband noise in the signal and non-ideal filters. However, the signal intensity from an ideal step varies as $I = {}^{1}/\omega$: consequently high frequency amplitudes are small, though finite.

Truncation errors arise from examining the time domain signals over a discrete time interval and neglecting all events occuring before or after this interval. (We may recall that truncation errors may also be introduced by incorrect application of the DFT to effect the transformation of the time domain data into the frequency domain.) To avoid truncation errors, sampling must be continued until the information loss is insignificant.

2.3.3 Other Sources of Errors.

The presence of noise in the signal waveform has already been noted. This arises from the use of a tunnel diode pulse generator for which the spectral intensity is low. This means a high amplifier gain is needed with the noise thus introduced being a limitation on the measurement accuracy. To this noise must be added a component arising from quantisation, the effect of which is to add uncorrelated noise to the signal noise (Kelly and Horlick, 1973). Apart from noise errors, timing jitter (Nicolson, 1968) must also be considered : this is seen when a voltage, held on a fixed point of the waveform, fluctuates about a mean position. Finally rounding errors in the computer calculation of the Fourier transformation

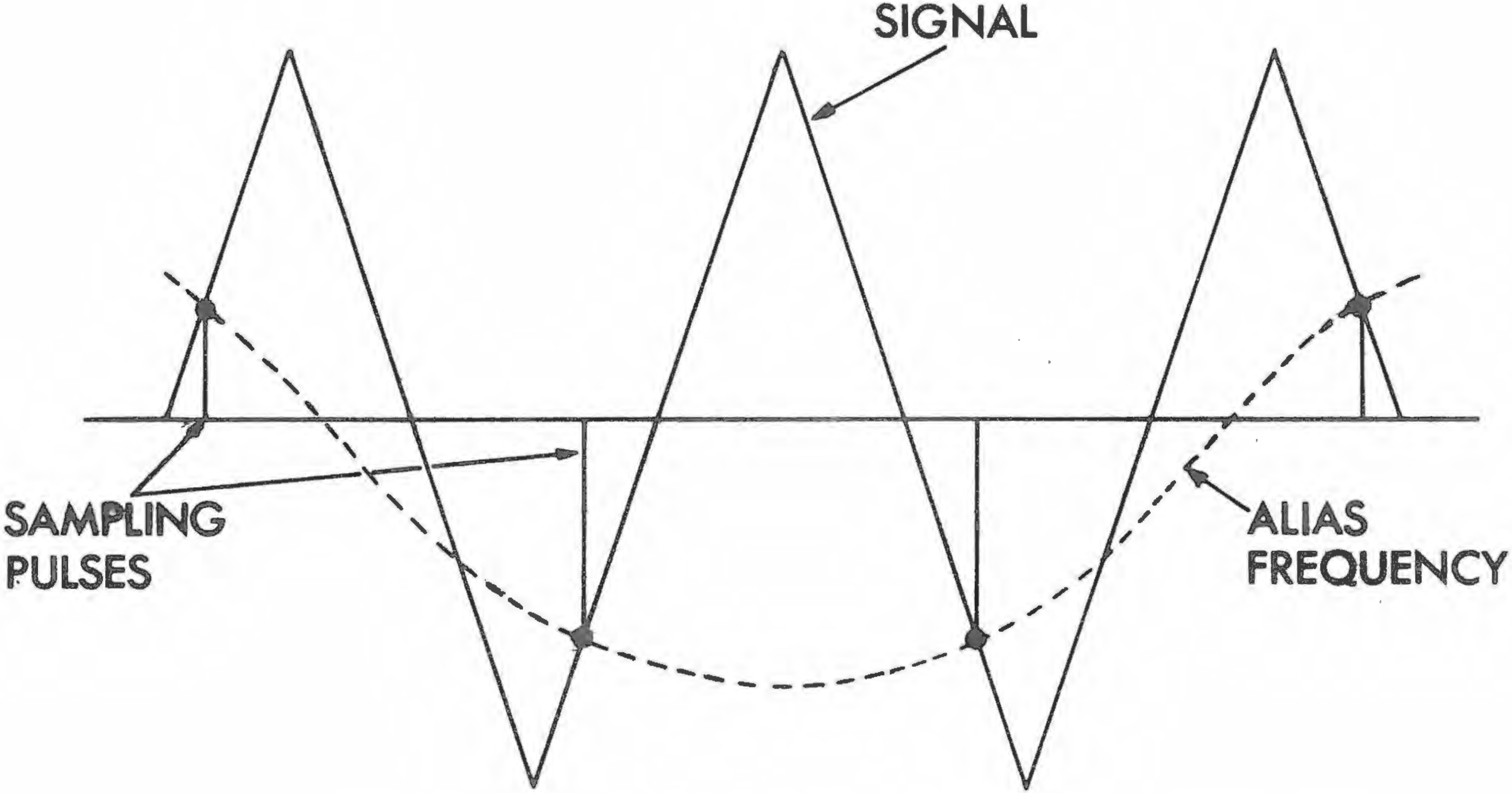


FIGURE 2.4
Alias frequency (dashed line) caused by inadequate sampling rate.

procedure should be noted (although these errors are probably very small).

This brief description of the techniques of TDS shows the rapid development in a relatively short period. Although the technique has so far only been applied to high and moderate dielectric loss materials ($\varepsilon''_{max} > 1$), it is to be hoped that continuing progress will allow the investigation of materials with medium and low losses.

Note Added in Proof

In a recent publication, Suggett (1975) discussed refinements in earlier experiments which combined the TCR and single reflection methods (Loeb *et al.*, 1971; discussed in sub-section 2.2.1). The decreased uncertainty with which the time domain waveforms can be referred to a common time reference point was found to result in a significant increase in the level of accuracy for TDS microwave measurements of complex permittivity. The use of a high pass filter to minimise the effects of truncation errors at frequencies above 1 GHz was also discussed.

CHAPTER 3

EXPERIMENTAL TECHNIQUES

Section 3.1. Preparation of Samples

3.1.1. Purification of Compounds

The alcohols and solvents studied are listed, together with their sources and grades in Table 3.1. Before use, each of the alcohols was dried by refluxing, for some hours, over calcium hydride (CaH_2). They were then fractionally distilled, under reduced pressure, using a 1 metre spinning band column. Under these conditions, the alcohols were collected within a boiling range of 0.5°C. The distillation removed carbonyl impurities, seen at 1720 cm^{-1} in the infrared spectra, from the materials as supplied. The solvents, cyclohexane, carbon tetrachloride and benzene were refluxed over phosphorus pentoxide (P_2O_5) and distilled at atmospheric pressure through a 1 metre column, packed with glass helices, prior to use; hexadecane and n-hexane were used as supplied, without further purification. To ensure dryness, the materials were stored over molecular sieve (type 4A) for the short period before use.

All compounds were checked for purity using gas chromatography, infrared spectroscopy and refractive index measurements.

3.1.2. Preparation of solutions

All solutions were prepared gravimetrically. For dilute (less than about 0.1 mol ℓ^{-1}) alcohol solutions, for which the solute concentration was required with great accuracy, the weighings were effected using a Mettler H 16 balance, accurate to 0.01 mg, which was kept in an air thermostat. Solvent addition was performed in a dry box flushed with dry nitrogen.

3.2. Physical Measurements

TABLE 3.1

Alcohols and Solvents Studied

Compound	Source	Grade	n_D^{25} after purification
1-Propanol	B.D.H	–	1.3839
1-Butanol	B.D.H.	–	1.3973
t-Butanol	B.D.H.	–	1.3854
1-Hexanol	B.D.H.	–	1.4162
1-Heptanol	B.D.H.	–	1.4229
1-Octanol	Merck	pure	1.4277
2-Octanol	B.D.H.	–	1.4239
3-Octanol	Kock-Light	pure	1.4232
4-Octanol	Aldrich	–	1.4221
2,3,4-Trimethyl-3-Pentanol	Fluka	purum	1.4321
1-Decanol	B.D.H.	–	1.4351
Carbon Tetrachloride	Merck	analytical	1.4573
Cyclohexane	Merck	G.R.	1.4236
Benzene	Riedel de Haën	analytical	1.4978
Hexadecane	B.D.H.	–	1.4321
n-Hexane	Merck	spectroscopic	1.3721

3.2.1. Density

The densities of the more dilute alcohol solutions were measured using a bicapillary bottle (Weissberger, 1972) with a volume of about 20 ml. All measurements were conducted in an air thermostat. The volume of the bottle was calibrated against carbon tetrachloride, taken to have a density of 1.58454 g cm^{-3} (Timmermans, 1950). The bottle was placed in a thermostat bath controlled to ±0.02°C, with the capillary arms arranged vertically. After temperature equilibration, the height of the menisci above or below a reference mark on one of the capillary arms was measured using a cathetometer which had a micrometer adjustment. From a calibration curve of volume against meniscus height, the volume corresponding to the measured height was calculated; from the mass of the solution, found by difference, the density was calculated with an accuracy of ± 0.00002 g cm^{-3}.

For alcohol solutions of concentration greater than about 0.1 mol ℓ^{-1}, densities were measured by means of a 5 ml Lipkin pycnometer which had graduated scales etched onto the capillary arms. Again calibration of the volume was against carbon tetrachloride and, in this case, an accuracy of ± 0.001 g cm^{-3} was attained.

3.2.2. Infrared and NMR spectra

Infrared spectra were recorded on a Beckman IR-8 spectrophotometer except for solutions of 2,3,4-trimethyl-3-pentanol which were examined using a Beckman IR-10 spectrophotometer. The former instrument produces spectra linear in wavelength and the latter spectra linear in wavenumber. Frequencies for the -OH stretching vibration are accurate to ± 5 cm^{-1}. A variable path length cell was used to compensate for solvent absorption. The sample cell was thermostatted at 25°C. Additional results, described in the text, were recorded on a Perkin-Elmer

Model 180 spectrophotometer and are accurate to ± 1 cm^{-1}. Low temperature spectra were obtained using a Beckman VLT-2 cell and TEM-2 controller.

NMR spectra were recorded at 35°C using a Perkin-Elmer R12 spectrometer. Chemical shifts were measured relative to the alcohol methylene group as an internal reference while this was in turn referenced against tetramethyl silane to provide an accurate value of the chemical shift. The chemical shifts are accurate to ± 0.02 ppm.

3.2.3. Static Dielectric Permittivity

Static permittivity measurements were made at 2 MHz using a heterodyne-beat Wissenschaftlich-Technische Werkstätten "Dipolmeter" (Model DM 01) with a DFL 1 cell for dilute alcohol solutions and a DFL 2/D cell for more concentrated alcohol solutions. The cells were thermostatted by water pumped through their outer jackets from a bath controlled to ± 0.02°C. The precision of the permittivity measurements is better than 0.0001 for the low concentration solutions (DFL 1 cell) and about 0.0004 for the higher concentration solutions. The permittivities of the pure alcohols were measured, at 10 KHz, in the DFL 2/D cell using a General Radio 716C Bridge. The precision of the permittivities thus measured was about 0.01.

Since the "Dipolmeter" does not measure permittivity directly, it was necessary to prepare a calibration curve from the published dielectric permittivities of standard liquids. For this purpose, cyclohexane, carbon tetrachloride and benzene were used to calibrate the DFL 1 cell, and cyclohexane, carbon tetrachloride and n-dibutyl ether for the DFL 2/D cell. The permittivity values used were taken from the "Handbook for Dipolmeter" (1959). Table 3.2 lists the values used together with their original sources.

TABLE 3.2.

Permittivities Used for Calibration of the "Dipolmeter"

Compound	Permittivity at 25°C	Reference
Cyclohexane	2.0148	Rosswog (1953)
Carbon Tetrachloride	2.2263	Mecke & Rosswog (1956)
Benzene	2.2727	Mecke & Rosswog (1956)
n-Butyl Ether	3.0475	Mecke & Specht (1958)

To maintain the stated accuracy, it was necessary that each time a cell was removed from the measuring equipment, or its position altered in any way, a new calibration curve be established. A typical calibration curve is shown in Figure 3.1.

3.2.4. Dielectric Relaxation Properties

To examine the relaxation properties of alcohol solutions, a Tektronix 7S 12 time domain reflectometry system was used with an S-52 pulse generator (rise-time, 25 ps) and an S-6 sampling head (system rise-time, 35 ps). The pulse was fed through the loop-through sampler into 7 mm coaxial lines fitted with "Americon" connectors, and with a 20 cm precision air line interposed between the sample cell and sampling system. The experimental arrangement is similar to that depicted in Figure 2.2, the main difference being the omission of the precision air line from Figure 2.2.

The outer conductor of the coaxial line was glued, using electrically-conducting, silver impregnated,polymerised resin (Johnson-Matthey Type FSP49 H and R), to the terminating connector of the inner conductor. This prevented liquid leakage from the sample cell, which has been suggested (Suggett, 1974a) as causing a reduction in the high frequency response from coaxial cells.

The sample cell was thermostatted by means of a demountable jacket (Campbell, Glasser and Ranftelshofer, 1974), illustrated in Figure 3.2. The jacket, which was designed for use with commercial rigid coaxial lines, required no precision engineering and avoided the possibility of leakage and contamination of the sample. It is constructed from a cylindrical tube, the diameter of which is larger than that of the outer tubular coaxial conductor. The seal between the jacket and conductor is formed by O-rings, compressed by hexagon nuts which are countersunk to permit the jacket to cover the

FIGURE 3.1

Typical calibration curve for "Dipolmeter". The permittivities of the reference compounds are listed in Table 3.2 .

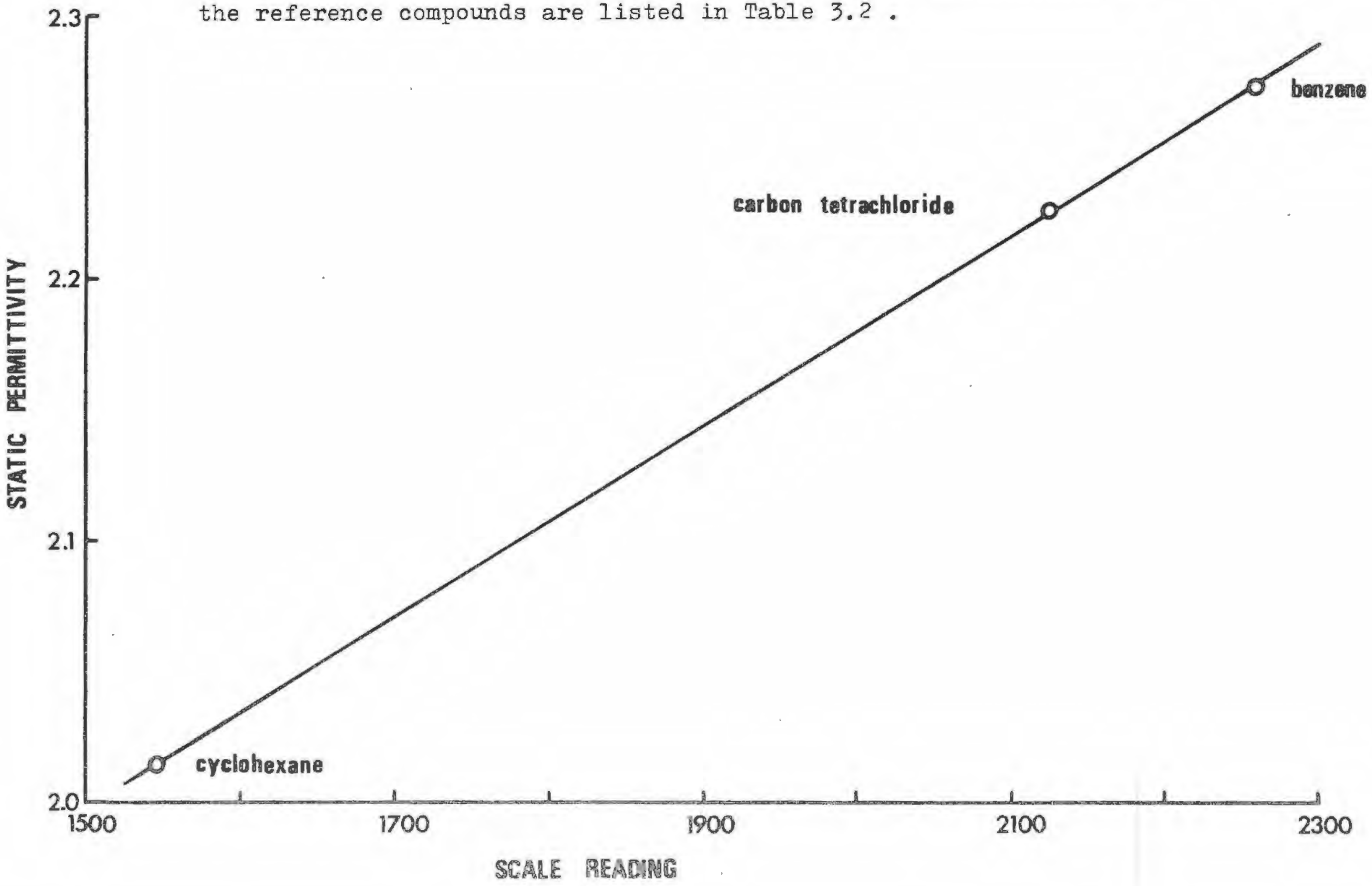
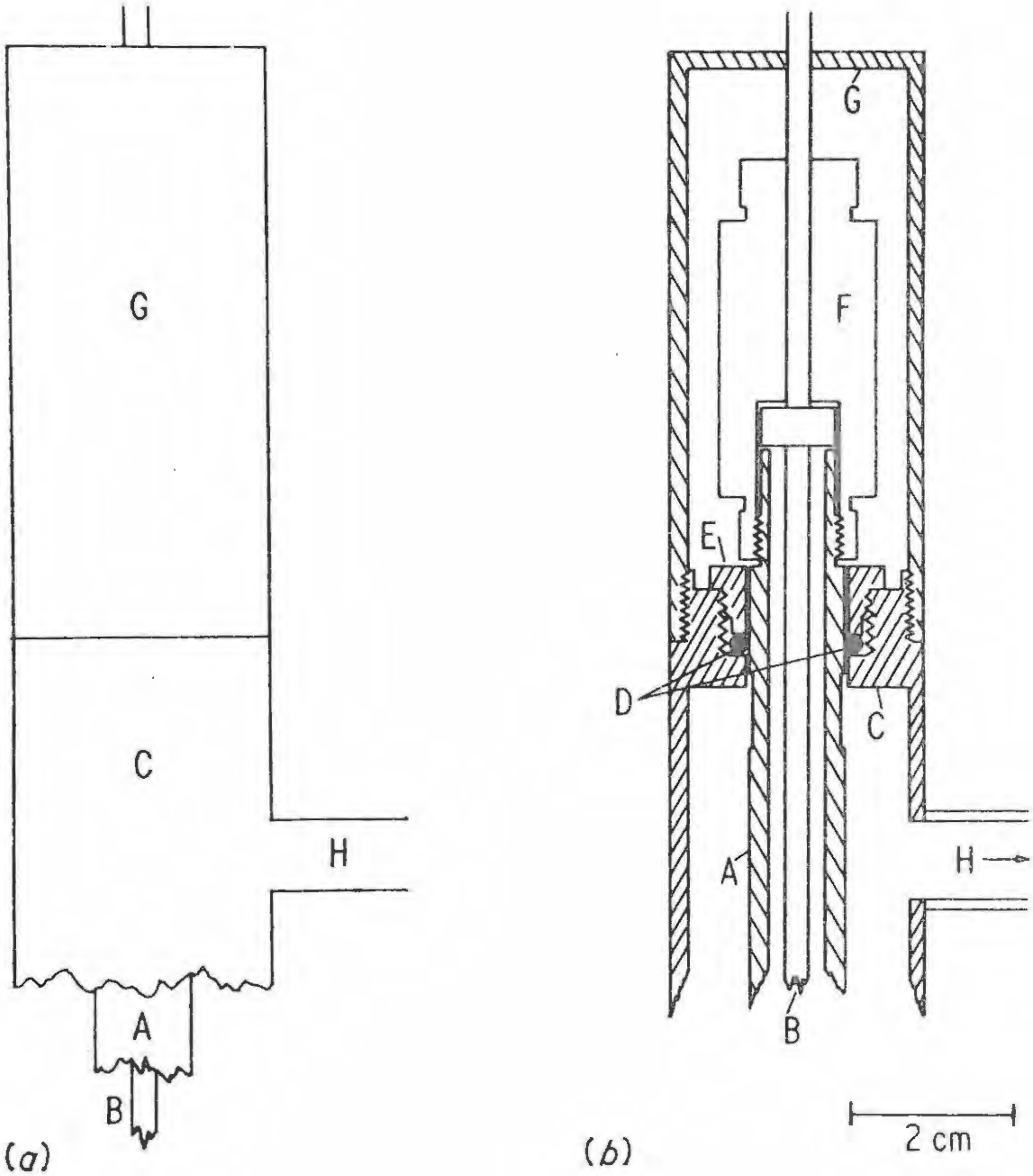


FIGURE 3.2

Demountable thermostat jacket: a) external view of one end of the jacket: A, outer conductor of coaxial line; B, inner conductor; C, thermostat jacket; G, thermostat cap; H, thermostat liquid inlet/outlet. b) Cutaway view of one end of the jacket: D, O-ring; E, hexagonal nut; F, connectors to external coaxial line. The outer conductor, A, is depicted with flats milled into it; these are intended to facilitate assembly of the line.



maximum possible area of the coaxial tube. This arrangement permits the connectors terminating the coaxial tube to be removed for filling and cleaning of the tube, without disturbing the jacket. When the coaxial line has been assembled, metal caps, internally insulated with polystyrene foam, may be screwed over the connectors to ensure that the ends of the tubes are at as uniform a temperature as possible. The metal caps are drilled to allow connecting cables to pass through to the coaxial assembly, thus permitting measurements to be made in either a reflection or transmission mode.

3.3. Processing of Time Domain Waveforms.

3.3.1. Digitisation of Waveform and Collection of Data.

Initially, the analyses were performed by hand-digitising an XY recording of the 7S 12 output; however, this process was inaccurate and slow and the need for automatic digital data collection procedures was evident. The techniques of TDS are singularly suited to such procedures because digital computer calculations, in which the time domain data are Fourier transformed into the frequency domain, are necessary to obtain the relaxation parameters describing a system. Another advantage of digital data acquisition is that it lends itself to the calculation of corrections to compensate for voltage drift and time jitter (Nicolson, 1968) which are significant, even during rapid scanning.

The modular, transient data collection system designed (Way-Jones and Glasser, 1974) was not adapted to particularly high data collection speeds since, although the signals contain very high effective frequencies (up to 15 GHz at 100 KHz repetition rate), they are sampled and presented at a much lower rate (a maximum of 50 Hz in the Tetronix system). A diagrammatic representation of the combined 7S 12 and data collection systems is shown in Figure 3.3.

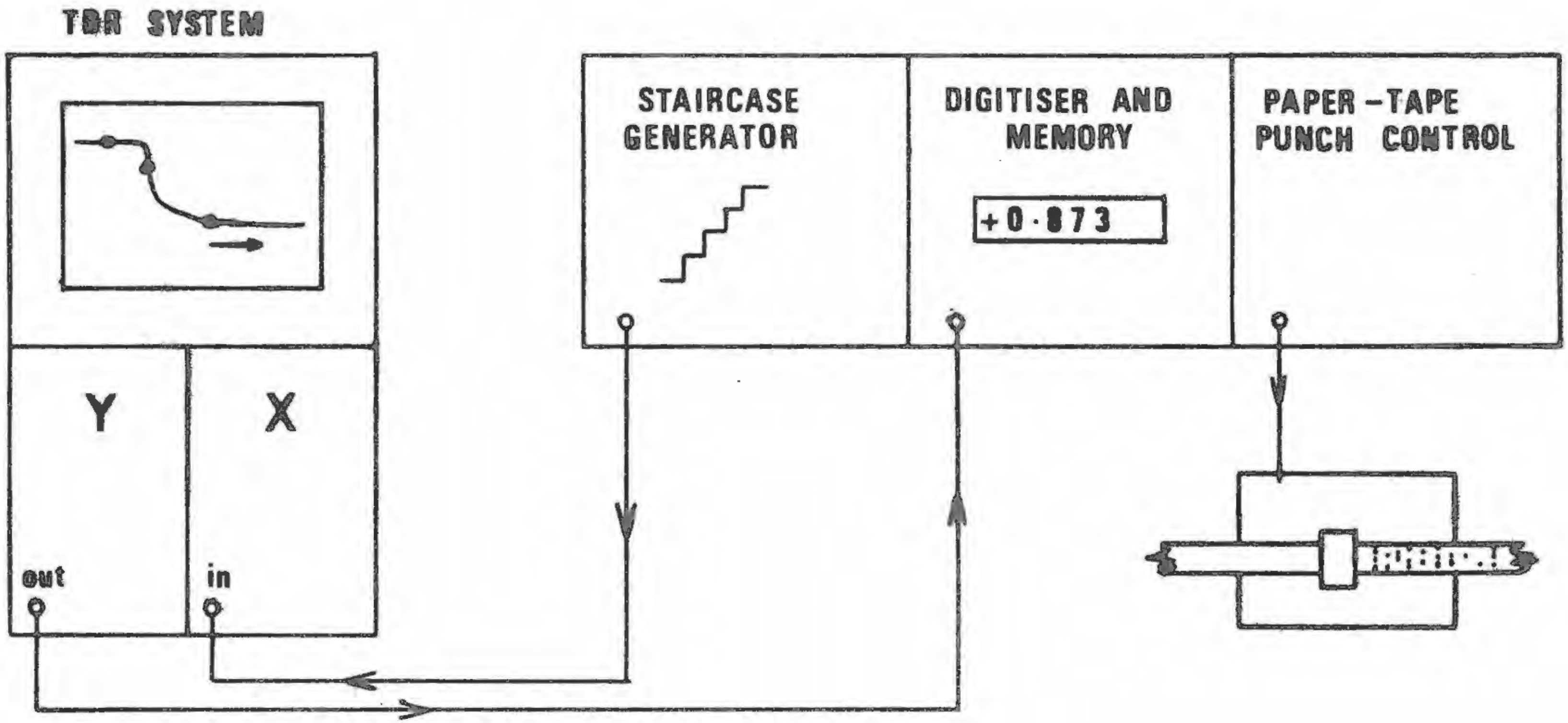


FIGURE 3.3

Diagrammatic representation of the interrelation between the time domain sampling equipment and the data acquisition system.

While considering the practical features of the data collection system, it is relevant to discuss how practical difficulties arising from the digitisation of an analogue signal (Kelly and Horlick, 1973) are overcome by its design.

The basic system provides a stepped voltage to act as a scan across the oscilloscope screen. The amplitude of the scan is variable and an offset is also provided; this allows for selection of that portion of the screen display which is of interest (the appropriate time window) to be digitised and so minimises errors arising from sampling an insufficient or inappropriate segment of the analogue signal.

The number of steps generated is switchable from 64 to 1024 per scan, in 9 settings. The voltage steps are provided by a digital ramp and a D/A converter, so that analogue voltage control problems are avoided. This range of voltage steps allows one to avoid aliasing errors, which have been discussed in sub-section 2.3.2. For single reflection experiments the time scale used was 2 ns with 256 samples being taken. This corresponds to a Nyquist frequency of 63.75 GHz, a value much larger than the upper limit of about 15 GHz provided by the sampling system. For total reflection experiments, a time scale of 35 ns, sampled at 1024 points was used : this provides a Nyquist frequency of 14.6 GHz which is near the upper frequency limit of the sampling system; furthermore calculations were not carried beyond 2 GHz. Thus, for experiments conducted in this study, aliasing errors are not a major factor to be considered.

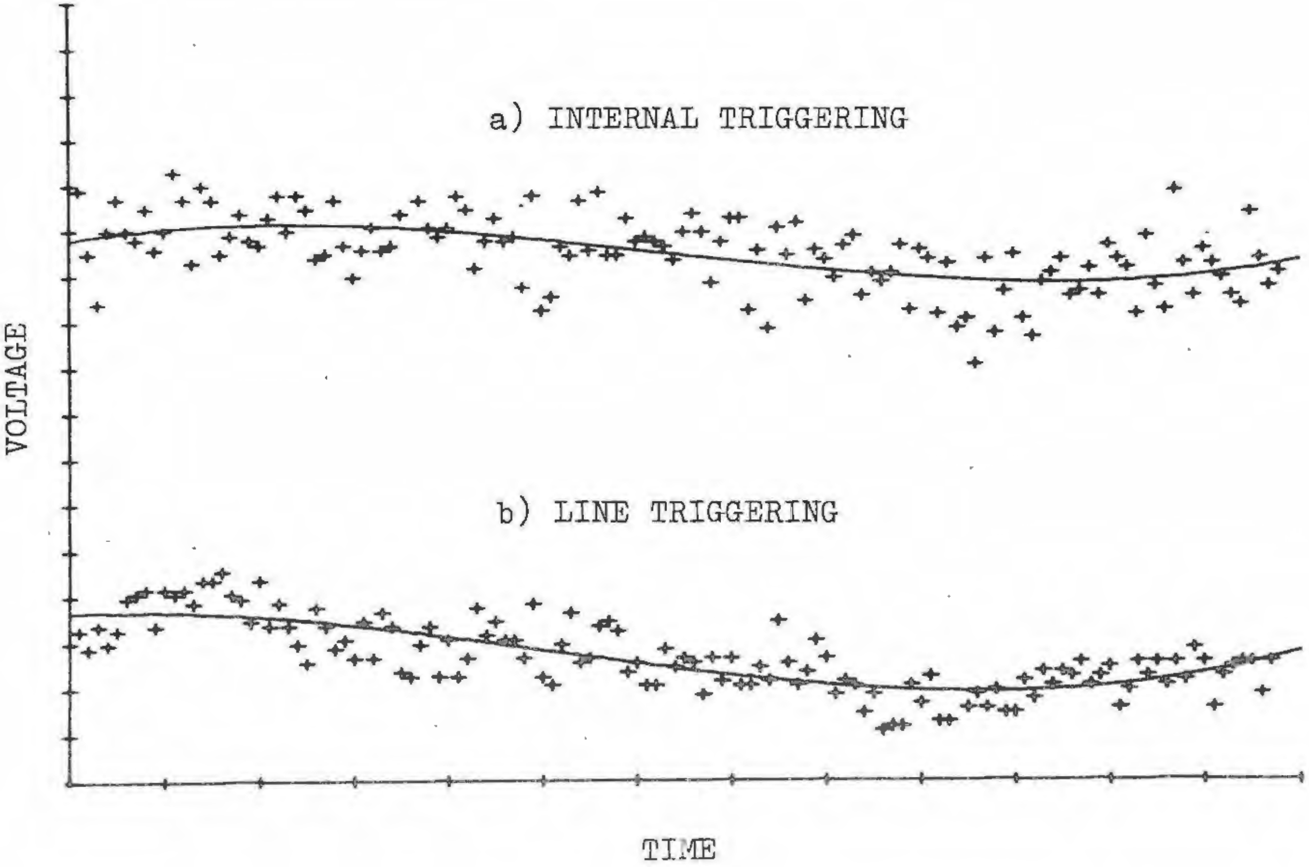
After a brief settling period for the analoque voltages, the output signal from the 7S 12 is applied to a dual-slope integrating A/D converter with an effective resolution of 1 part in 4000. To minimise the uncorrelated noise arising from quantisation errors, the vertical display of the oscilloscope was expanded as far as was experimentally possible. This provides a range of approximately 2.5 volts (beyond which saturation of the amplifiers occurs). The expected quantisation error is ± 1 mV, the minimum resolution of the digitiser, which is less than the uncertainty of ± 2.0 mV observed by measuring the voltage of a point on a non-sloping portion of the waveform.

The conversion time of the converter is approximately 5 ms; consequently a period of 6 ms is provided for digitisation of the 7S 12 output to allow settling of the analogue signals after switching. It was found that triggering at the line frequency (50 Hz) brings about a small reduction in the amplitude of the signal noise; this is illustrated in Figure 3.4. Consequently, the scan rate most often used was 20 ms per step, although digitisation was still completed in 6 ms. This practice allows the use of the "high resolution" setting of the Tektronix system, which reduces sampling noise by integrating over a period, the settling time of which is 7 ms. Thus, by incorporating an appropriate time delay before sampling, the high resolution settling may be used in conjunction with line triggering and sampling. However, little reduction in the apparent signal noise occurs, suggesting that the integration time constant of the A/D converter is similar to that inserted in the "high resolution" setting. It can thus be seen that errors caused by changes in the analogue output voltage, occuring during the period of digitisation, are avoided since sampling only takes place after the 7S 12 output has stabilised.

Finally, the digitised data are collected and are fed into and stored,in a BCD coding, in an MOS circulating memory of 512 steps. They may then be fed asynchronously to a paper tape punch which

FIGURE 3.4

Signal noise observed at a steeply sloping portion of the time domain waveform: a) depicts the noise observed when the sampling signal is internally triggered while b) depicts the noise observed when the signal is triggered at the line frequency (50Hz).



operates at about 40 characters s^{-1}: thus about 50s are required to output the data from the full memory.

3.3.2. Correction for Time Jitter.

An additional feature of the data collection system has proved very valuable. As has been described, digitisation may occur from the external input. It may also occur, alternately, from the input and from the stepped ramp output, to provide a check on the actual ramp voltage. During these alternate steps, the ramp voltage may be replaced by one, or alternately one of two, reference voltages which can be independently set. Figure 3.5 illustrates the sequence in which the voltages may be applied.

These voltages are usually set to the initial horizontal portion of the trace to check for voltage drift and to a steeply sloping portion to check for time jitter, following the suggestion of Nicholson (1968).

A reference voltage located on the most steeply sloping section of a reflected signal is highly elongated, having a measured r.m.s. of approximately 33 mV. This corresponds to a time jitter of about 20 ps in a total display of 2 ns, whereas the timer and amplifiers controlling the time interval selected for sampling are accurate to within 0.01% of the time interval. This implies that errors arising from random variations in the selected time interval are negligible compared to those arising from time jitter.

The time jitter is calculated from the change in voltage, as a function of time, of the points on the horizontal section of the waveform and of the points on a steeply sloping section which are smoothed over the whole period of data collection, arbitrarly by a second order equation, to remove the noise noted above. A corresponding time is added algebraically to the assumed time for

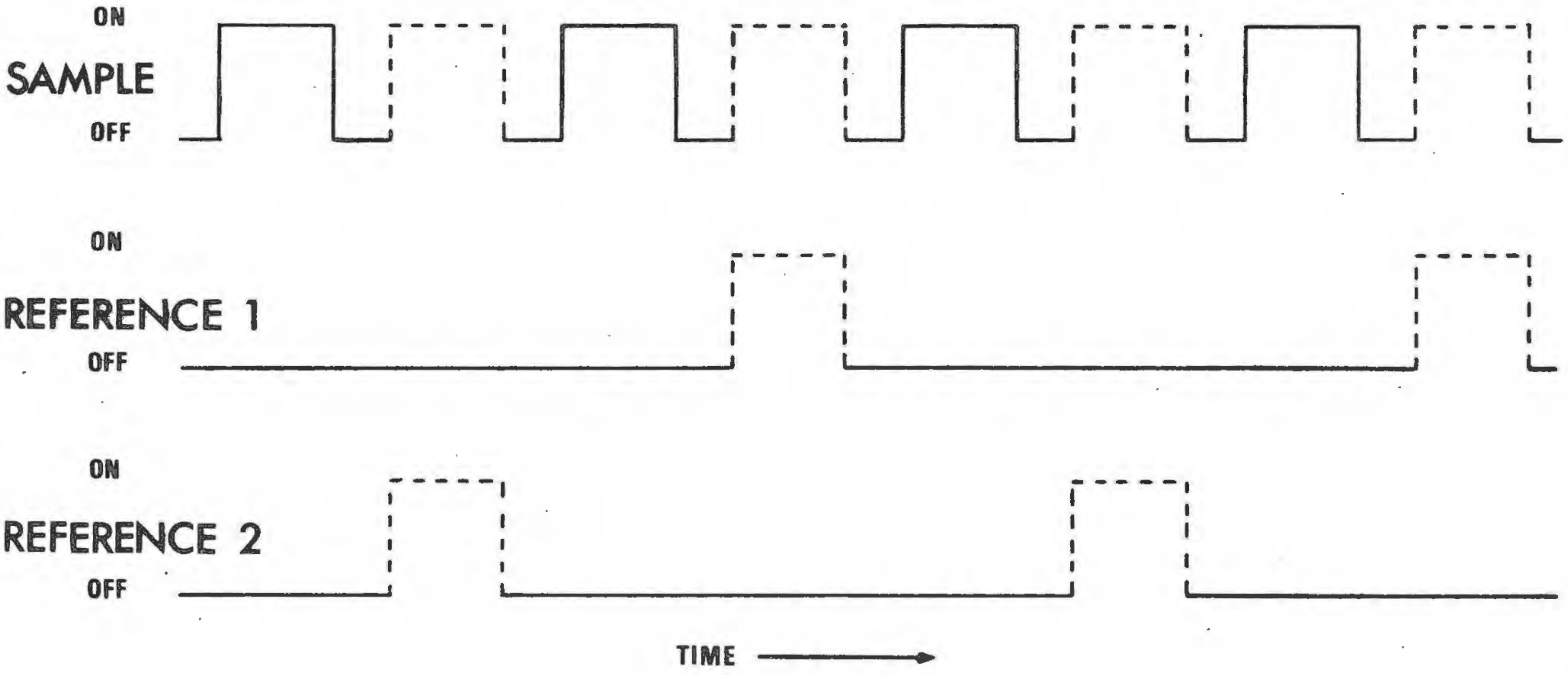


FIGURE 3.5

Diagrammatic representation of the switching sequence of the sample and reference voltages of the data acquisition system.

each discretely measured point. Similarly, all measured voltages are referred to the voltages on the horizontal portion of the time domain signal and are thus corrected for any "vertical" voltage drift occuring in the course of the experiment.

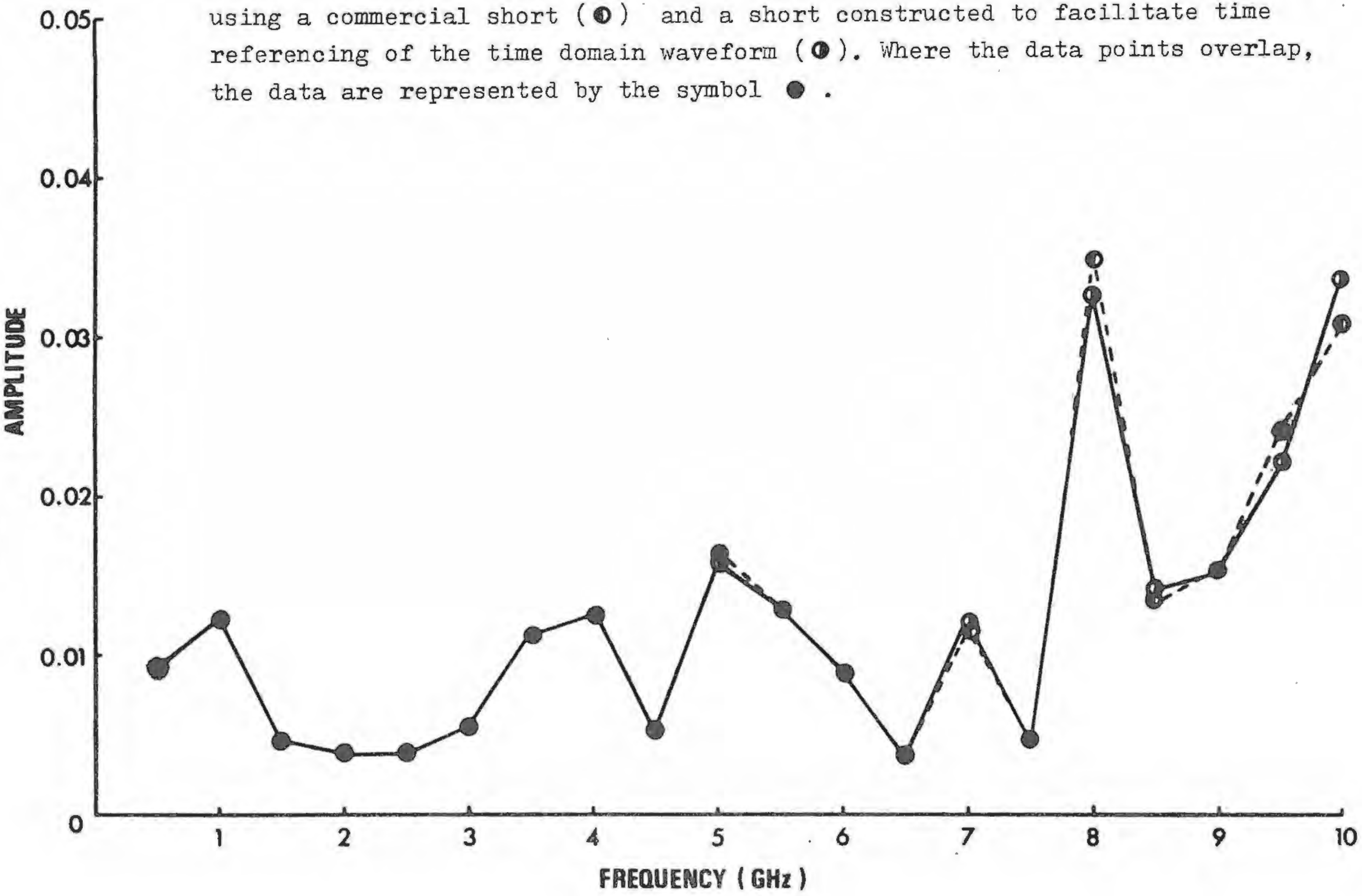
3.3.3. Time Referencing of the Waveform.

The need for relative time referencing of the traces from the incident and reflected signals has been noted in sub-section 2.2.1. To reduce the problems involved, a short was constructed such that the position of the discontinuity with respect to the external connecting bead matched that of the air/dielectric interface when the sample cell was in position. The properties of this short and of a commercial short, when compared in the frequency domain, were found to be closely similar; this is illustrated in Figure 3.6.

Time reference points for the time domain signals were measured by performing a computer calculation of the gradients of the horizontal and most steeply sloping sections of the trace. The time corresponding to the intersection of these gradients was used as the time reference point and all discrete, sampled voltages were referred to this point. No systematic error in this reference point could be seen from the Cole-Cole plots of the complex permittivities obtained, as contrasted with the error which has been noted when the inflection point on the time domain waveform was used as the time reference point (Suggett, 1974b).

FIGURE 3.6

Comparison in the frequency domain of the incident signal spectra obtained using a commercial short (◐) and a short constructed to facilitate time referencing of the time domain waveform (◑). Where the data points overlap, the data are represented by the symbol ● .



CHAPTER 4

EXPERIMENTAL RESULTS

Section 4.1 Static Permittivity, Infrared and NMR Studies

4.1.1. Calculation of the Apparent Dipole Moment

The measured static permittivities and densities of the solutions studied are listed in Tables A: 1-17 of the Appendix.

From these data, the apparent dipole moments of the solutions were calculated using a generalised form of the Kirkwood-Fröhlich equation which, for the case of a dipolar material in a non-polar solvent, may be written:

$$\mu_{app}^2 = g\mu_g^2 = \frac{9kT}{4\pi L} \cdot \frac{M_2}{\rho w_2} \cdot \frac{(\varepsilon-\varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} , \qquad 4.i$$

where k, L and T are the Boltzmann constant, Avogadro's number and absolute temperature respectively; M, ρ and w refer to the molecular mass, density and mass fraction respectively and subscript 2 refers to the solute. ε_∞ is the limiting high frequency permittivity of the solution, and, from Maxwell's relation, is often taken as n^2, n being the refractive index at such a frequency that the orientation polarisation contributes nothing to the permittivity while electronic and atomic polarisations each make their full contribution. As has been discussed, the correlation factor, g, in relating the gas phase dipole moment squared, μ_g^2, to the experimentally determined value for μ_{app}^2, provides information on the association of solute molecules. This form of the Kirkwood-Fröhlich equation is actually a special case of an Onsager- based equation (Böttcher, 1973b) when the permittivity of the solute and solvent are the same. We have found, however, that the relative shapes of the curves representing the concentration dependence of the dipole moment squared, when calculated using either equation, cannot be distinguished while there is only a minor difference in the magnitudes of the dipole moments so calculated. In view of the scatter in the experimental data, these differences appear not to be significant and either equation may be used.

The choice of a value for ε_∞ presents a problem since substituting the value of ε_∞ given by Maxwell's relation using the refractive index at the Na_D - line, n_D, into the above equation gives values of g which are quite meaningless. In fact, it is generally found that the calculated value of g is very sensitive to the value assumed for the refractive index (Hill, 1969b). It has often been noted that $\varepsilon_\infty \neq n_D^2$, but the difference, which arises from atomic polarisation and Poley absorptions, can only be estimated. Therefore, since the subsequent analysis of the data demands a consistent treatment for ε_∞ to allow meaningful comparisons among the g values for the alcohol solutions studied, an approximation for the above contributions was allowed for by considering $\varepsilon_\infty = m.\, n_D^2$. Following Dannhauser (1968a), a value of 1.05 for m was selected and the following procedure applied consistently. The specific refraction:

$$R_i = (m_i . n_i^2 - 1)/[(m_i . n_i^2 + 2)\rho_i] \qquad 4.ii$$

is, to a good approximation an additive quantity (Böttcher, 1952). Therefore, for a solution, the following relation may be written:

$$R = w_1 R_1 + w_2 R_2 \quad . \qquad 4.iii$$

As described, n_2^2 for the alcohols studied, was taken to be $1.05\, n_D^2$ while, for the solvents, n_1^2 was taken as the intercept, at infinite dilution, obtained from a least squares fit to the low concentration permittivity data.

4.1.2. Study of 1-Octanol Solutions.

The study was initiated by investigating the association behaviour of 1-octanol solutions. Figure 4.1 shows the concentration dependence of μ^2_{app} for 1-octanol in hexane, cyclohexane, carbon tetrachloride and benzene solutions with a logarithmic scale along the abscissa, which allows the interesting behaviour of μ^2_{app} to be presented over the whole concentration range. Although the use of a logarithmic scale on the abscissa distorts the curves, the maxima and minima are not shifted and the various regions of interest are consequently accurately defined. The molar (rather than mole fraction) concentration scale is used to facilitate comparison of different molecular mass materials at similar molecular concentrations.

From the curves, it can be noted that, as the solute/solvent interactions increase on going from cyclohexane to carbon tetrachloride to benzene (Huyskens, Henry and Gillerot, 1962), the maximum in μ^2_{app}, seen at low concentrations when solutions in carbon tetrachloride are examined, shifts to higher concentration when benzene is used as the solvent. The minimum in μ^2_{app}, observed at higher concentration, becomes less pronounced as the solute/solvent interaction increases. The similarity between the concentration dependencies of μ^2_{app}, when solutions in cyclohexane and in n-hexane are examined, is evident. Attention will be focussed on the association behaviour of solutions in cyclohexane and the data for solutions in n-hexane will not be further analysed.

Infrared spectra, recorded at the concentrations indicated by the arrows in Figure 4.1, are depicted in Figure 4.2. These spectra lie in the fundamental -OH stretching region.

FIGURE 4.1

μ^2_{app} versus the logarithm of molar solute concentration for 1-octanol in hexane (●), cyclohexane (○), carbon tetrachloride (◐) and benzene (◑) solutions at 25°C. The curves drawn through the data points are not mathematical fits. Curves (ii) and (iii) are each displaced upward from the one below by 0.5D^2. The value of μ^2 (in D^2) for pure 1-octanol is given in parentheses. The arrows indicate the concentrations at which the infrared spectra in Figure 4.2 were recorded.

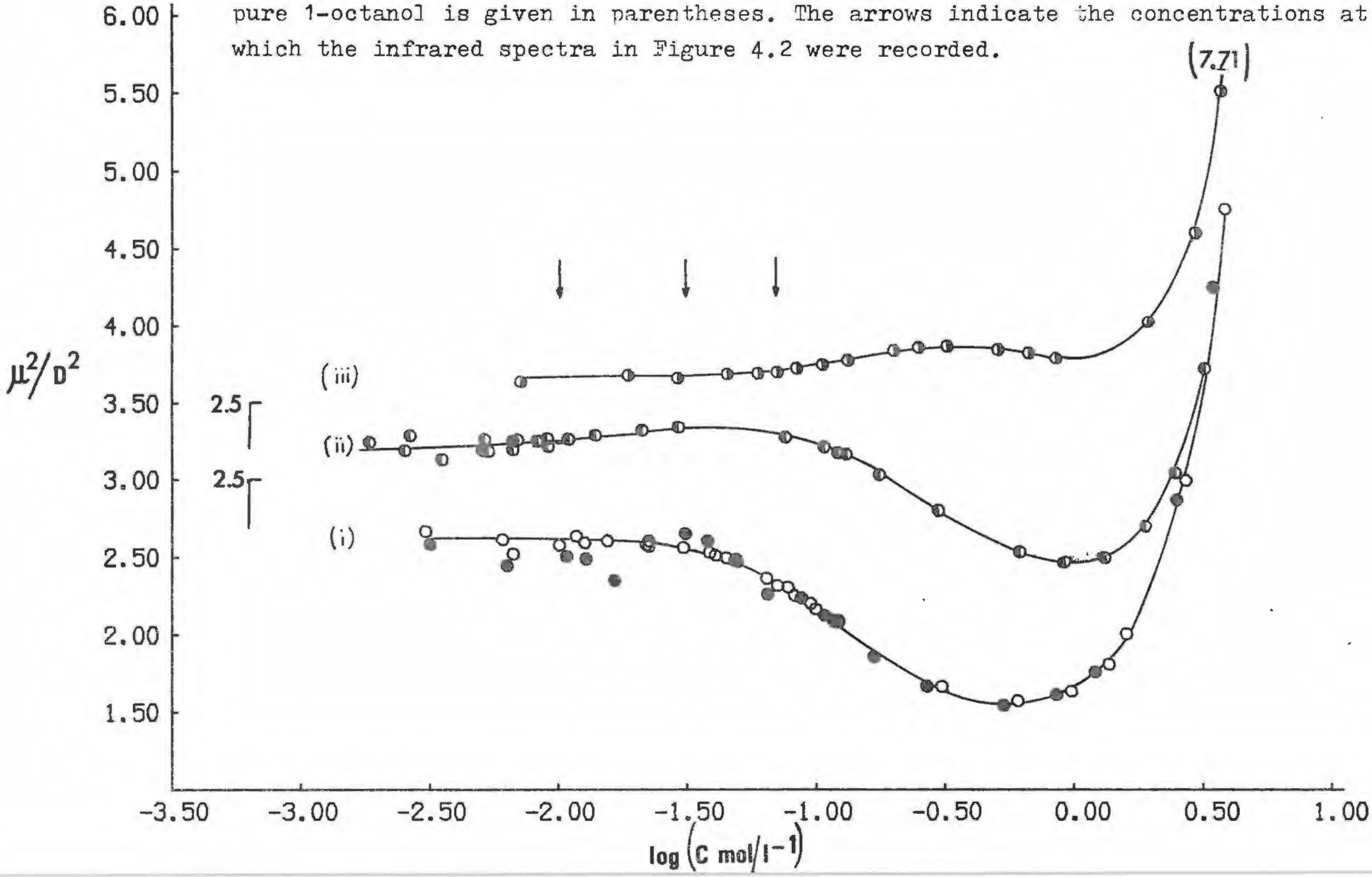
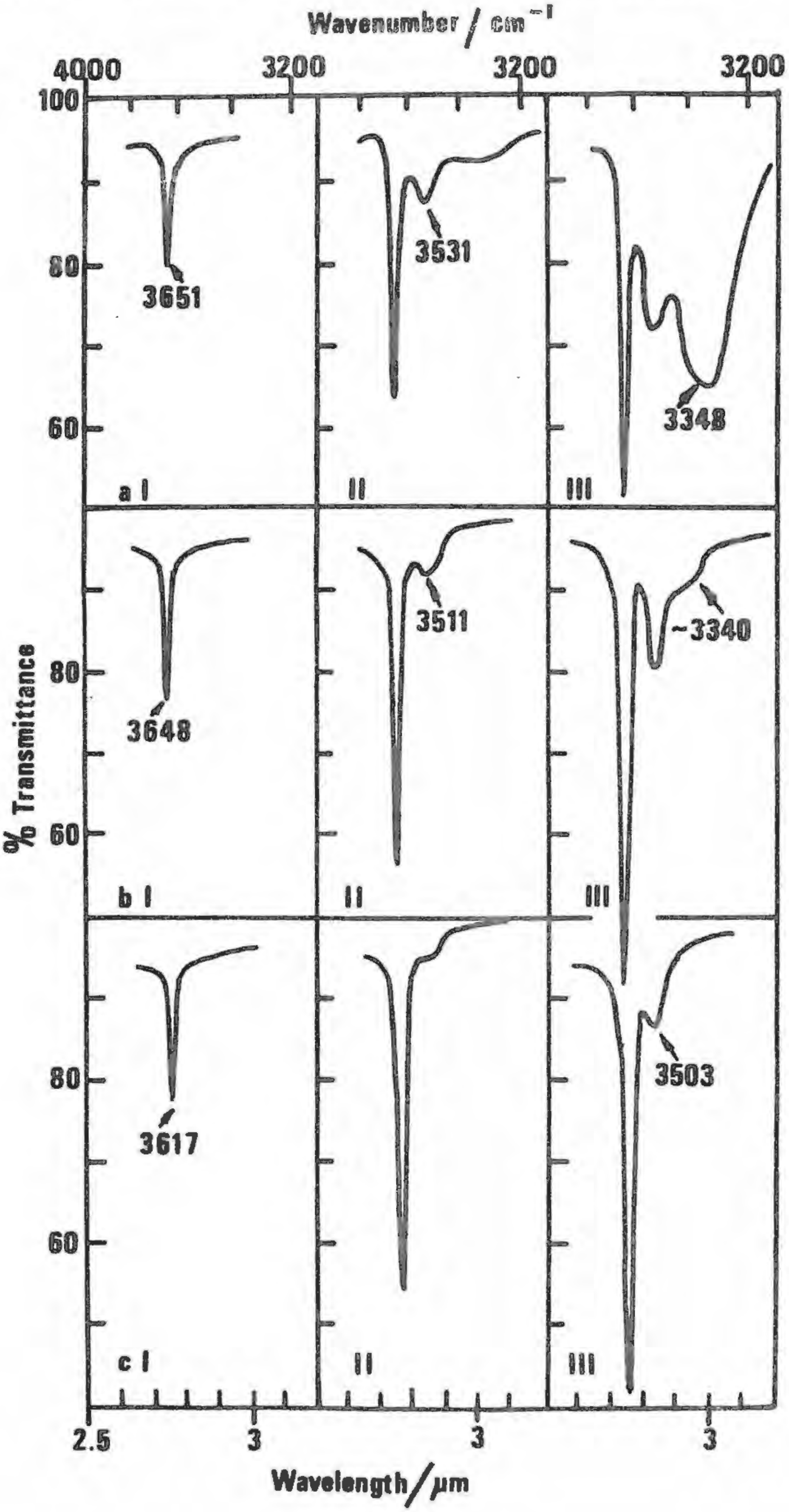


FIGURE 4.2

Infrared spectra at 25°C of 1- octanol solutions in a) cyclohexane, b) carbon tetrachloride and c) benzene at concentrations (I) 0.0107 mol l^{-1}, (II) 0.0339 mol l^{-1} and (III) 0.0650 mol l^{-1}, using a 1mm sample cell.



4.1.3. Study of 2-, 3- and 4- Octanol Solutions

The concentration dependencies of μ^2_{app} for the straight-chain, isomeric octanols in carbon tetrachloride, cyclohexane and benzene solutions are shown in Figures 4.3, 4 and 5 respectively. The solid line through the low concentration data, shown in Figure 4.3, represents a least squares fit for an equilibrium model which will be discussed in the subsequent chapter. The broken lines at the higher concentrations simply follow the trend through the data points. In Figures 4.4 and 5, the data points are joined by curves which are not mathematical fits.

The influence of the solvent on the concentration dependence of μ^2_{app}, noted for 1-octanol solutions, is maintained for each of the octanols studied : a pronounced maximum in μ^2_{app} is not observed for alcohol solutions in cyclohexane, but does appear for solutions in carbon tetrachloride and, at higher concentrations, for solutions in benzene. Similarly the minima in μ^2_{app} observed at the higher concentrations become more pronounced on going from cyclohexane to carbon tetrachloride to benzene as solvent. The depth of the minimum observed for any alcohol/solvent system is also influenced by the steric environment of the alcohol -OH group : whereas there is little change in the height of the maxima, observed at low concentrations, as the hydroxyl group is moved towards the centre of the alkyl chain and becomes sterically more hindered (from 1- to 4-octanol), the minima become more pronounced. The value of μ^2_{app} for the pure alcohol is also observed to decrease on going from 1-octanol to 4-octanol.

The arrows in Figures 4.3-5 indicate the concentration (0.065 mol ℓ^{-1}) at which the infrared spectra, shown in Figure 4.6,

FIGURE 4.3

μ^2_{app} versus the logarithm of molar solute concentration for (i) 1-octanol, (ii) 2-octanol, (iii) 3-octanol and (iv) 4-octanol solutions in carbon tetrachloride at 25°C. The solid lines at low concentrations represent the least-squares fits for 1-2-3 models; the broken lines follow the trends through the data points which were not included in the least-squares fits. Curves (ii), (iii) and (iv) are each displaced downwards from the one above by $0.25D^2$. Values of μ^2 (in D^2) for the pure solutes are given in parentheses. The arrow indicates the concentration at which the infrared spectra in Figure 4.6 were recorded.

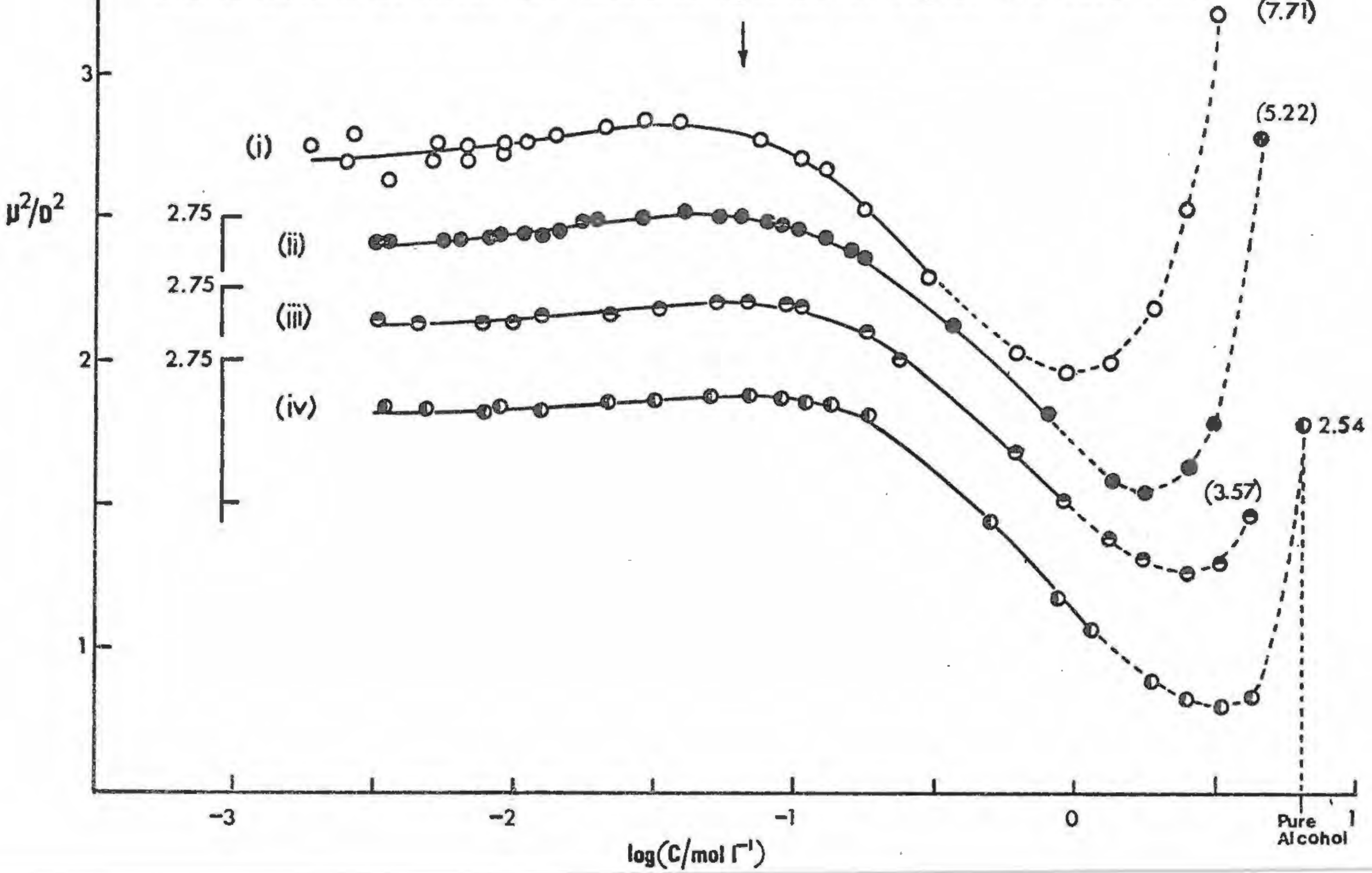


FIGURE 4.4

μ^2_{app} versus the logarithm of solute concentration for 1-, 2-, 3- and 4-octanol solutions in cyclohexane at 25°C. The curves drawn through the data points are not mathematical fits. The arrow indicates the concentration at which the spectra in Figure 4.6 were recorded.

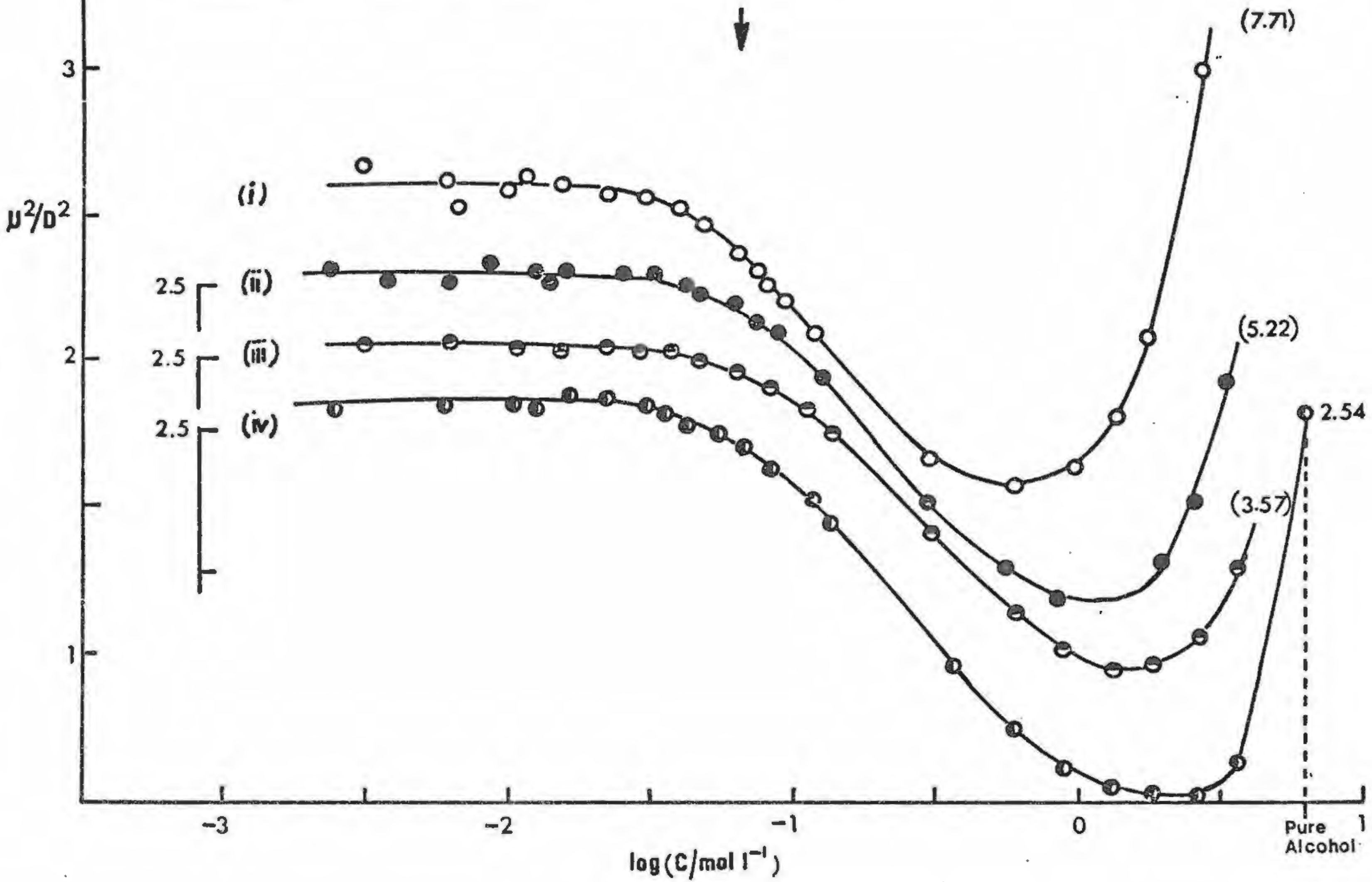


FIGURE 4.5

μ^2_{app} versus the logarithm of solute concentration for 1-, 2-, 3- and 4-octanol solutions in benzene at 25°C. The curves drawn through the data points are not mathematical fits. The arrow indicates the concentration at which the spectra in Figure 4.6 were recorded.

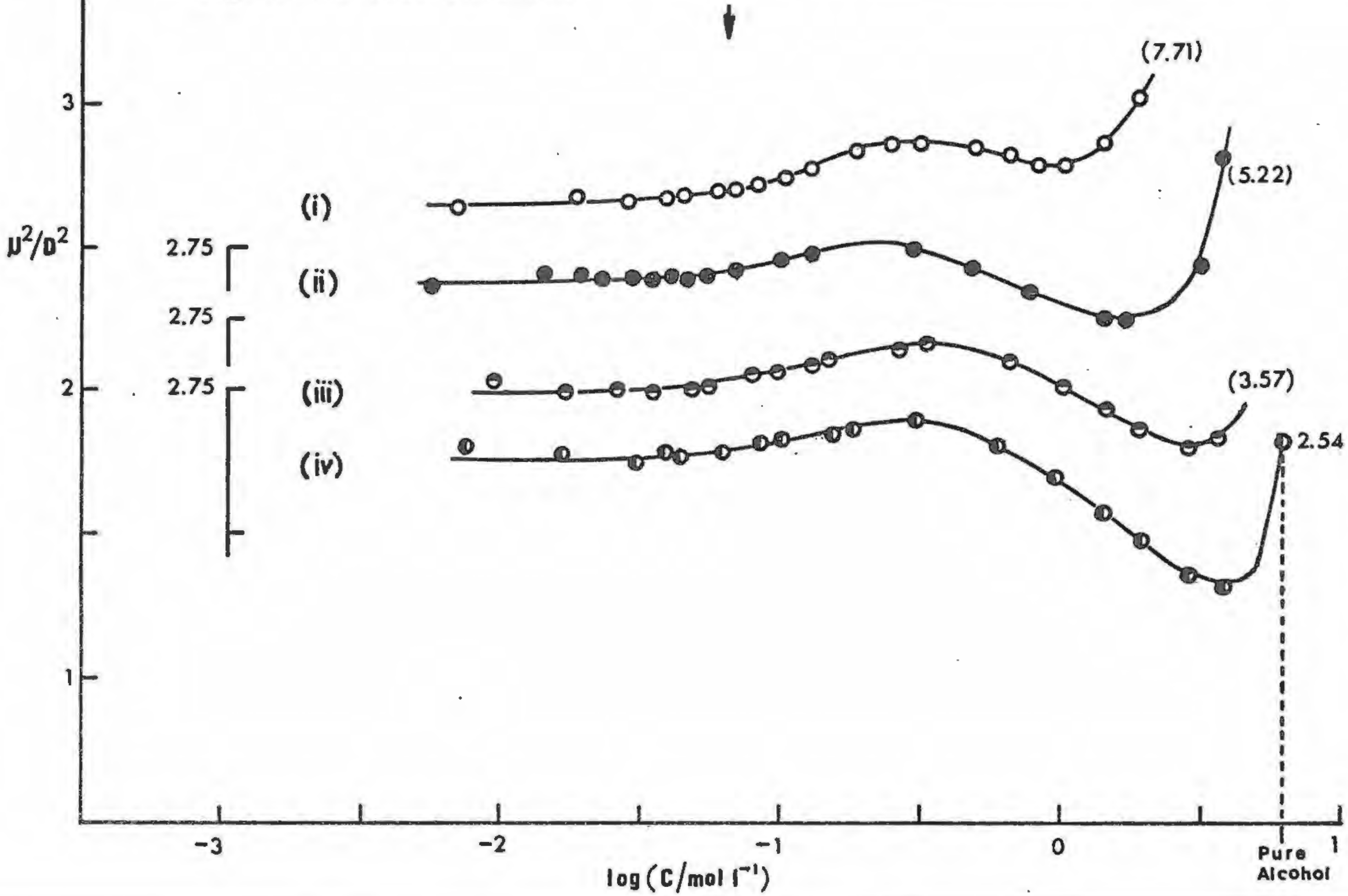
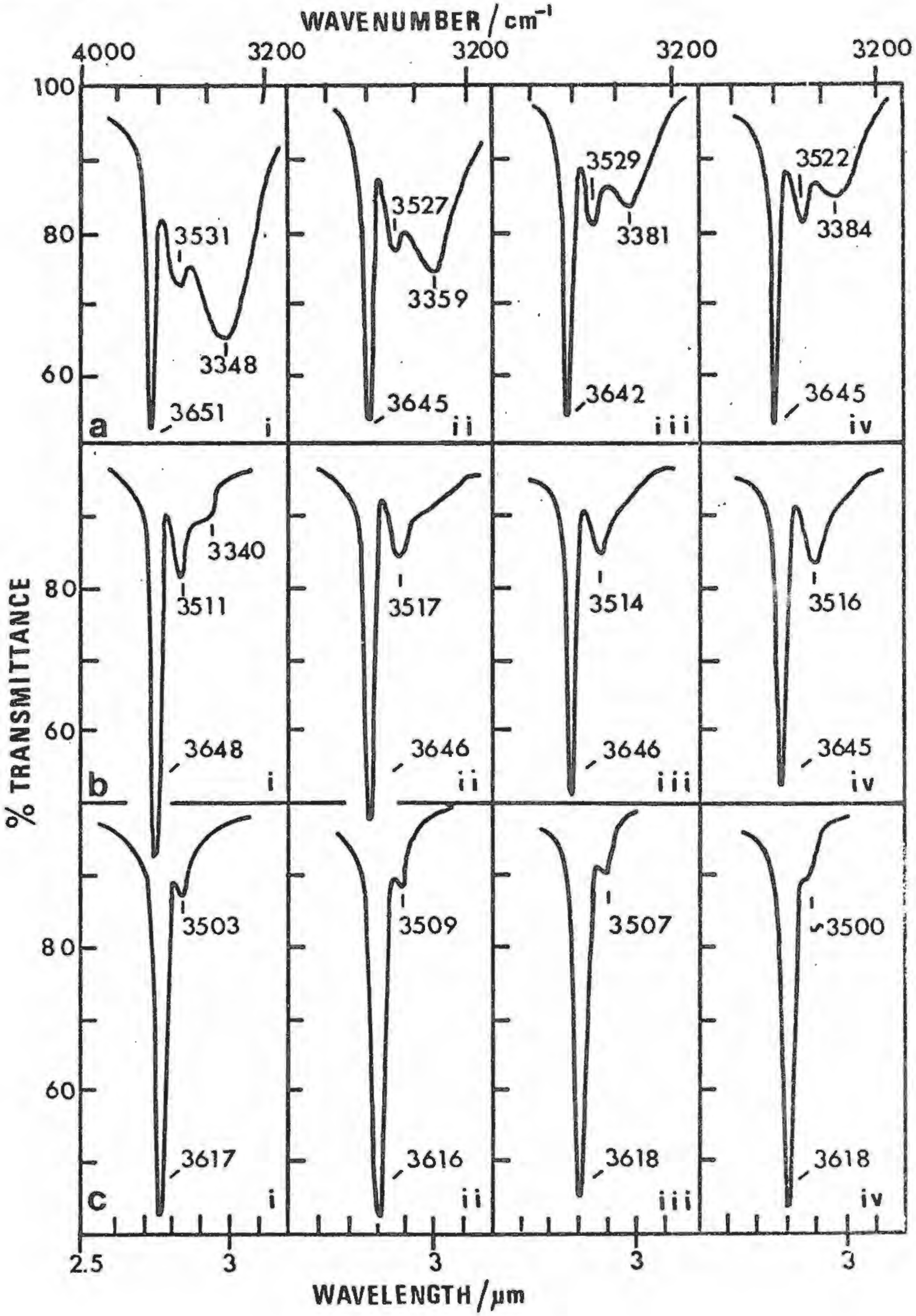


FIGURE 4.6

Infrared spectra at 25°C of (i) 1-octanol, (ii) 2-octanol, (iii) 3-octanol and (iv) 4-octanol solutions in (a) cyclohexane, (b) carbon tetrachloride and (c) benzene, all at 0.0650 mol l^{-1}, using a 1mm sample cell.



were recorded. As before, these spectra lie in the fundamental -OH stretching region. Infrared spectra were also recorded at the other, lower concentrations for which spectra were recorded for 1-octanol solutions (Figure 4.2.), but are not illustrated here because the information provided is parallelled by that of Figure 4.2.

4.1.4 Study of 2,3,4-Trimethyl-3-Pentanol Solutions

The interesting trends observed in the concentration dependence of μ^2_{app} on changing the steric environment of the -OH group in the alkyl chain suggested that it would be rewarding to investigate similarly an alcohol in which the -OH group experiences a very restricted environment. Accordingly, the concentration dependence of μ^2_{app} for 2,3,4-trimethyl-3-pentanol (2,3,4-TMP) was studied in each of the above three solvents and is shown in Figure 4.7. Infrared spectra were recorded at the concentrations indicated by the arrows drawn in Figure 4.7 and are illustrated in Figure 4.8., while the concentration dependence of the NMR chemical shift of the hydroxyl group proton of this alcohol in carbon tetrachloride solutions is shown in Figure 4.9. In view of the monotonic change observed in the chemical shift of the -OH proton, it was felt that little extra definitive information beyond that observed from an analysis of the concentration dependencies of μ^2_{app} for the various alcohol/solvent systems could be obtained; therefore NMR studies were restricted to this single system.

The most striking difference between the curves relating the change in μ^2_{app} to concentration for 2,3,4-TMP and for the other alcohols studied is that no rise in μ^2_{app} is observed at high alcohol concentrations for solutions of the former alcohol :

FIGURE 4.7

μ^2_{app} versus the logarithm of molar solute concentration for 2,3,4-trimethyl-3-pentanol solutions in (i) cyclohexane, (ii) carbon tetrachloride and (iii) benzene at 25°C. The lines through the data points represent the best least-squares fits: 1-2-3 model for cyclohexane solutions and 1-2-4 model for carbon tetrachloride and benzene solutions. Curves (ii) and (iii) are each displaced upwards from the one below by $0.5D^2$. The arrows indicate the concentrations at which the infrared spectra in Figure 4.8 were recorded.

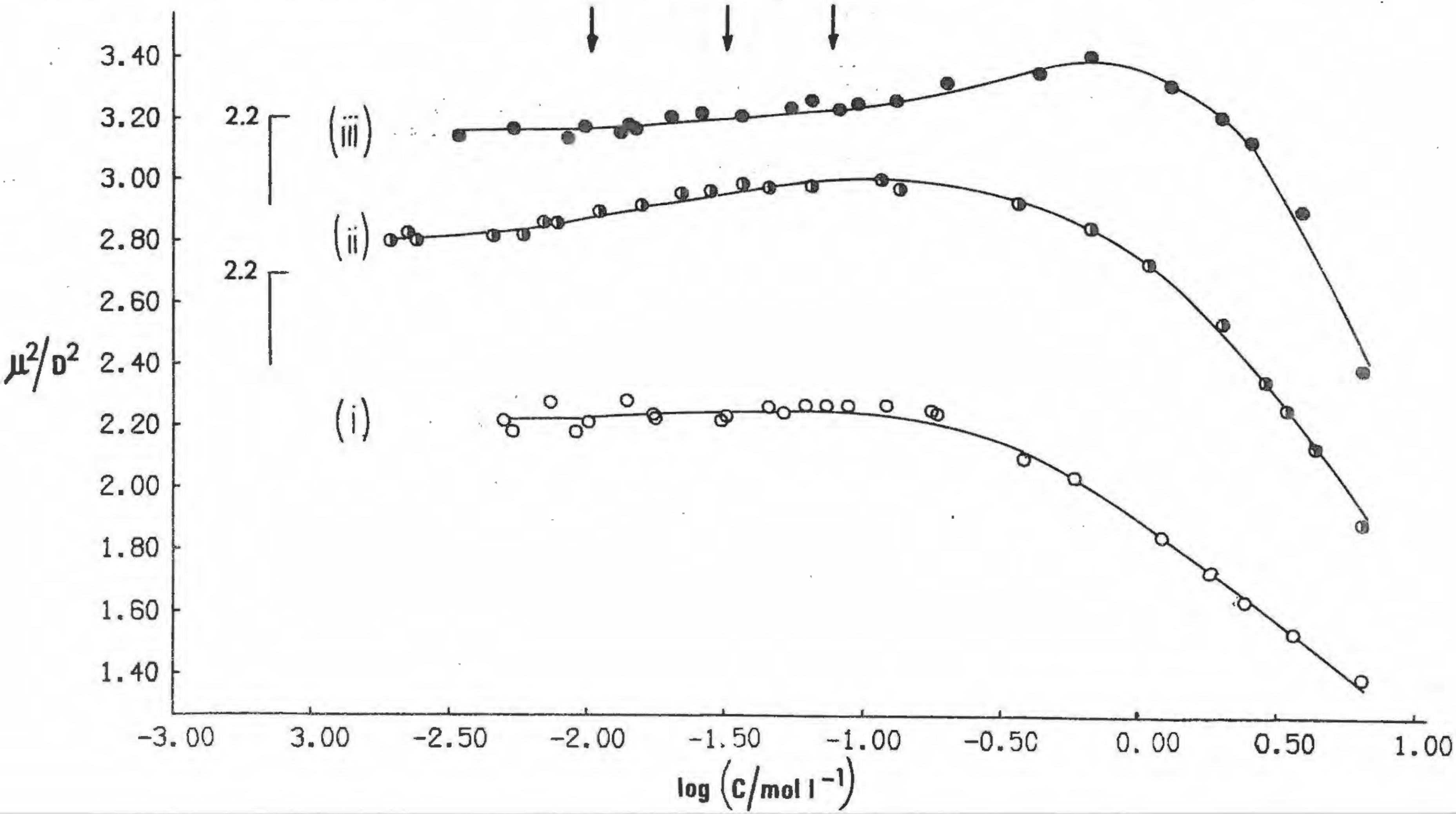


FIGURE 4.8

Infrared spectra at 25°C of 2,3,4-trimethyl-3-pentanol solutions in (a) cyclohexane, (b) carbon tetrachloride and (c) benzene at concentrations (I) 0.0107 mol l^{-1}, (II) 0.0339 mol l^{-1} and (III) 0.0650 mol l^{-1}, using a 1mm sample cell.

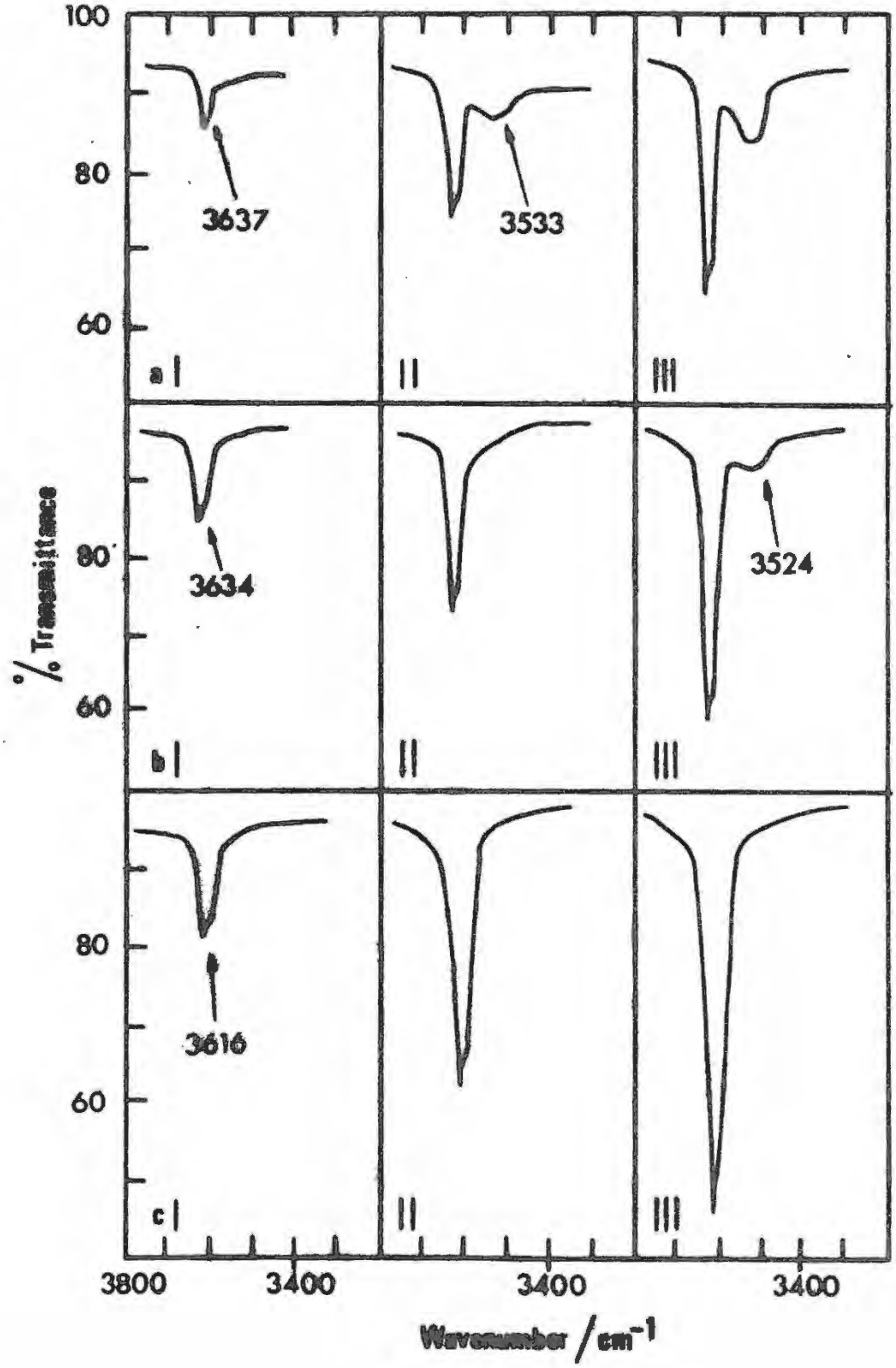
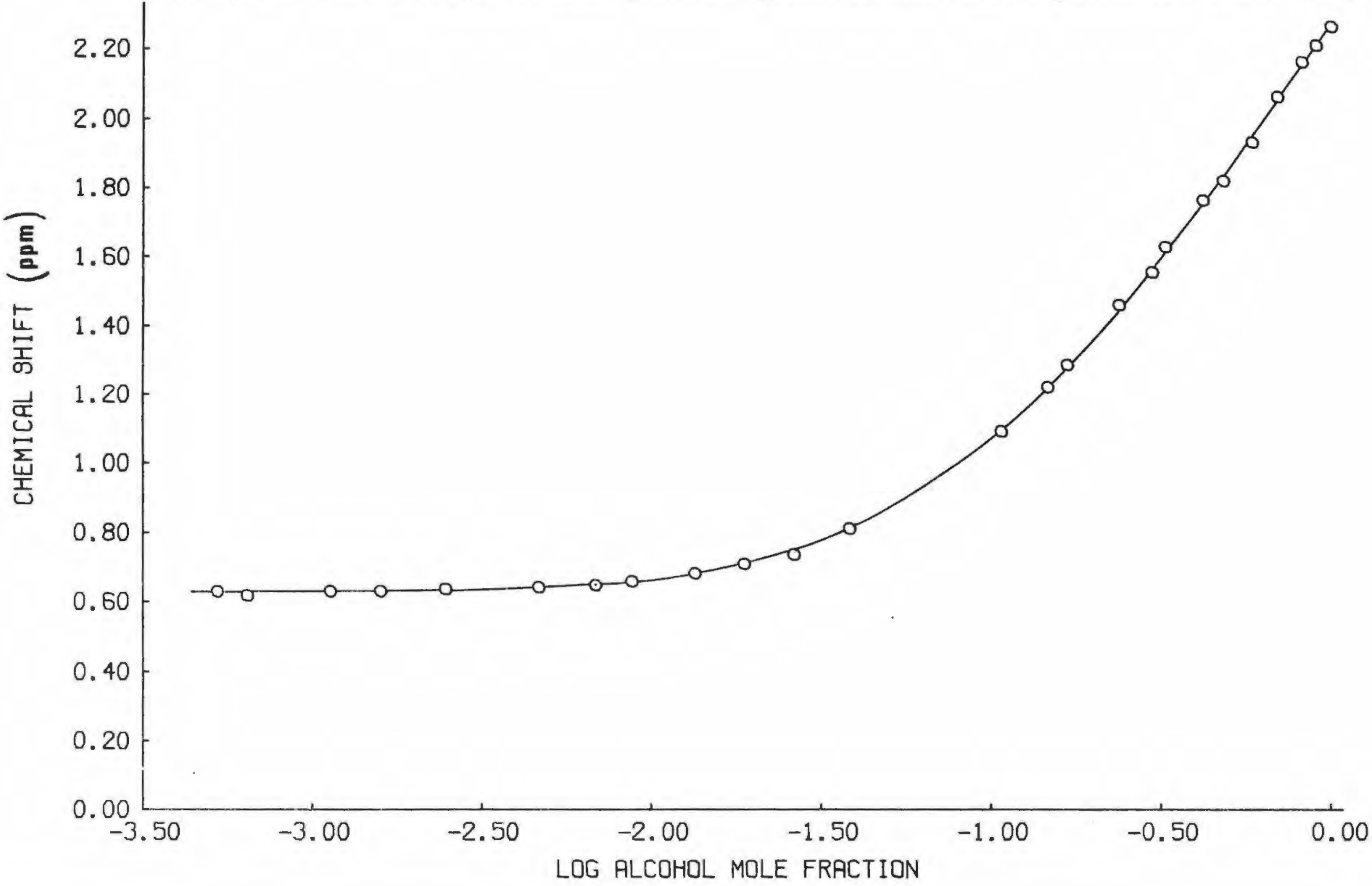


FIGURE 4.9

Proton magnetic resonance chemical shifts versus the logarithm of solute mole fraction for the hydroxyl proton of 2,3,4-trimethyl-3-pentanol in carbon tetrachloride solution at 35°. The line through the data points represents the least-squares fit for a 1-2-3 model.



instead μ^2_{app} decreases continuously, after the maximum at low concentration, without passing through a further turning point.

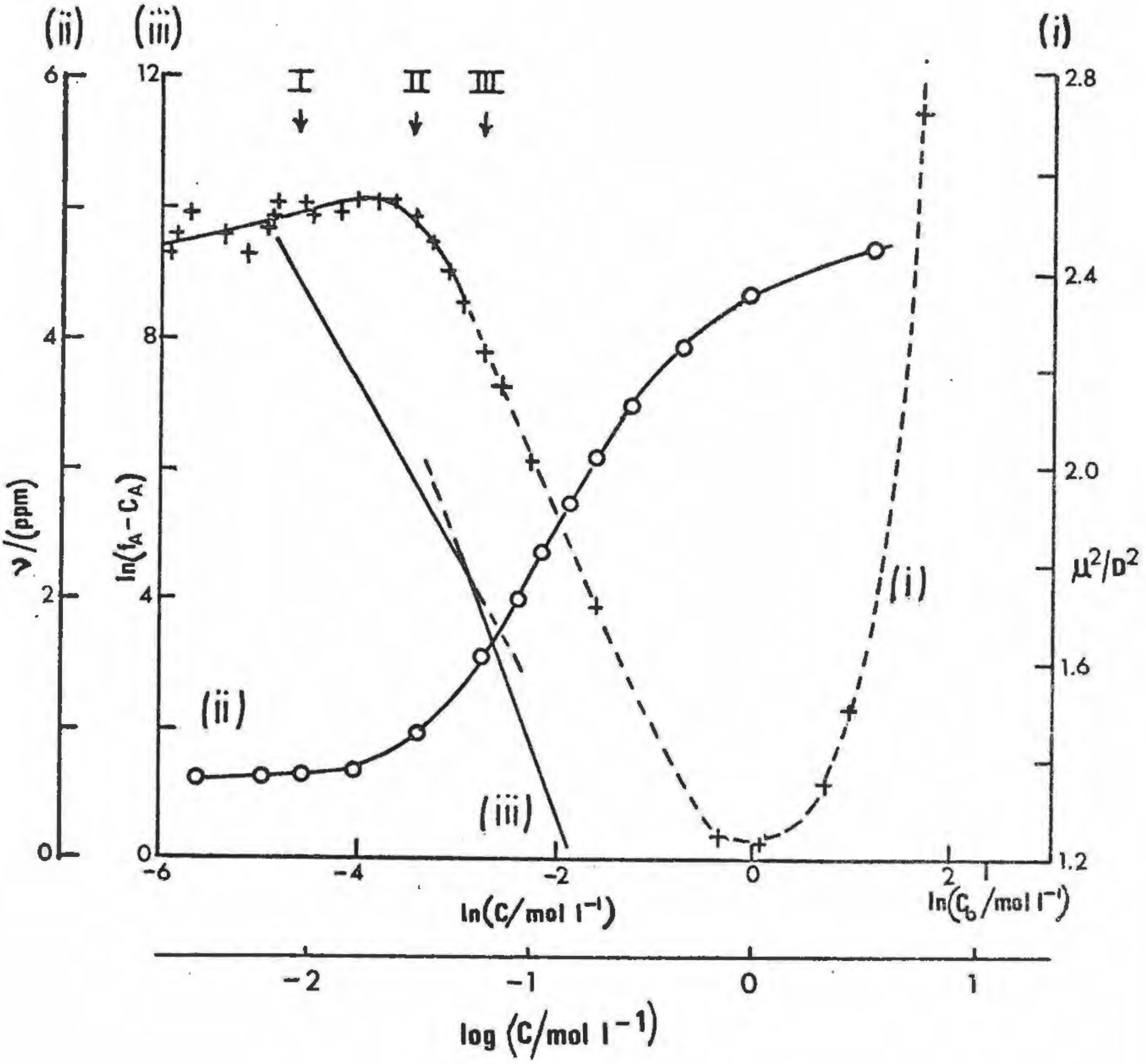
4.1.5. Study of t-Butanol in Hexadecane Solutions.

The highly structured curves obtained from the permittivity studies facilitate an explanation of the association behaviour of alcohol solutions. As has been discussed in Chapter 1, hydrogen bonded species which are not permanent entities, but rather have a certain stability so that they can be considered to have finite lifetimes, influence the physical properties of alcohol solutions. It is possible to associate features of the above curves with physical properties of the postulated oligomers, in particular the alignment of dipoles within these species. However, the alcohols described, to this point, have all been octanols which would restrict any conclusions from this study; consequently it was attractive to extend the investigation to include solutions of other alcohols. A particularly attractive system is t-butanol with hexadecane as solvent. Tucker and Becker (1973) recently completed an extensive investigation of the association behaviour of this system and it was thought that application of the experimental techniques described in this study could meaningfully extend understanding of this system. It was also hoped that the results obtained could be correlated with those obtained for the octanols studied.

For these reasons, an investigation of the association of t-butanol in hexadecane was undertaken. In Figure 4.10, a composite graph compares results obtained from a permittivity study with NMR and vapour pressure results obtained by Tucker and Becker on the same system. Curve (i) shows the concentration dependence of μ^2_{app} against both the natural logarithm and the common logarithm of

FIGURE 4.10

Concentration dependence (using both the natural and common logarithm of solute concentration) of three physical properties of t-butanol in hexadecane solutions: (i) experimentally determined values of μ^2_{app} at 25°C; the continuous line is the best least-squares fit assuming a 1-2-3 model, while the broken line joins the experimental points not involved in the fit; (ii) chemical shift of proton resonance relative to TMS at 220MHz and 21°C (Tucker and Becker, 1973); (iii) logarithm of the difference between formal alcohol concentration and monomer concentration at 30°C from vapour measurements (Tucker and Becker, 1973). The arrows indicate the concentrations at which the infrared spectra in Figure 4.11 were recorded.



concentration, while curves (ii) and (iii) depict results derived from Tucker and Becker's NMR chemical shift and vapour pressure studies respectively. The features of curve (i), which occur at roughly the same concentration for curves (ii) and (iii), are also similar to those found in Figures 4. 3-5 : there is an initial maximum in μ^2_{app} followed, at higher concentrations, by a minimum with the curve finally rising continuously to the value of μ^2_{app} for the pure, liquid alcohol.

The arrows in Figure 4.10 indicate the concentration at which the infrared spectra, shown in Figure 4.11, were recorded. Spectra were recorded for t-butanol solutions in carbon tetrachloride as well as hexadecane to facilitate interpretation of the association behaviour. As before, these spectra lie in the fundamental -OH stretching region.

4.2. Numerical Analysis of Simple Association Models.

Introduction.

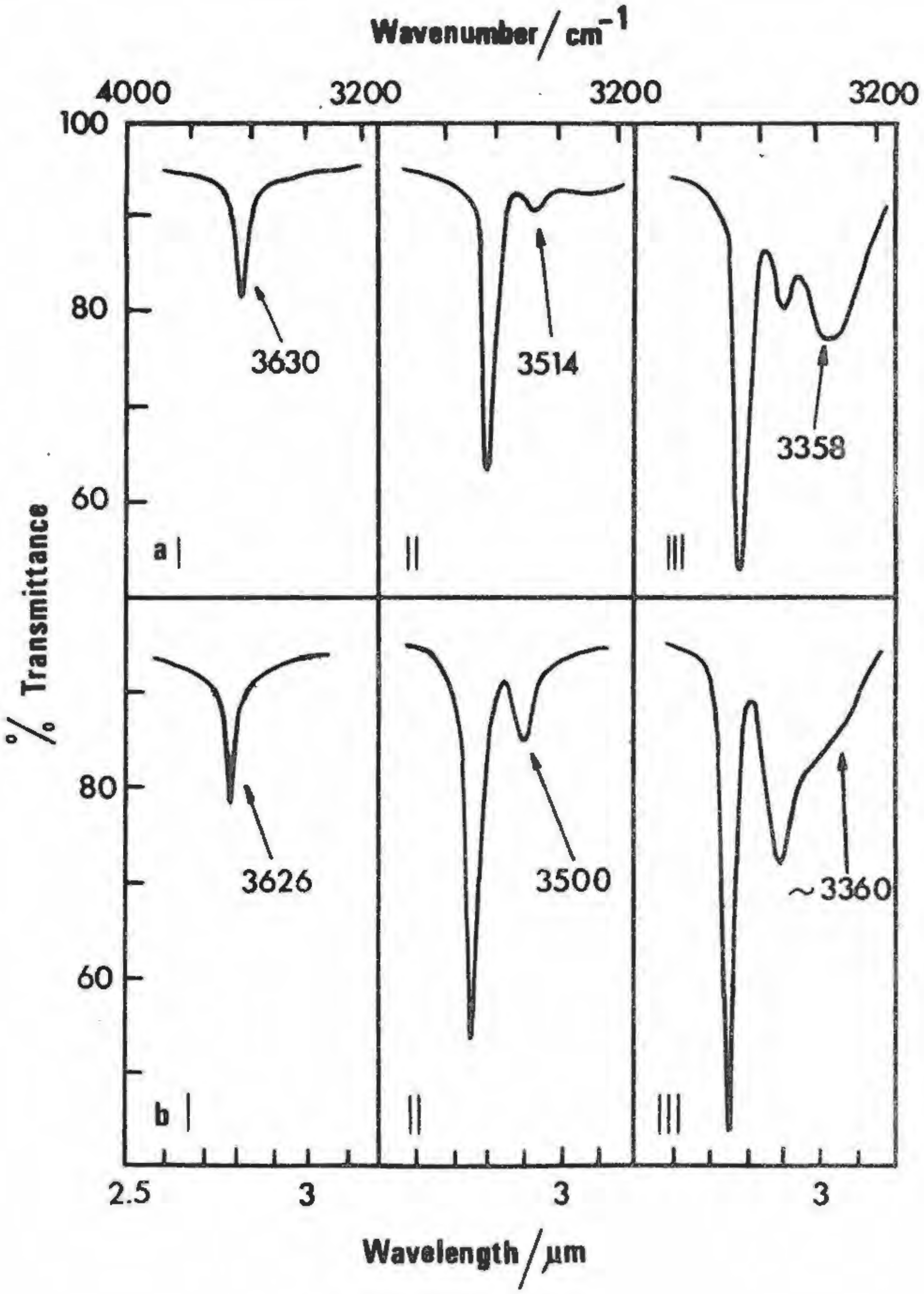
It has been noted that the distinct regions, observed in the concentration dependence of μ^2_{app} for the alcohol solutions studied, may be associated with the presence of discrete, hydrogen bonded oligomers in solution. While a qualitative understanding of the characteristics of these species may be obtained by correlating the data obtained from permittivity and infrared studies, it is also valuable to attempt to obtain a quantitative measure of their dipole moments and the equilibrium constants for their formation.

4.2.1. Some Fundamental Equations.

If we consider an equilibrium between alcohol monomer molecules and an associated species formed from i alcohol molecules, we may

FIGURE 4.11

Infrared spectra at 25°C of t-butanol solutions in (a) cyclohexane and (b) carbon tetrachloride at concentrations (I) 0.0107 mol l^{-1}, (II) 0.0339 mol l^{-1} and (III) 0.0650 mol l^{-1}, using a 1mm sample cell.



write

i (monomer) → "i-mer".

Assuming ideal association, the concentration of the i^{th} species, c_i, may be related to the concentration of monomer molecules, c_1, by a corresponding equilibrium constant K_i :

$$c_i = K_i \cdot (c_1)^i \quad . \qquad 4.iv$$

From the mass balance, the formal concentration of alcohol, c, may be described:

$$c = \sum_i i\ c_i = \sum_i i.K_i(c_1)^i \quad . \qquad 4.v$$

The experimentally determined dipole moment squared can be calculated as an average over all types of multimers present (Huyskens and Cracco, 1960) :

$$c\mu^2_{app} = \sum_i c_i\mu_i^2 = \sum_i c_i g_i \mu_1^2 \quad . \qquad 4.vi$$

By combination of equations 4.v and vi, a generally applicable equation follows (Bordewijk <u>et al</u>., 1973):

$$\mu^2_{app} = \frac{1}{c}\left[\sum_i iK_i(c_1)^i g_i \mu_1^2\right] . \qquad 4.vii$$

Two different curve-fitting techniques were utilised to optimise the values of K_i and μ_i such that a minimum sum of squares of errors between the experimental and fitted values of μ^2_{app} results. Initially, this optimisation was achieved by application of a simplex least squares procedure, described by Deming and Morgan (1973); however, the more efficient Newton-Raphson iterative procedure was subsequently applied. The Newton-Raphson procedure was also applied to the NMR data discussed in sub-section 4.1.4. The algorithm used to evaluate the second procedure has been described by Pitha and Jones (1966), having originally been developed by Meiron (1965).

4.2.2. Simplex Procedure.

Of the methods available to optimise parameters, the sequential simplex method and its modifications are probably the most simple both to understand and apply. To optimise n parameters, the objective is to force the simplex, which is an n-dimensional geometric figure, defined by n + 1 points, (e.g. a simplex in two dimensions is a triangle) to the region of optimum response which, for the purpose of this study, is the minimum in the sum of squares of errors between the observed dipole moment and that calculated from equations 4.v and vii. The movement of the simplex is governed by the so-called "rules" of simplex procedure (Deming and Morgan, 1973).

4.2.3. Newton-Raphson Procedure

The application of the Newton-Raphson procedure is conceptually more difficult. In general, the vector, X, defines the variables to be optimised; considering N variables

$$X = X_1, X_2, - - - - - X_N \quad . \qquad 4.\text{viii}$$

Values obtained from the mth iteration are modified in the next iteration by application of a correction vector:

$$X_{m+1} = X_m - (B_m + p.\ C_m)^{-1}\ G_m, \qquad 4.\text{ix}$$

where G and X are vectors, B and C are matrices and p is a scalar quantity; $(B_m + p.C_m)^{-1}\ G_m$ is a vector. The quantities B, C, G and p are defined below.

For each of the M data points, we obtain

$$f_i = I_i(\text{obs}) - I_i(\text{calc}) \quad , \qquad 4.\text{x}$$

from which is calculated the error function:

$$\phi = \sum_{i=1}^{M} f_i^2 \quad . \qquad 4.xi$$

From the partial derivative of the error, f_i, with respect to the variable to be optimised, an $M \times N$ matrix, A, is obtained such that

$$A_{jk} = \partial f_j / \partial X_k \quad . \qquad 4.xii$$

B, an $N \times N$ matrix, is determined from the operation:

$$B = A^T . A \quad , \qquad 4.xiii$$

where A^T is the transpose of matrix A. C, also an $N \times N$ matrix, is obtained from B by setting the off-diagenal terms of matrix B to zero. G is obtained as a vector of N elements by the operation:

$$G = A^T . f \quad . \qquad 4.xiv$$

The value used for p controls the efficiency with which the procedure converges and a method of determining p has been given by Pitha and Jones (1966). The program used to implement these procedures is given in part C of the appendix. By making suitable adjustments to the relevant subroutines, one can use this program, which was developed by Dr. G. Brink, to provide equilibrium parameters for any desired association model.

4.2.4. Calculation of Goodness of Fit and Uncertainty in Estimated Parameters.

The overall goodness of fit is given by the standard deviation

$$S = \sqrt{\frac{(Iobs - Icalc)^2}{M - N}} \quad .$$

The standard deviation of each estimated parameter, S_i, may be written (Bennett and Franklin, 1954) :

$$S_i = S \cdot \sqrt{\frac{|\det B_{ii}|}{|\det B|}} ,$$

where $|\det B|$ is the determinant of matrix B and $|\det B_{ii}|$ is the determinant of matrix B omitting row i and column i. The uncertainties (± values) given in Tables 5. 1,2 and 3 are the conventionally quoted standard deviations, S_i, as described above. However, it is probably more realistic to quote the uncertainties at the higher confidence level of $\pm 2 S_i$.

4.3. Dielectric Relaxation and Viscosity Studies

4.3.1. Application of TDS Techniques to Relaxation Studies

Studies of the dielectric relaxation behaviour exhibited by concentrated alcohol solutions were conducted to supplement the information provided by static permittivity and spectroscopic data on such solutions. As has been discussed in Chapter 2, TDS techniques have proved singularly suited to investigating that frequency range in which the major, Debye dispersion, characteristic of most primary and secondary alcohols and their concentrated solutions in non-polar solvents, is evident. Accordingly, TDS experiments, as described below, were conducted.

In Figures 4.12 and 13 are plotted the time-dependent reflection coefficients, as a function of concentration, observed for butanol and for octanol solutions respectively in cyclohexane at 20°C. These are representative of the curves obtained from single reflection and from total reflection experiments respectively. For alcohols with more than four carbon atoms in the alkyl chain, it was necessary, because of the long relaxation times involved, to use total reflection methods to obtain relaxation parameters at 20°C.

The digitised data obtained on paper tape from such time domain signals were first output, through an I.C.L. 1901 series computer,

FIGURE 4.12

Time domain waveforms observed for 1-butanol solutions in cyclohexane at 20°C. The waveforms, which are typical of those observed for single reflection experiments, show the effect of increasing solute concentration on the reflection coefficient (as a function of time): the X-axis is a function of time, the Y-axis is a function of voltage and the Z-axis is a function of concentration. The alcohol mole fractions for the various waveforms are as follows: i, 0.3714; ii, 0.4923; iii, 0.6086; iv, 0.6973; v, 0.8027; vi, 0.9009; vii, 1.0 .

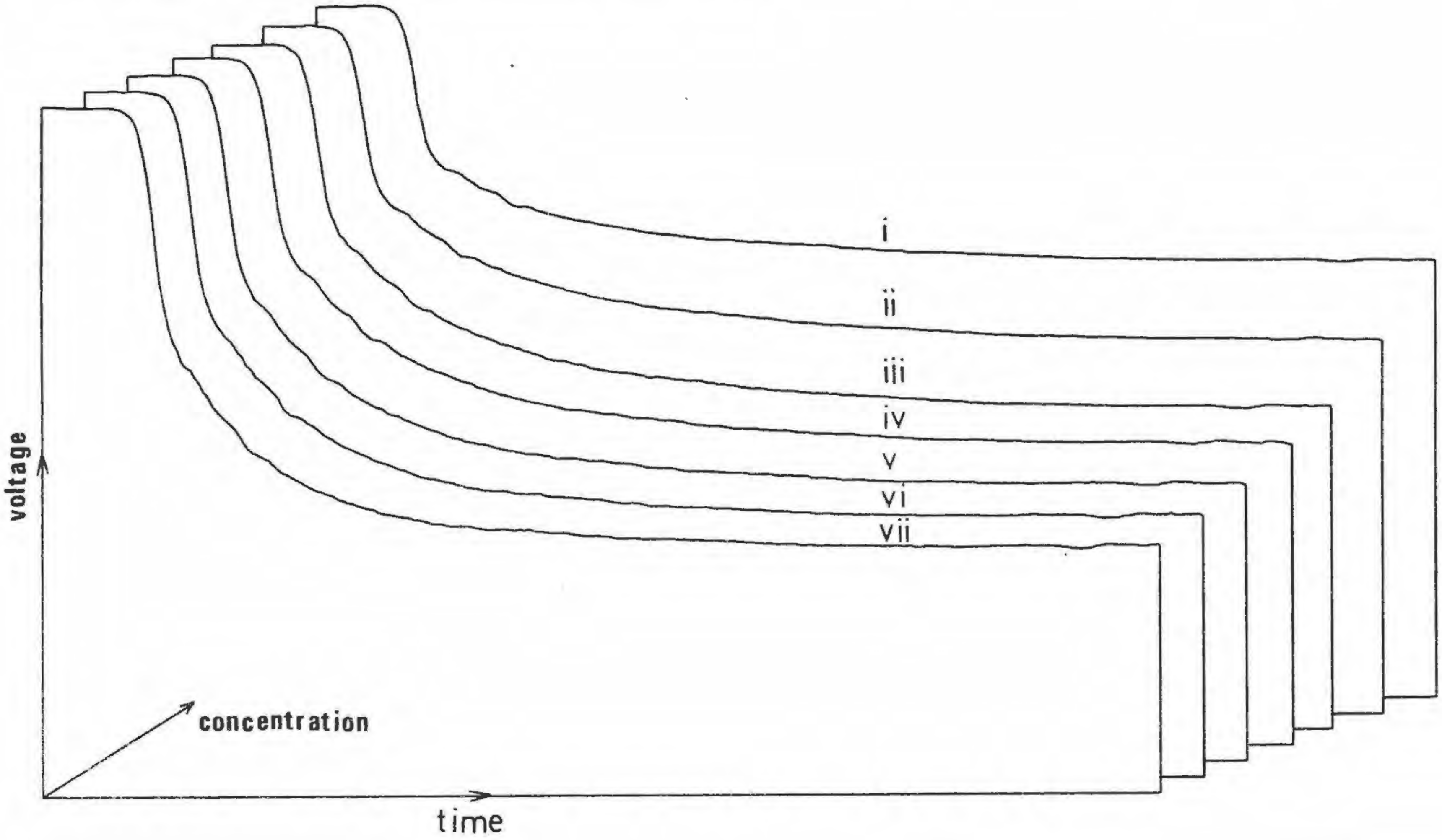
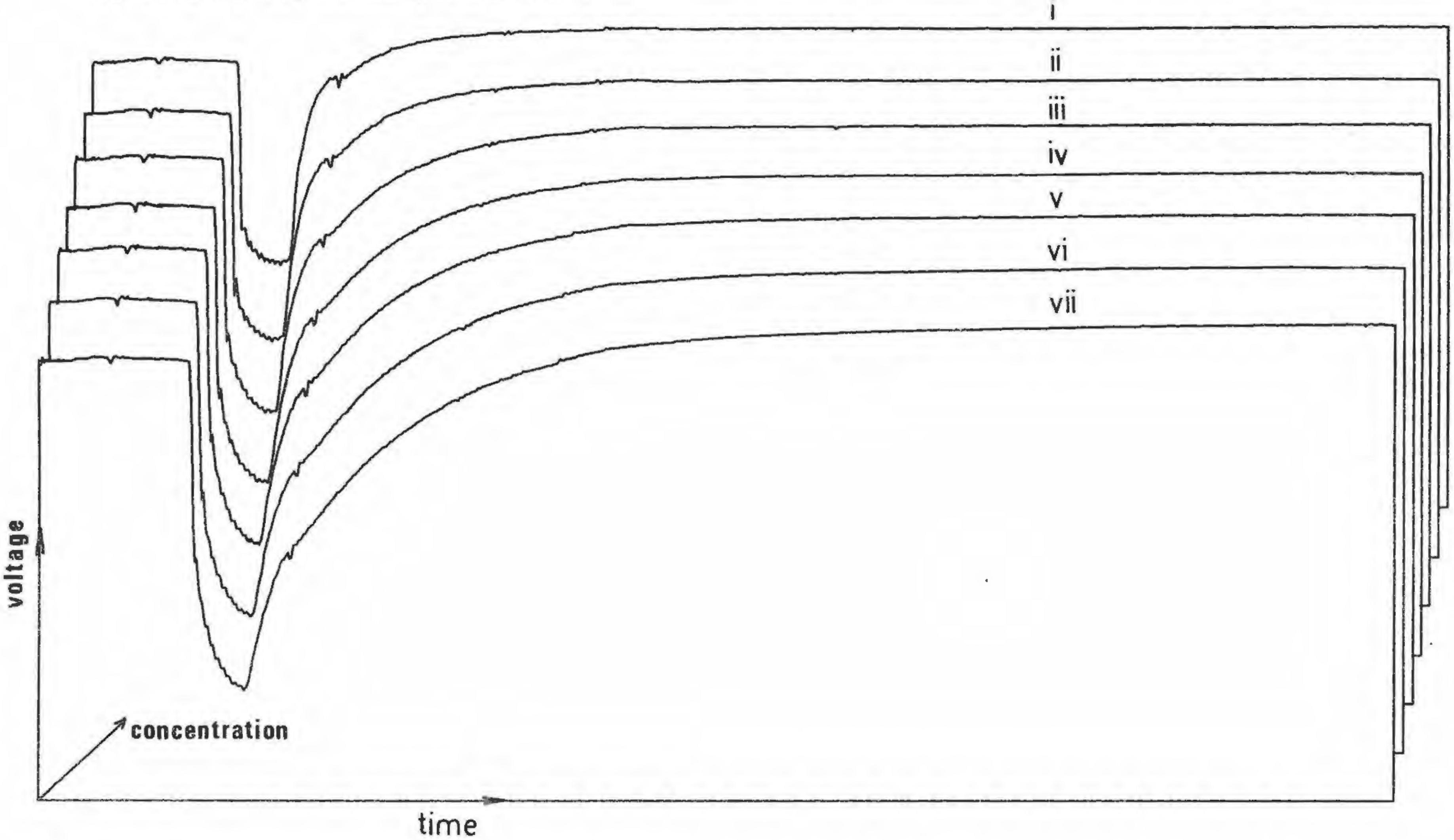


FIGURE 4.13

Time domain waveforms observed for 1-octanol solutions in cyclohexane at 20°C. The waveforms are typical of those observed for total reflection experiments. (See legend to Figure 4.12 for other details.) The alcohol mole fractions for the various waveforms are as follows: i, 0.3951; ii, 0.4958; iii, 0.5979; iv, 0.6881; v, 0.7833; vi, 0.8887; vii, 1.0 .



to a digital graph plotter in order to check for character misreading or mispunching by the paper-tape punch of the data acquisition system. Any errors in the data were found by inspection and corrected.

For single reflection experiments, the data were corrected for time jitter (Nicolson, 1968) and voltage drift by application of a computer program named DATA. The corrected voltages, in the time domain, were then transformed into the frequency domain by application of the Samulon modification (1951) of the Shannon sampling theorem (1949), discussed in sub-section 2.1.4. This was achieved by a program named SHANTDR (considerably developed from a program of the same name written by van Gemert (1972)). Data from total reflection experiments were analysed directly, also by SHANTDR, without applying corrections for voltage drift and time jitter; the limited storage of the computer used did not readily allow such corrections to be applied when more than 256 data points and the associated 256 reference points were considered. The program also permitted the calculation of frequency domain reflection coefficients for the reference spectrum as obtained by Glasser's method (1975) : to obtain these values, heptanol was used as a reference liquid, the relaxation parameters at 20^{0}C taken to be

$$\varepsilon_0 = 11.67$$

$$\varepsilon_\infty = 3.14$$

$$\tau = 1.38 \text{ ns} \quad ,$$

as reported by Middelhoek and Böttcher (1966).

The frequency domain values were then utilised by a program, EPSILON (developed from van Gemert's program (1972) SHANTDR), which calculated the complex, relative permittivity for either single or total reflection experiments. For the former data, the corrections suggested by Giese (1974) were applied, benzene being used as the reference liquid. Whenever it was necessary to disconnect the sample cell from the sampling equipment and also for each alcohol/solvent system examined, the behaviour of benzene (for single reflection experiments) and of heptanol (for total reflection experiments) was redetermined. The newly measured parameters thus corrected for any changes in the signal intensity of the pulse generator and also for changes in the reflection characteristics of the connectors joining the sample cell to the sampling equipment.

After preliminary measurements on selected alcohols whose relaxation parameters are reliably reported, it was observed that application of Giese's corrections, as described in sub-section 2.3.1., led to values of the relative permittivity, ε_0, which differed consistently from literature values. To overcome this problem, the reflection coefficient used for benzene,

$$R = (1 - \sqrt{\varepsilon})/(1 + \sqrt{\varepsilon})$$

where ε is the permittivity of benzene at the appropriate temperature, was adjusted to give a value of ε_0 which, for the sample being studied, agreed with the literature values. This correction was found to have a negligible influence on the observed relaxation times. Therefore, for each alcohol/solvent system studied, the reflection coefficient for the benzene data, taken in conjunction with the appropriate set of solutions, was adjusted to give a value of ε_0, for the pure alcohol, which agreed with the reported values. This adjusted value of R was then applied, without further change, in the calculation of the relaxation parameters of the solutions of that particular system.

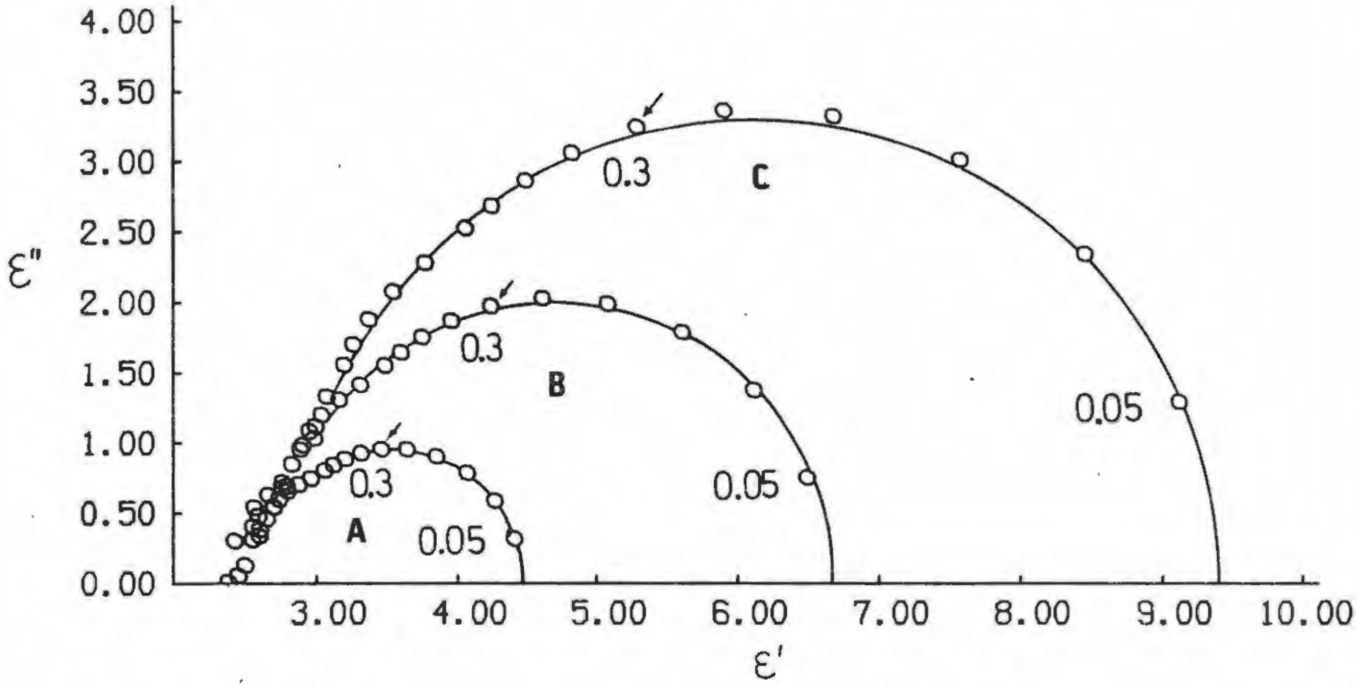
The complex relative permittivities and corresponding frequencies of the systems which have been examined in this study are presented in Section B of the Appendix. The programs utilized to obtain the above data are listed in Section C.

The Cole-Cole plots in Figures 4.14 and 15 show the complex relative permittivities obtained from an analysis, as described above, of the time domain data illustrated in Figures 4.12 and 13. The semi-circles drawn through the data points of these Figures are not mathematical fits. These plots are representative of the quality of the results. The experimentally determined real permittivity (ε') and loss factor (ε'') values fit the semi-circle as well as is generally observed for results obtained from frequency domain measurements. Solutions in which the alcohol mole fraction was less than 40 mole % were not examined (except for propanol solutions in cyclohexane in which the concentration range was extended down to 20 mole %) : below this concentration contributions from the high frequency processes and the small observed ε'' values made the observed relaxation times unreliable.

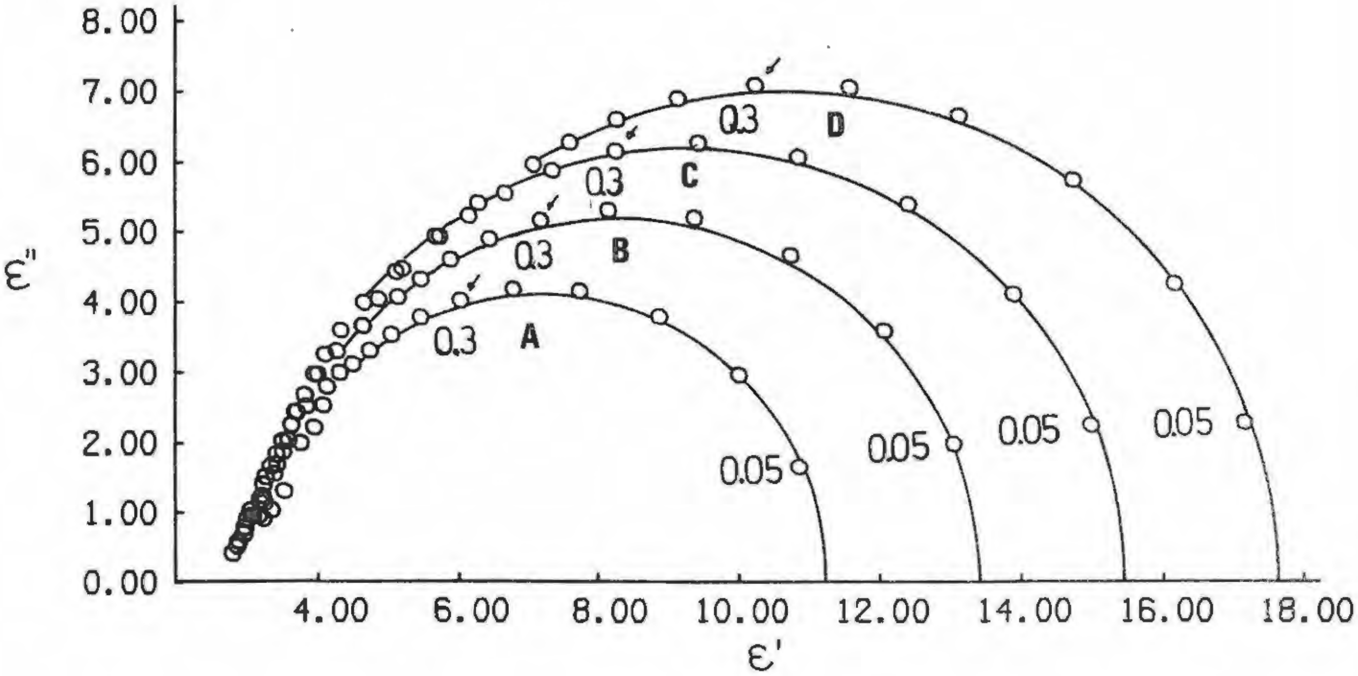
The Cole-Cole plots obtained from time domain and from frequency domain (Garg and Smyth, 1965) methods are compared in Figure 4.16: part (a) compares the results obtained for pure 1-butanol, while in part (b) the results for pure 1-octanol are compared. As above, the semi-circle drawn through the data points is not a mathematical fit. The results of Garg and Smyth have been criticised (Middelhoek and Böttcher, 1966) as being systematically in error, so that a strict evaluation of accuracy is not possible;but, in general, the deviations of the results presented in this study from those of Garg and Smyth are similar to those reported by other workers (Middelhoek and Böttcher, 1966; van Gemert, 1972).

FIGURE 4.14

Cole-Cole plots for 1-butanol solutions in cyclohexane at 20°C. Frequencies, in GHz, are printed alongside selected points. The plots were obtained by analysis of the time domain waveforms depicted in Figure 4.12. The semi-circles drawn through the experimental points are not mathematical fits.



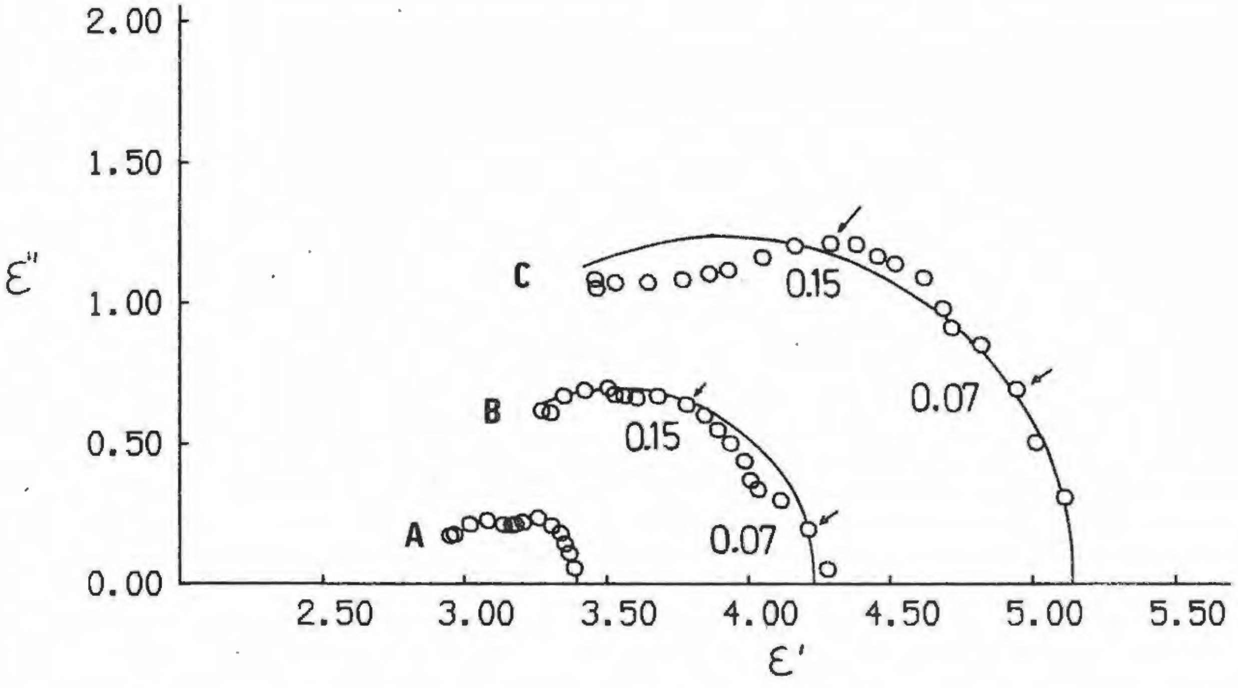
A : plots A-C calculated from waveforms i-iii respectively.



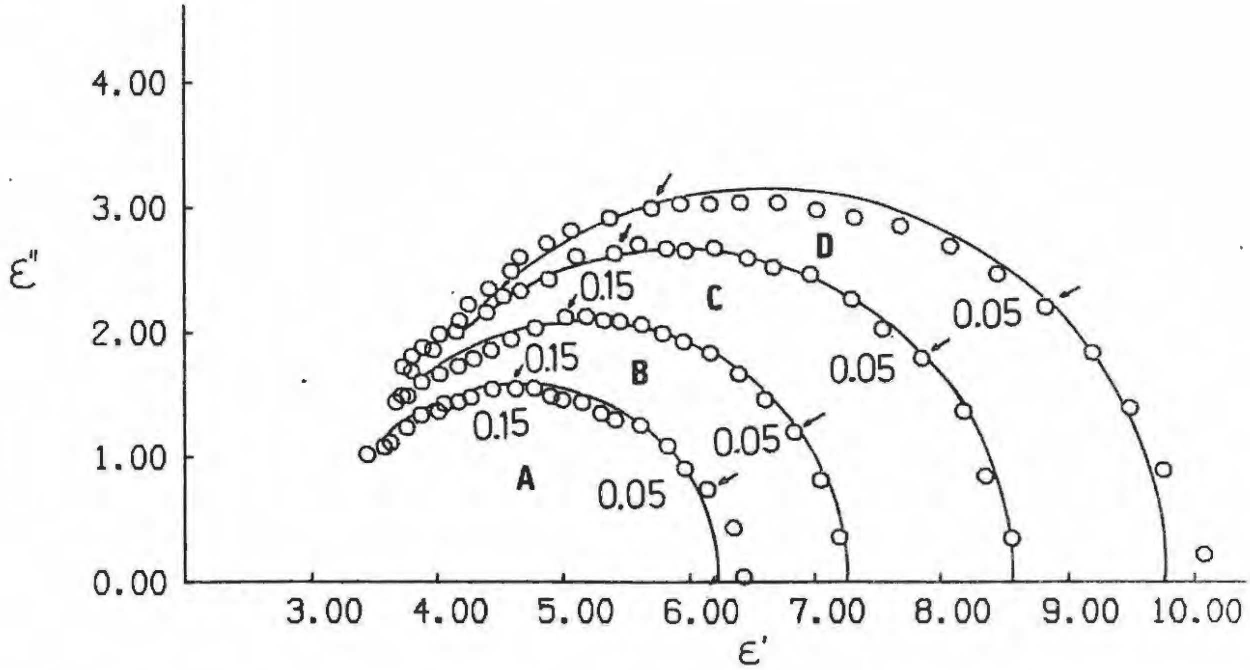
B : plots A-D calculated from waveforms iv-vii respectively.

FIGURE 4.15

Cole-Cole plots for 1-octanol solutions in cyclohexane at 20°C. Frequencies, in GHz, are printed alongside selected points. The plots were obtained by analysis of the time domain waveforms depicted in Figure 4.13. The semi-circles drawn through the experimental points are not mathematical fits.



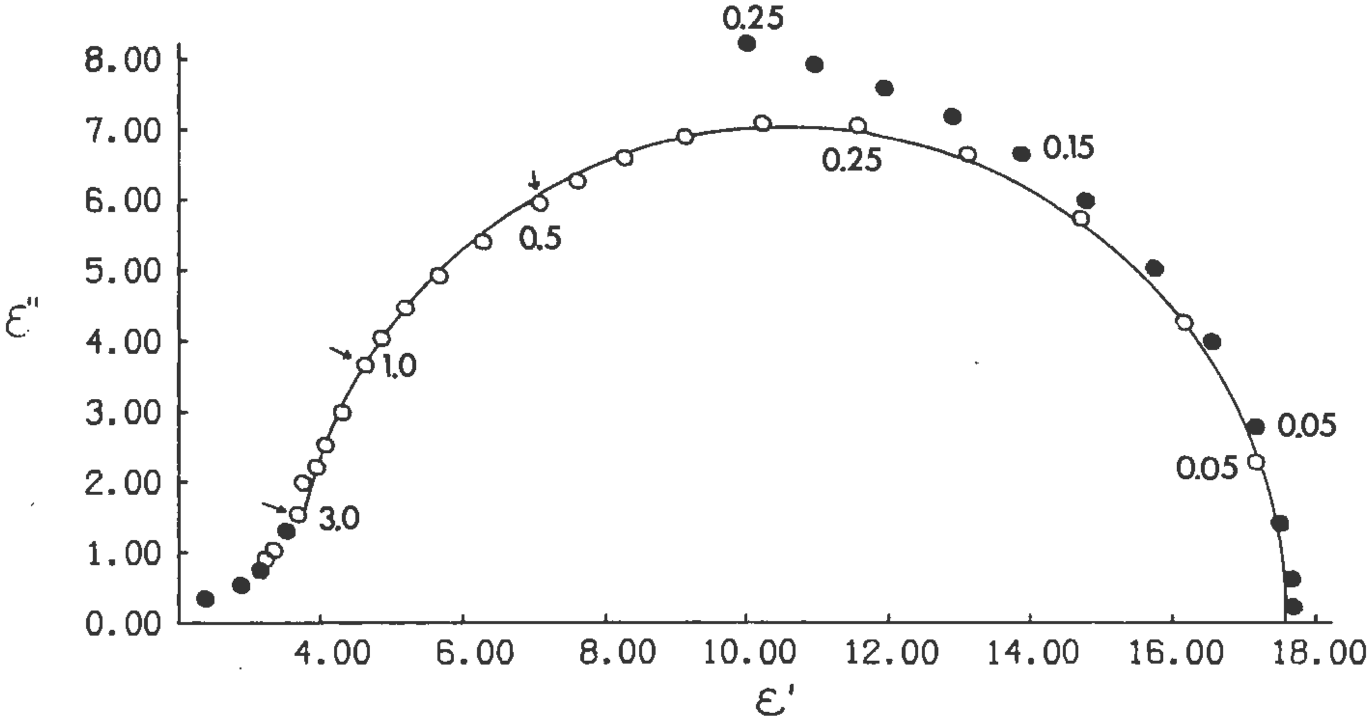
A : plots A-C calculated from waveforms i-iii respectively.



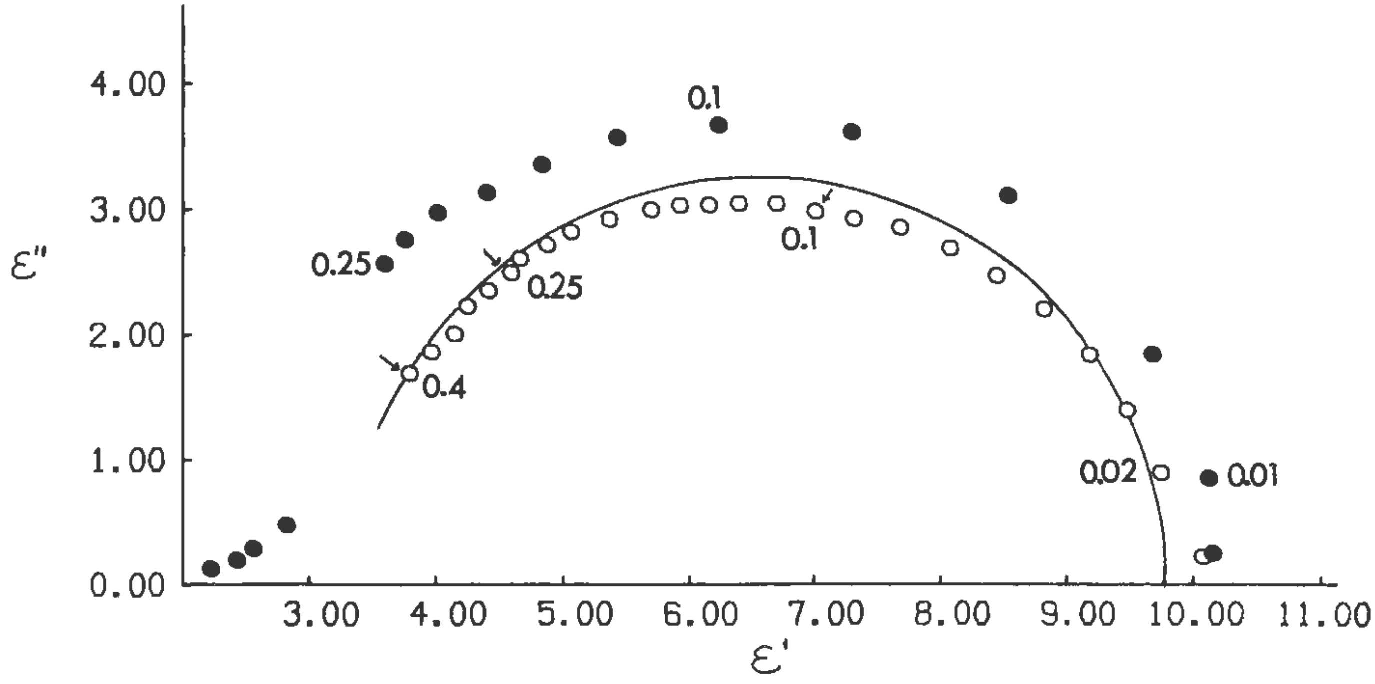
B : plots A-D calculated from waveforms iv-vii respectively.

FIGURE 4.16.

Comparison of the Cole-Cole plots obtained from time domain (O) and frequency domain (●; Garg and Smyth, 1965) studies. Frequencies, in GHz, are printed alongside selected points. The semi-circles drawn through the experimental points are not mathematical fits.



A : plots obtained for pure 1-butanol at 20°C.



B : plots obtained for pure 1-octanol at 20°C.

4.3.2. Calculation of Relaxation Parameters

The relaxation times, τ, and relative permittivities, ε_0, which characterise the solutions and which are presented in Tables 4.1-10 were obtained from the slope and intercept, respectively, of ε' against $\varepsilon''\omega$ plots (Hill, 1969c), where ω is the angular frequency.

For single reflection experiments, a least squares fit to the data, up to 0.7 GHz, was used to obtain the results; beyond this frequency the data, in most cases, gradually deviated from a straight line, possibly because of contributions from high frequency relaxation processes. From the few time and frequency domain values available for comparison (van Gemert, 1973; Sagal, 1962 (by interpolation)), it appears that the relaxation times thus obtained are probably accurate to ± 5%.

For total reflection experiments, least squares fits to the plots of ε' against $\varepsilon''\omega$ (up to 0.15 GHz) were, where possible, used, as above, to obtain the relaxation parameters; but where the least squares procedure could not be reliably applied because of poor accuracy of the data (particularly at the lower concentrations), a fair straight line drawn through the above plots permitted the relaxation times to be estimated. Where comparisons with frequency domain results may be drawn (Garg and Smyth, 1965; Komooka, 1972) it is generally observed that the results obtained from total reflection studies were subject to greater inaccuracies, in the interesting frequency range 0.01 to 0.15 GHz, than results obtained from frequency domain studies and from single reflection experiments. (This may be seen by inspection of the results obtained for solutions of 1-octanol and of 1-hexanol in cyclohexane which are included in Figure 4.17.) These inaccuracies, which are associated with the low frequencies required and with only

Table 4.1

Relaxation and Viscosity Data for 1-Propanol in Cyclohexane at 20°C

X	τ (ps)	ε_0	η (cp)
1.0	370	20.62	2.150
0.9078	430	18.62	1.915
0.8097	460	15.59	1.693
0.6967	500	12.60	1.491
0.6224	515	10.63	1.387
0.5058	525	7.65	1.221
0.4068	480	5.52	1.122
0.2849	295	3.45	1.027
0.1919	225	2.62	0.985

Table 4.2

Relaxation and Viscosity Data for 1-Propanol in Benzene at 20°C

X	τ (ps)	ε_0	η (cp)
1.0	370	20.62	2.150
0.8827	369	16.72	1.557
0.7802	336	14.45	1.294
0.6776	300	11.90	1.089
0.5669	267	9.32	0.925
0.4698	234	7.43	0.823
0.3790	195	5.70	0.753

Table 4.3

Relaxation and Viscosity Data for 1-Butanol in Cyclohexane at 20°C

X	τ (ps)	ε_0	η (cp)
1.0	561	17.67	2.859
0.9009	626	15.50	2.510
0.8027	648	13.50	2.171
0.6973	682	11.23	1.873
0.6086	661	9.39	1.657
0.4923	629	6.62	1.394
0.3714	532	4.44	1.201

Table 4.4

Relaxation and Viscosity Data for 1-Butanol in Carbon Tetrachloride at 20°C

X	τ (ps)	ε_0	η (cp)
1.0	561	17.67	2.859
0.8989	628	14.99	2.192
0.7986	653	13.38	1.965
0.6957	634	10.77	1.728
0.5949	597	8.77	1.498
0.4974	537	6.82	1.307
0.4034	445	5.15	1.174

Table 4.5

Relaxation and Viscosity Data for 1-Butanol in Benzene at 20^{o}C

X	τ (ps)	ε_o	η (cp)
1.0	561	17.67	2.859
0.8705	532	14.67	1.991
0.7591	472	12.54	1.586
0.6567	409	10.37	1.293
0.5587	344	8.38	1.076
0.4502	285	6.45	0.908
0.3425	214	4.74	0.788

Table 4.6

Relaxation Data for 1-Hexanol in Cyclohexane at 20^{o}C

X	τ (ps)	ε_o
1.0	1311	13.45
0.8701	1119	11.62
0.8054	1370	11.03
0.7181	1253	9.48
0.6255	1136	8.30
0.5158	906	6.15
0.4144	873	4.74

Table 4.7

Relaxation Data for 1-Octanol in Cyclohexane at 20^{o}C

X	τ (ps)	ε_o
1.0	1519	9.91
0.8887	1277	8.57
0.7833	1125	7.24
0.6881	1261	6.42
0.5979	747	5.16
0.4958	800	4.24
0.3951	500*	3.45*

Results denoted * obtained by drawing a fair straight line through a graph of ε' against $\varepsilon''\omega$

Table 4.8

Relaxation Data for 1-Octanol in Carbon Tetrachloride at 20^{o}C

X	τ (ps)	ε_o
1.0	1519	9.91
0.8629	1289	8.54
0.7907	1194	7.65
0.6986	1111	6.70
0.5879	706	5.43
0.4812	545	4.43
0.3954	460	4.44

Table 4.9

Relaxation Data for 1-Octanol in Benzene at 20°C

X	τ (ps)	ε_0
1.0	1519	9.91
0.8818	1066	8.66
0.7564	992	7.64
0.6530	606	6.52
0.5382	592	5.31
0.4439	407	4.69
0.3498	354	4.00

Table 4.10

Relaxation Data for 1-Decanol in Cyclohexane at 20°C

X	τ (ps)	ε_0
1.0	2180*	6.83*
0.9085	2010*	6.64*
0.8120	1690*	6.00*
0.6903	1470*	5.46*
0.5912	1350*	4.59*

Results denoted * obtained by drawing a fair straight line through a a graph of ε' against $\varepsilon''\omega$

moderate values of ε'', indicate the need for more thorough investigation of total reflection methods in this frequency range. Therefore, although the trends which result from systematic changes in the alcohols and solvents studied can be readily distinguished, the scatter of the data precludes the development of a description, in terms of molecular behaviour, of the association of those alcohol solutions studied by total reflection methods.

4.3.3. Study of the Concentration Dependence of the Relaxation Time

Figure 4.17 shows the concentration dependence at 20°C of relaxation times for 1-propanol, 1-butanol, 1-hexanol, 1-octanol and 1-decanol solutions in cyclohexane. Also included are results obtained, by interpolation to 20°C, of the data reported by Sagal (1962) on ethanol solutions in cyclohexane. The solid lines drawn in Figure 4.17 merely follow the trends exhibited by the various sets of data. The mole fraction concentration scale facilitates comparison of the results obtained in this study with other reported values (Sagal, 1962; Komooka, 1972; Koshii et al., 1974a,b). An interesting feature of the curves is the maximum in relaxation time observed for the short chain length alcohols (less than six carbon atoms). As the chain-length of the alcohol increases, the maximum moves to higher concentration and eventually shifts out of the available concentration range, so that the curve for decanol solutions exhibits a monotonous rise in relaxation time with concentration.

However, the maximum in relaxation time observed for solutions of short chain-length alcohols is also influenced by the solvent, as shown in Figure 4.18 which illustrates the concentration dependence of the relaxation times observed for 1-butanol in cyclohexane, carbon

FIGURE 4.17

Relaxation time versus solute mole fraction for ethanol (○), 1-propanol (◑), 1-butanol (◓), 1-hexanol (◐), 1-octanol (◒) and 1-decanol (●) solutions in cyclohexane at 20°C. The curves drawn through the data points are not mathematical fits. The data points for ethanol solutions are interpolated from Sagal's results (1962).

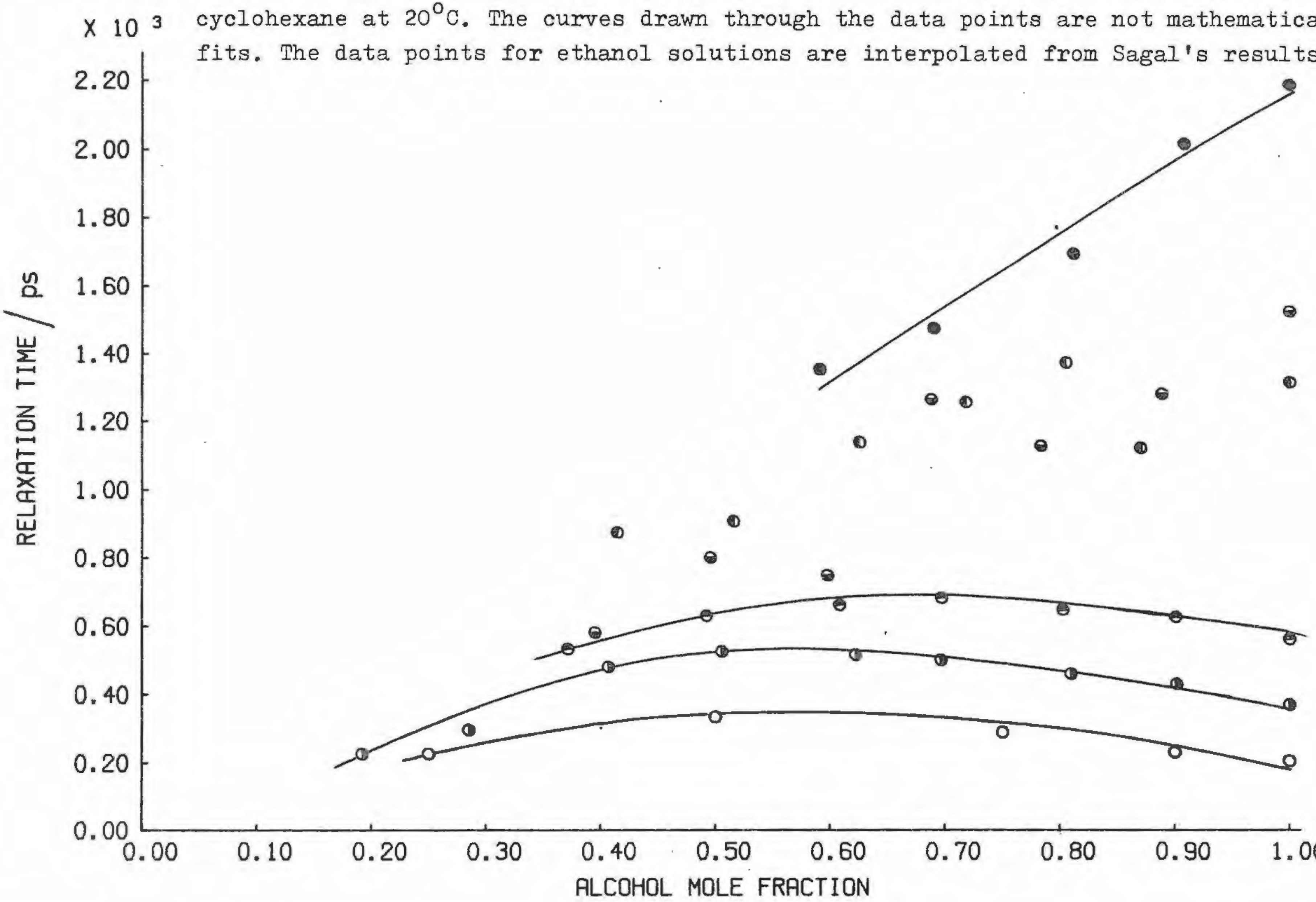
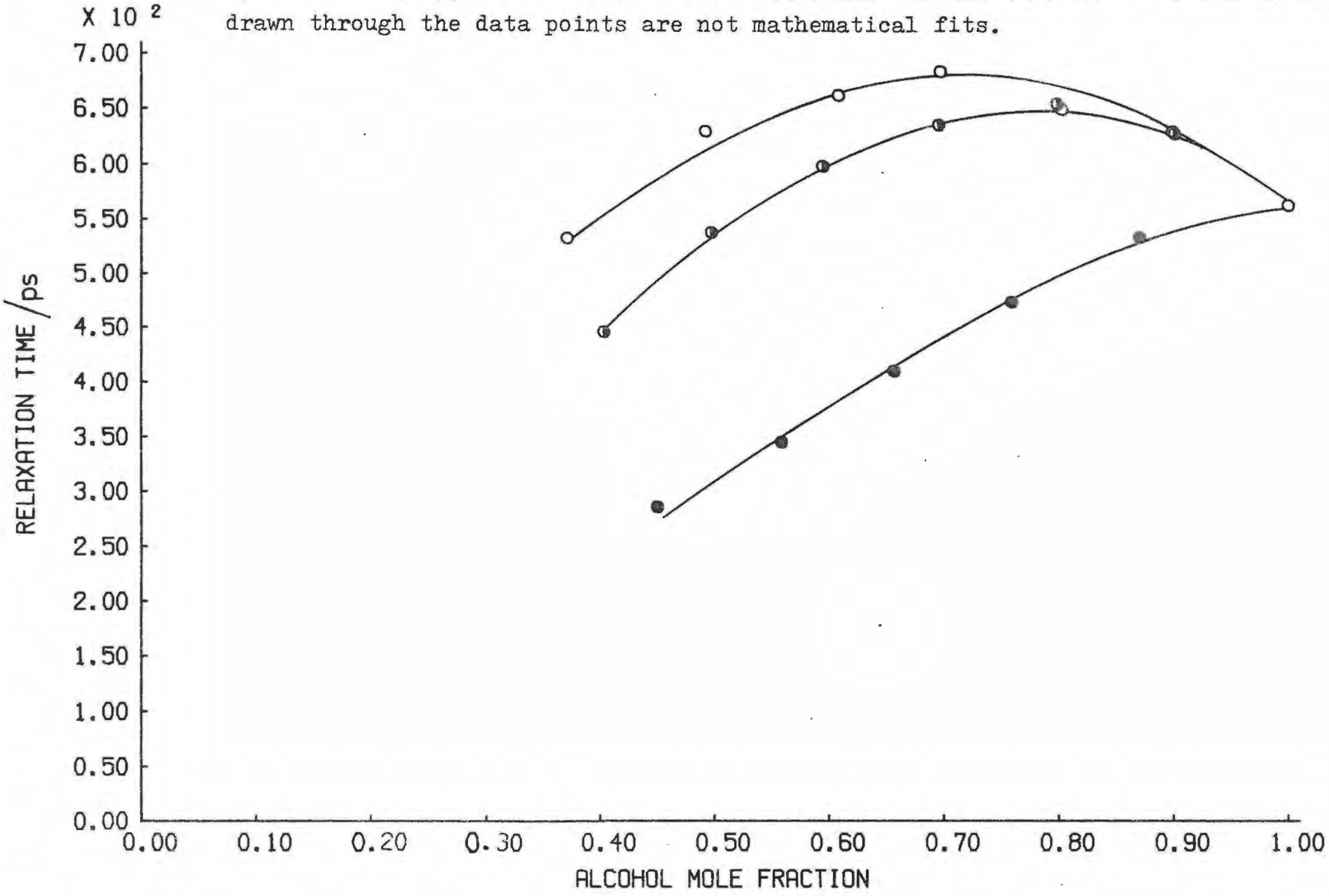


FIGURE 4.18

Relaxation time versus solute mole fraction for 1-butanol solutions in cyclohexane (○), carbon tetrachloride (◑) and benzene (●) at 20°C. The curves drawn through the data points are not mathematical fits.



tetrachloride and benzene solutions. In carbon tetrachloride solutions, the maximum in relaxation time is less pronounced than for cyclohexane solutions while no maximum appears for benzene solutions. (Similarly no maximum appears in 1-propanol solutions in benzene, although this is not shown in a graph.) Higasi and coworkers (Koshii et al., 1974a) noted a similar solvent-dependent influence on the relaxation times observed for solutions of 1-propanol and 1-butanol in a variety of solvents at 25°C. For octanol solutions in the above solvents, a decrease in the relaxation time, at any given concentration, is observed on changing the solvent successively from cyclohexane to carbon tetrachloride to benzene. This behaviour is shown in Figure 4.19. However, the scatter in the data, which occurs for reasons noted above, presently permits this trend merely to be noted and no further use of the data is warranted. As above, the solid lines of Figures 4. 18 merely follow the trends exhibited by the data. To extend the investigation of the influence of alcohol chain length on the concentration dependence of the relaxation time, the data for 1-hexanol and 1-octanol solutions in cyclohexane, reported by Komooka (1972) and listed in Table 4.11, were utilised in the analysis which follows.

4.3.4. Viscosity Studies

To this point, the relaxation times observed for alcohol solutions have exhibited consistent, although perhaps unexpected behaviour. It has been noted that the relaxation time is often viscosity-dependent and many attempts have been made to correlate τ and the macroscopic viscosity, η, for polar molecules (Davies, 1969a). One such relationship is the Debye equation which may be written as

$$\tau/\eta = 3V_D/RT \quad , \qquad 4.xv$$

Table 4.11

Relaxation Data Reported by H. Komooka (1972), with Viscosity Data measured by G. Höll

A. 1-Hexanol in Cyclohexane at 20°C

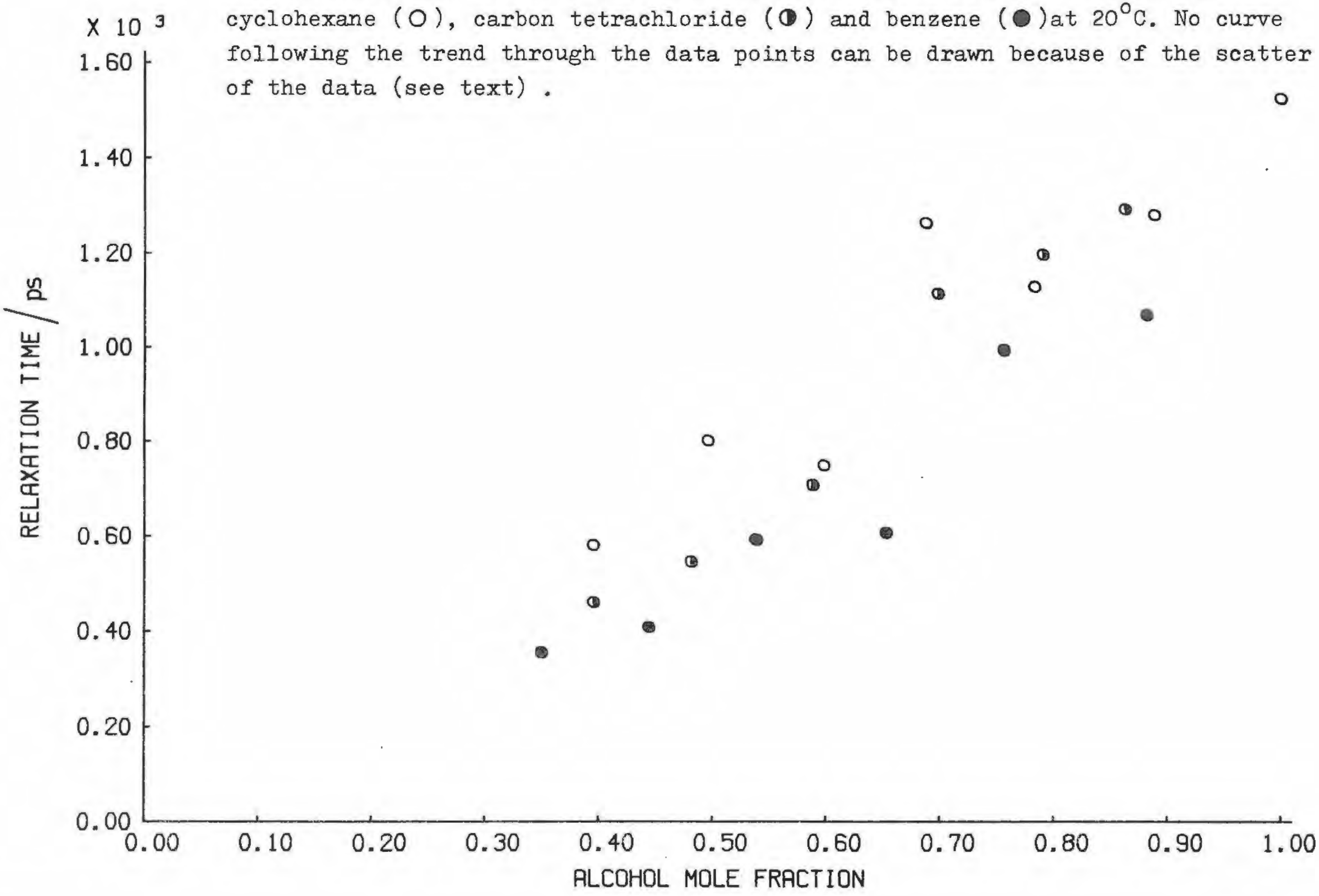
X	τ (ps)	ε_0	η (cp)
1.0	1180	13.66	5.225
0.8988	1210	12.18	4.379
0.7976	1210	10.81	3.702
0.7010	1180	9.21	3.069
0.5992	1100	7.40	2.492
0.5068	990	5.80	2.038
0.4015	820	4.21	1.666
0.3014	630	3.15	1.392

B. 1-Octanol in Cyclohexane at 20°C

X	τ (ps)	ε_0	η (cp)
1.0	1790	10.56	8.819
0.9091	1770	9.69	7.448
0.8093	1690	8.61	6.159
0.7007	1560	7.23	4.861
0.6032	1420	6.02	3.871
0.5069	1190	4.78	3.053
0.4041	930	3.68	2.377
0.3008	680	2.93	1.833

FIGURE 4.19

Relaxation time versus solute mole fraction for 1-octanol solutions in cyclohexane (○), carbon tetrachloride (◑) and benzene (●) at 20°C. No curve following the trend through the data points can be drawn because of the scatter of the data (see text).



where V_D is the molar volume. In view of the Debye-type relaxation behaviour of concentrated solutions of most primary and secondary alcohols, it may be profitable to extend the use of the equation by examining the ratio, τ/η. Assuming the relaxation process to be a cooperative movement, under the influence of an external field, of a molecular species and its environment (Dannhauser and Flueckinger, 1970), one may, as a first approximation, consider there to be two contributions to the process : one contribution is from the movement of the molecular dipole while the second, which may be associated with η, is the motion of the hydrocarbon part of the species through its environment. Therefore the ratio τ/η, referred to as the reduced relaxation time (Antony and Smyth, 1964), might be expected to refer to the relaxation time for reorientation of the dipole in the absence of the contribution from the hydrocarbon part of the molecule. It is necessary to note, however, that only trends in the behaviour of τ/η should be considered and not the absolute values in view of the recognised inadequacy of the Debye equation in describing relaxation characteristics (Davies, 1969b).

Studies of the reduced relaxation time for a series of bromoalkanes and alkenes, as a function of the number of carbon atoms in the alkyl chain have been conducted by Crossley (1973, 1974). He observed a maximum in τ/η for the pure liquids but no maximum was noted for their solutions in non-polar solvents. Following Hennelly et al. (1948), Crossley interpreted his results in terms of increasing internal orientation and molecular coiling with increasing chain length. Antony and Smyth (1964) studied the behaviour of τ/η for solutions of chloroform in a series of solvents of differing proton accepting ability. They found that τ/η decreased with decreasing proton accepting ability of the solvent.

Such studies have, in general, not provided detailed information on molecular association. However, it was hoped that studies of the reduced relaxation time as a function of concentration for alcohol solutions (in which solute self-association is of major importance and could reasonably be expected to influence τ/η) might provide interesting results. Accordingly, the concentration dependence of viscosity for selected alcohol/solvent systems was measured in this laboratory by G. Höll (using a capillary viscometer) and the results are included where available in Tables 4. 1-10. In all cases, viscosity was observed to be a monotonously increasing function of alcohol concentration.

Figure 4.20 shows the concentration dependencies of the reduced relaxation times for 1-propanol, 1-butanol, 1-hexanol and 1-octanol solutions in cyclohexane (the relaxation times for 1-hexanol and 1-octanol solutions being taken, as noted above, from Komooka's work (1972)), and in Figure 4.21 is shown the concentration dependencies of the reduced relaxation times for 1-butanol solutions in cyclohexane, carbon tetrachloride and benzene. As before, the solid lines are not mathematical fits. From these Figures, it can be seen that each alcohol/solvent system studied exhibits a maximum in τ/η near an alcohol concentration of about 50 mole %. The curves of Figure 4.21 indicate that the height and position, in terms of concentration, of the maxima are solvent dependent. The implications of this behaviour will be discussed in the subsequent chapter.

FIGURE 4.20

Reduced relaxation time versus solute mole fraction for 1-propanol (◑), 1-butanol (◓), 1-hexanol (◒) and 1-octanol (◐) solutions in cyclohexane at 20°C. The curves drawn through the data points are not mathematical fits.

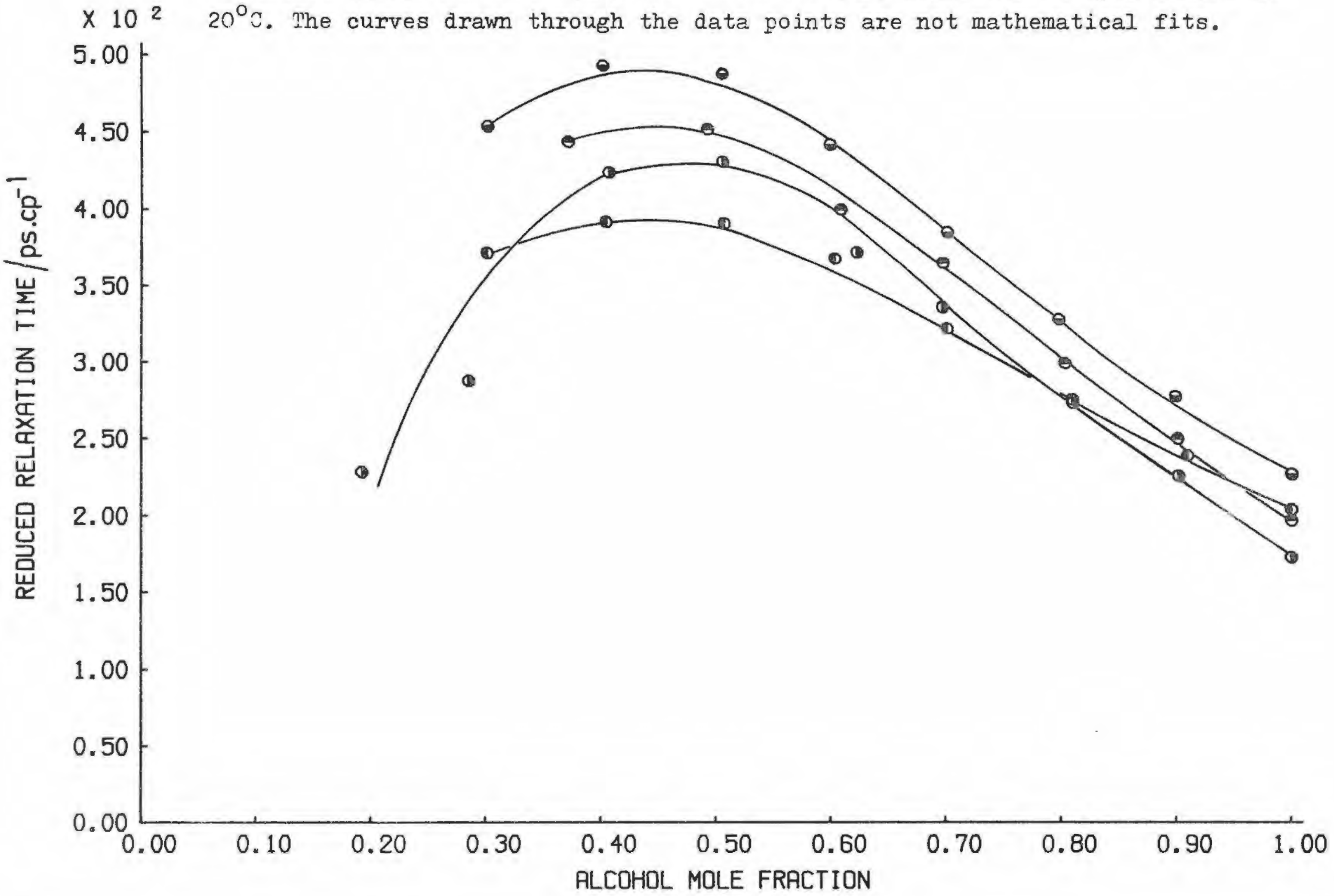
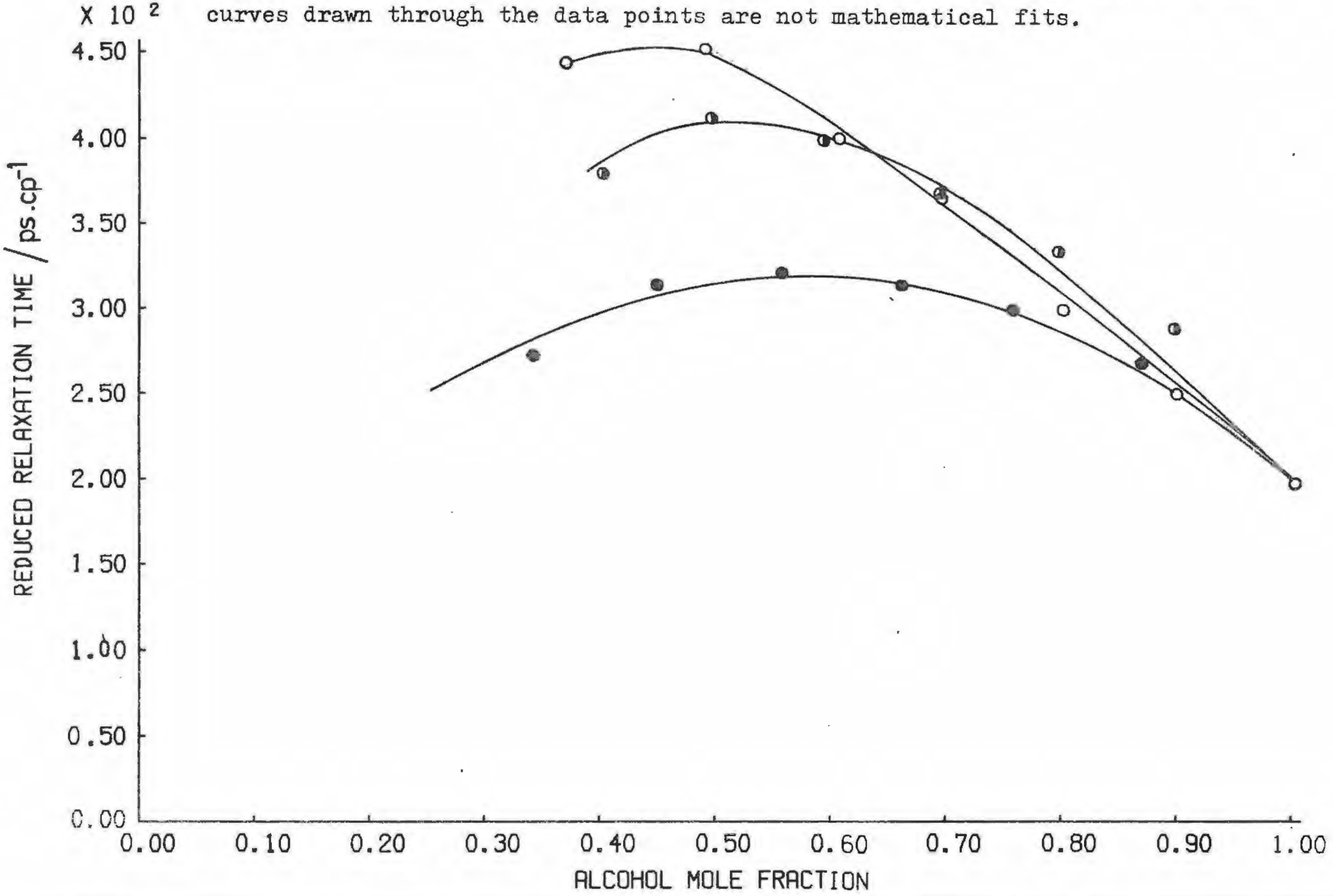


FIGURE 4.21

Reduced relaxation time versus solute mole fraction for 1-butanol solutions in cyclohexane (○), carbon tetrachloride (◑) and benzene (●) at 20°C. The curves drawn through the data points are not mathematical fits.



CHAPTER 5

Alcohol Association in Solutions of non-Polar Solvents

Section 5.1. Outline of Discussion

In this chapter, an interpretation of the association of alcohol solutions, based on the results described in the preceding chapter, will be attempted. The low concentration range will initially be examined, utilising the information available from static permittivity and infrared studies to gain an understanding of the influence of solvents on the equilibrium behaviour of 1-octanol solutions. Solutions of 2-, 3- and 4-octanols will then be similarly examined to investigate the influence, on the equilibrium behaviour, of progressively altering the steric environment of the -OH group. The qualitative information thus gained will be quantised by applying molecular models, consistent with the qualitative information, to the data using least-squares, curve-fitting procedures.

The interesting trends noted on going from 1-octanol to 4-octanol suggested that it would be interesting to examine an alcohol in which the -OH experienced a very restricted environment; accordingly similar studies were undertaken on solutions of 2,3,4-trimethyl-3-pentanol. NMR studies were also conducted on solutions of this alcohol. As a final aspect of the low concentration studies, static permittivity and infrared studies were used to further the experimental information available on solutions of t-butanol in hexadecane, a system which has been extensively investigated by Tucker and Becker (1973).

At high alcohol concentrations, it is necessary to apply different experimental techniques to gain insight into the association behaviour because of the unremarkable information available from the above methods. Dielectric relaxation studies on solutions of several primary alcohols were thus undertaken, using TDS techniques.

Finally, a description of alcohol association will be summarised. The limitations of the techniques and approach used will be noted and suggestions as to experiments which could clarify and remove ambiguities in the association behaviour will be presented.

5.2. Solvent Effect on the Association of 1-Octanol Solutions

5.2.1. Description of Permittivity and Infrared Results

The concentration dependencies of μ^2_{app} for solutions of 1-octanol in hexane, cyclohexane, carbon tetrachloride and benzene have been shown in Figure 4.1. The distinct regions observed in the curves have been discussed as resulting from the presence of different hydrogen bonded species in solution. Evidence for the presence of such postulated species comes from an examination of the infrared spectra shown in Figure 4.2. At the lowest concentrations in each of the solvents, only a single -OH stretching vibration (at about 3650 cm^{-1}) is observed when a 1 mm sample cell is used : this is the non-bonded -OH stretching vibration. This does not mean that self-associated species are entirely absent at the concentration at which the spectra were recorded, but rather that their concentrations are too small to be observed under the experimental conditions. As the concentration is increased, two additional bands appear, in the region of 3500 cm^{-1} and 3350 cm^{-1}. A significant point is the rate at which the low frequency (3350 cm^{-1}) band increases with concentration, compared to the 3500 cm^{-1} band, in the various solvents. In cyclohexane solution the low frequency band increases rapidly with concentration; in carbon tetrachloride it increases more slowly, and in benzene this band is absent at the concentrations shown, but does appear at higher concentrations. In addition, the peak near 3500 cm^{-1} grows more slowly for benzene solutions than for solutions in the other two solvents.

The three peaks (at about 3650 cm^{-1}, 3500 cm^{-1} and 3350 cm^{-1}) are usually attributed to monomer, dimer and higher multimeric hydrogen bonded species respectively, as has been noted in Section 1.3. However, as has also been discussed in that Section, there is by no means total agreement as to the configuration of the dimer, both cyclic and open forms being put forward to explain experimental data. Furthermore, there is not even agreement that a dimer, either cyclic or linear, is in fact the first associated species : Tucker and Becker (1973), from an analysis of infrared spectroscopic, vapour pressure and NMR data, favour a linear trimer as the first associated species. Fletcher and Heller (1967, 1968) conclude that their results for several alcohol/solvent systems are adequately explained by an equilibrium of monomer and linear and cyclic tetramers; however, from Table III of their results (Fletcher and Heller, 1967), monomer-dimer-tetramer and monomer-trimer-tetramer models also seem to fit the data well.

5.2.2. Correlation of Information Provided by Permittivity and Infrared Studies.

Information on the structure of the associated species giving rise to an absorption in the spectra near 3500 cm^{-1} may be obtained from a correlation of information available from the infrared spectra shown in Figure 4.2. and the concentration dependencies of μ^2_{app} for 1-octanol solutions (Figure 4.1). In carbon tetrachloride solutions, the appearance of the "dimer" band in the infrared spectrum is associated with an increase in μ^2_{app}; with further increase in concentration, μ^2_{app} decreases and this is accompanied by the first appearance of the "multimer" band in the infrared spectrum. The initial increase in μ^2_{app}

indicates an increase in the dipole moment above that for a single molecule, implying a parallel alignment of dipoles as a result of hydrogen bonding. The infrared peak near 3500 cm^{-1} consequently arises from an open dimer or perhaps an open trimer, but certainly not from a small, closed cyclic species (cyclic species usually being assumed to have a low (zero) dipole moment).

The subsequent decrease in μ^2_{app} with concentration represents a situation where the associated species are still small (because the concentrations are still low), but have a low dipole moment, for example cyclic trimers or tetramers. This behaviour is accompanied by the appearance of a peak near 3350 cm^{-1} in the infrared spectrum. If the concentration of alcohol is increased still further, μ^2_{app} again increases owing to formation of associated species of high dipole moment, perhaps chains of four or more alcohol molecules. No additional peaks appear in the -OH stretching region of the infrared spectrum to accompany this behaviour; however, the lowest frequency peak grows in intensity compared to the two other peaks and eventually dominates the spectrum. This implies that the force constants of the -O-H bond in the various types of hydrogen bonded species, the dimer excepted, do not differ greatly and give rise to a broad peak centered at about 3350 cm^{-1}. The dimer and multimer peaks grow less rapidly with alcohol concentration in carbon tetrachloride than in cyclohexane solutions. This indicates that the monomer is stabilised by an association with carbon tetrachloride. Fletcher (1969) has gone so far as to postulate a formal 1:1 complex between the 1-octanol monomers and carbon tetrachloride; however, his analysis has been critised by Christian and Tucker (1970).

The dielectric behaviour of 1-octanol solutions in benzene is similar to that in carbon tetrachloride. However, the formation of the first, high dipole moment species is delayed to higher concentrations as is shown both by the dipole moment behaviour, depicted in Figure 4.1, and by the infrared spectra in Figure 4.2. The infrared spectra show that the appearance of the low dipole moment species is similarly delayed. This suggests that the alcohol monomer is stabilised by an association with benzene, even more than with carbon tetrachloride. Several independent studies (Pimentel and McClellan, 1960b) show that benzene has behaviour which correlates very well with the criteria for well-recognised hydrogen bonding systems. Huyskens and co-workers (Mullens, Hanssens and Huyskens, 1971), from their studies of the partition coefficients of alcohols between water and each of cyclohexane, carbon tetrachloride and benzene, and from infrared spectroscopic studies, have shown that alcohol self-association occurs to a smaller extent in benzene than in carbon tetrachloride and, in turn, is less in carbon tetrachloride than in cyclohexane. These findings agree with the conclusions of Woolley and Hepler (1972) based on thermochemical data obtained from studies of phenol in the above solvents.

Solutions of 1-octanol in cyclohexane present an interesting situation. Apparently the high dipole moment species, including both the monomer and the linear species formed at low concentrations, are little stabilised by interaction with this relatively inert solvent. This results in the early appearance in the infrared spectrum of the absorption band associated with the low dipole moment species. The combined effect of the nearly simultaneous appearance of a high and a low dipole moment species results in a balance which keeps μ^2_{app} approximately constant until the larger, low dipole moment species dominates the equilibrium. The initial, almost horizontal, region seen for cyclohexane solutions in Figure 4.1 illustrates this balance. Ibbitson and Moore (1967a,b), who observed similar behaviour, have suggested that μ^2_{app} remains constant at low concentrations because alcohol association is delayed until the concentration is sufficiently great for cyclic polymers to form. This suggestion was based on the argument that the free end of an open alcohol dimer would not be stabilised by an interaction with cyclohexane. It is clear, however, from the infrared results that a dimer (or trimer) does form and that the balance, suggested above, accounts for the lack of an initial increase in μ^2_{app} with increasing concentration.

As shown in Figure 4.1, the behaviour of 1-octanol solutions in n-hexane is almost identical to that in cyclohexane over the concentration range studied. These two saturated alkanes would be expected to exhibit similar solvent behaviours. Huyskens et al. (1962) similarly observed little difference between the solvent behaviours of cyclohexane and hexane at low concentrations, although a measurable difference did exist at high alcohol concentrations. On the other hand, Malecki and Jadzyn (1974), who examined the dipole polarisation, $Rp = \mu^2_{app}/\mu^2_1$, in dilute solutions of some butanols and phenol in hydrocarbon solvents, considered there to be measurable differences, even at low concentrations, between the solvent behaviours of cyclohexane and hexane. They also considered there to be no initial balance region as discussed above. However, their published diagrams indicate that their data, which are few, are subject to relatively large errors, so that their findings must be regarded with some caution.

Fletcher and Heller (1967) conclude, from a near infrared study of the association of 1-octanol in n-decane, that the equilibrium behaviour, over the whole concentration range, can be explained in terms of a monomer and only two associated species, an open and a closed tetramer. However, from the dielectric and infrared data presented here for 1-octanol in cyclohexane, it is evident that at least two associated species are present from about 0.03 mol ℓ^{-1} and at least one other associated species must be present to account for the increasing dipole moment for concentrations greater than about 0.5 mol ℓ^{-1}. It is not expected that the association behaviour in n-decane would be markedly different from that observed in cyclohexane.

The dielectric behaviour in the three solvents at low concentrations requires at least two associated species for adequate description of the observed association behaviour. The first associate may be an open dimer whose dipole moment is greater than that of the monomer; an alternative is an open trimer as suggested by Tucker and Becker (1973). The next species, which has a low dipole moment, is perhaps a cyclic trimer or tetramer. The infrared results probably exclude a cyclic dimer at these concentrations since each hydrogen bond of such a species, because of its non-linearity, would be expected to be weaker than the bond in an open dimer; absorption bands would then be found at frequencies between those of the monomer and open dimer (or trimer). (Such bands have in fact been observed by Kuhn (1952) for polyalcohols in which the hydrogen bonds formed between two -OH groups must be weak because of the relatively large distance between them.) Finally, the increase in μ^2_{app} at high alcohol concentrations indicates the formation of long, open-chain multimers (which could possibly interconnect to form a three-dimensional network) or perhaps a special configuration of a cyclic multimer having a large dipole moment as earlier suggested by Bordewijk *et al*. (1969).

The possibility of network formation will be considered in the following Section.

Some confirmation of this model of alcohol self association appears from studies of water self-association. Kistenmacher and co-workers (Kistenmacher, Lie, Popkie and Clementi, 1974) and also Scheraga and colleagues (Shipman, Owickji and Scheraga, 1974) have made a large number of computations for water-water interactions. The conclusions reached are that the open form of the dimer is more stable than the cyclic form and that the cyclic forms of the trimer and tetramer are more stable than the analogous open structures. Furthermore, Kistenmacher et al. point out that for large clusters, configurations with significantly different geometries have nearly the same energy. It would seem that these structural ideas are also relevant in alcohol association.

5.3. Influence of -OH Steric Environment on the Association of the Straight Chain Octanols.

5.3.1 Information Provided by Permittivity and Infrared Studies.

Having interpreted the concentration dependence of the association of 1-octanol in solution in terms of multimers of varying size and configuration, it is of interest to ascertain whether similar species account for the association behaviour of alcohols whose -OH groups experience a more restricted environment. Accordingly the effect on multimer formation of moving the hydroxyl group to different positions along the octyl chain was investigated. To this end, the behaviours of 2-, 3- and 4-octanols in the same solvents (with the exception of n-hexane) were examined.

The similarity of the concentration dependencies of μ^2_{app} for the four alcohols in each of the solvents (Figures 4.3, 4 and 5) shows that the solvent influences the association of 2-, 3- and 4-octanols in a manner similar to that observed for solutions of 1-octanol. Similarly, the infrared spectra exhibited analogous behaviour for each alcohol so that the assignments of the peaks were the same as for 1-octanol solutions.

The formation of the first, high dipole moment species occasions the initial rise in μ^2_{app} at a concentration largely independent of the position of the -OH group in the alkyl chain. A similar conclusion is obtained from examination of the infrared spectra. However, the concentration range over which the second, low dipole moment species is prominent is very dependent on the alcohol studied. The intensity of the multimer band near 3350 cm^{-1} in the infrared spectra is highly sensitive to the -OH position; this is most clearly seen at the solute concentration (0.065 mol ℓ^{-1}) of the spectra, obtained from cyclohexane solutions, in Figure 4.6. Evidently the cyclic multimer, which this peak represents at this concentration, forms most readily with 1-octanol and least readily with 4-octanol (assuming the absorption coefficients of this species, for the different alcohols, to be similar). Consequently, in each of the solvents, the minimum in μ^2_{app} occurs at higher concentrations going from 1-octanol to 4-octanol; in addition, the depth of the minimum increases in the same order (which may be less obvious from the diagrams as drawn).

5.3.2. Interpretation of Alcohol Association Using Thermodynamic Arguments.

The concentration dependence of the association behaviour of octanol solutions at low concentrations may be described using thermodynamic arguments. The Gibbs function, G, of the solution is reduced by the enthalpy release (-ΔH) which occurs with increasing intermolecular association and which overshadows any entropy decrease associated with the ordering process of association. The presence of solute/solvent interactions, which partially offset $-\Delta H$, is most apparent at the lowest concentrations where the monomer is the most stable species. At higher concentrations, a small, open multimer (usually considered to be a dimer) forms. However, there seems to be no tendency to form a closed species of the same size, implying that the enthalpy gain from the two, presumably weaker, hydrogen bonds which would form cannot compensate for the entropy decrease involved. Furthermore, as the proton-accepting ability of the solvent increases, these open multimers will be increasingly favoured. This is seen by the longer concentration range over which μ^2_{app} increases in benzene solutions compared to carbon tetrachloride and to cyclohexane solutions.

As the concentration increases further, the formation of large, cyclic multimers does become favoured : the enthalpy release obtained from the formation of an extra hydrogen bond to form a cyclic species (with less strain than is involved in forming a smaller, closed multimer) is more favourable than that from an open chain with the terminal -OH stabilised by the solvent. It is also sufficient to overcome the unfavourable entropy decrease involved.

5.3.3. High Concentration Multimers.

The increase of μ^2_{app} at the higher concentrations indicates that multimers of high dipole moment are formed. Because of the large dipole moment, the most likely form of these species are linear chains rather than closed rings. This implies that the terminal -OH groups of these chains are in some way stabilised. For alcohols with a non-hindered hydroxyl group, there is the possibility of two hydroxyl protons binding to a single oxygen of a third alcohol molecule *i.e.*

forming bifurcated hydrogen bonds (Huyskens, Zeegers-Huyskens, Dierckx, 1964). Consequently, one may envisage that as the concentration increases, there will be an increased possibility of the end hydroxyl group of a chain bonding to an hydroxyl group at any point along a neighbouring hydrogen bonded chain. (Since one would expect relatively few chain ends, one would not envisage this behaviour as substantially influencing the average coordination number of an alcohol molecule which, from X-ray studies (Pierce and MacMillan, 1938), is observed to be 2.) Such bonding would stabilise the terminal end groups and, coupled with the enthalpy gain resulting from less strained hydrogen bonds and a less negative entropy, the linear chains would then be expected to form preferentially to the cyclic oligomers at the higher concentrations. The interconnected chains would constitute a three-dimensional network so that to speak of associates of a particular size in this concentration range is probably inappropriate.

As the steric hindrance around the alcohol hydroxyl group increases, network formation would be expected to become increasingly difficult because of the steric difficulties associated with the hydroxyl groups sharing an acceptor atom. Consequently the network would be expected to form readily in 1-octanol solutions, but increasingly less so in solutions of 2-, 3- and 4-octanols. One would thus expect the concentration at which the high dipole moment species first appears to increase from 1- to 4-octanol with a resultant decrease in the value for the dipole moment of the pure alcohol in the above order. This is consistent with the observed behaviour.

A qualitative understanding of the self-association of solutions of the four straight chain octanols is thus obtained and the model is probably applicable to other alcohols.

5.4. Quantisation of the Association Model.

5.4.1. General Principles of the Models Considered.

To obtain a quantitative description of alcohol association, it is necessary to determine dipole moments for the hydrogen bonded species and equilibrium constants for their formation. For example, if the species responsible for the behaviour of μ_{app}^2 as a function of concentration are considered to be monomers, dimers and trimers, the appropriate equilibrium equations may be written

$$2\ (\text{monomer}) \rightleftharpoons \text{dimer};$$

$$3\ (\text{monomer}) \rightleftharpoons \text{trimer};$$

with corresponding equilibrium constants K_2 and K_3. These equilibria may be described by application of equation 4.vii :

$$\mu_{app}^2 = {}^1/c(c_1\mu_1^2 + 2K_2c_1^2g_2\mu_1^2 + 3K_3c_1^3g_3\mu_1^2) , \qquad 5.i$$

where subscripts 1, 2 and 3 refer to monomer, dimer and trimer respectively. c_1 may be obtained from the mass balance equation, 4.v :

$$c = c_1 + 2K_2c_1^2 + 3K_3c_1^3 . \qquad 5.ii$$

Similarly, equations can be developed to allow investigation of other models. This description is, however, somewhat idealised in that no account is taken of various factors (for example change in permittivity) which could cause equilibrium constants to change as a function of concentration.

Further, no account is taken of solute/solvent interactions incorporation of which has been suggested (Fletcher, 1969; Bordewijk, 1975) as being necessary to fully allow for the observed differences on using solvents of different proton-accepting abilities.

The interpretation to be developed is based on an application of Occam's Razor, viz., that the least number of species compatible with the experimental observations should be considered. Undoubtedly, more complex models than those to be discussed, with more adjustable parameters, may be fitted to the above data, but they can only be justified if the simpler models are shown, operationally, to be inadequate.

The variables were optimised over the low concentration range only, excluding the species which cause the final increase in μ^2_{app} since their influence would swamp the interesting low concentration behaviour. Confining the analysis to the low concentration range also has the advantage of minimising errors that might arise from neglecting the non-ideality, as discussed above, of alcohol solutions : such errors would be expected to be small for this concentration range since only small changes in the permittivities of the solutions occur.

5.4.2. Quantisation of Data for Octanol Solutions.

The model initially considered has the form : monomer-open dimer- closed trimer (1-2-3). To simplify the calculations (since there are five unknown parameters), the dipole moment of the cyclic trimer is assumed to be zero. For 1-octanol in the three solvents, the results were initially obtained by application of a simplex least squares procedure, as described in sub-section 4.2.2; essentially the same results were subsequently obtained, more rapidly, by application of the Newton-Raphson procedure, described in sub-section 4.2.3. In Figures 5.1-3 are plotted the values of μ^2_{app}, against a linear concentration scale, for 1-octanol solutions in carbon tetrachloride,

FIGURE 5.1

μ^2_{app} versus concentration (mol l^{-1}) for 1-octanol in carbon tetrachloride at low concentrations. Discrete points are experimental values; the continuous line is a least-squares fit assuming a monomer-dimer-trimer model. The arrows indicate the concentrations at which the infrared spectra in Figure 4.2 were recorded.

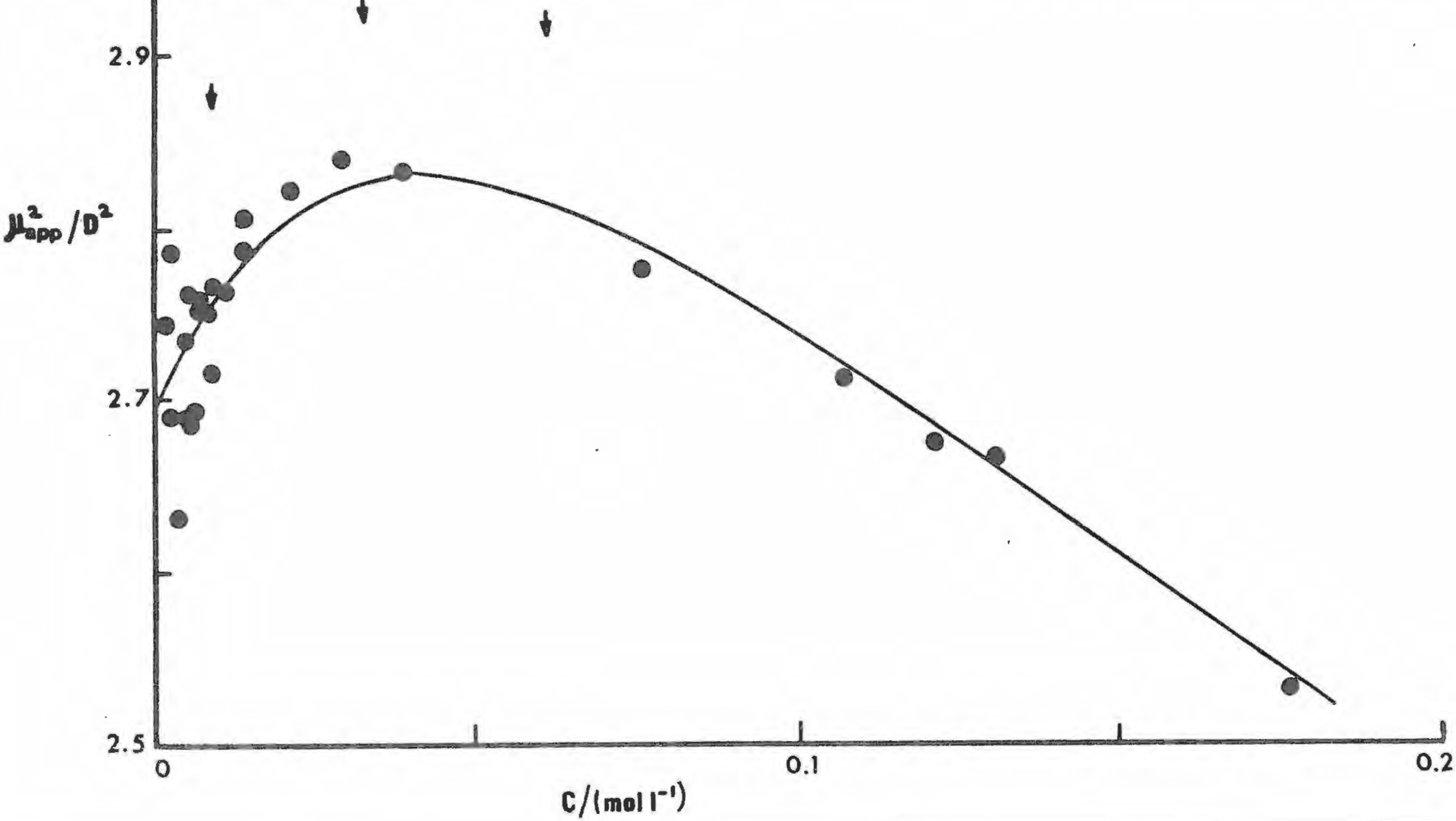


FIGURE 5.2

μ^2_{app} versus concentration (mol l^{-1}) for 1-octanol in benzene at low concentrations. See legend to Figure 5.1 for other details

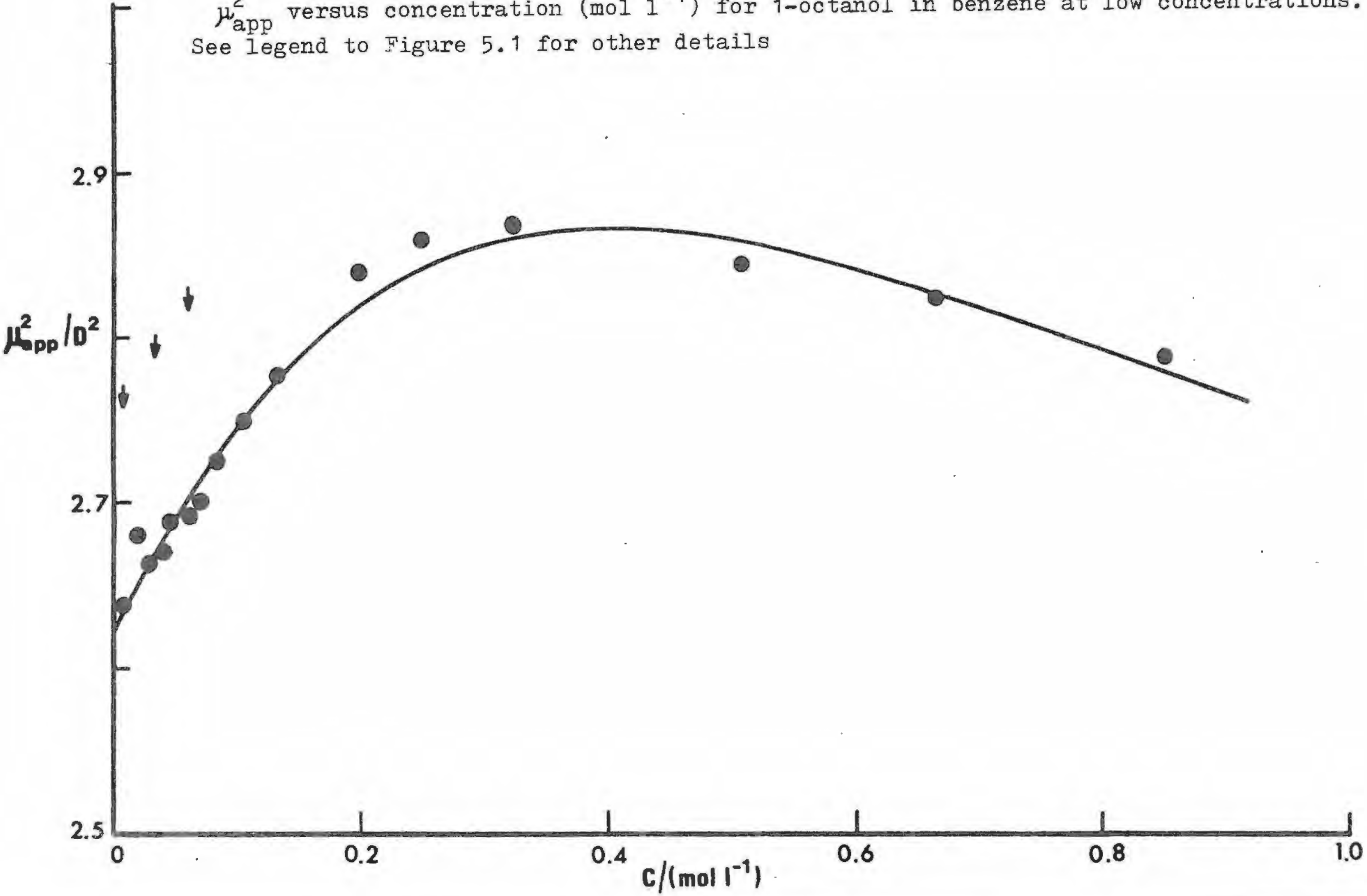
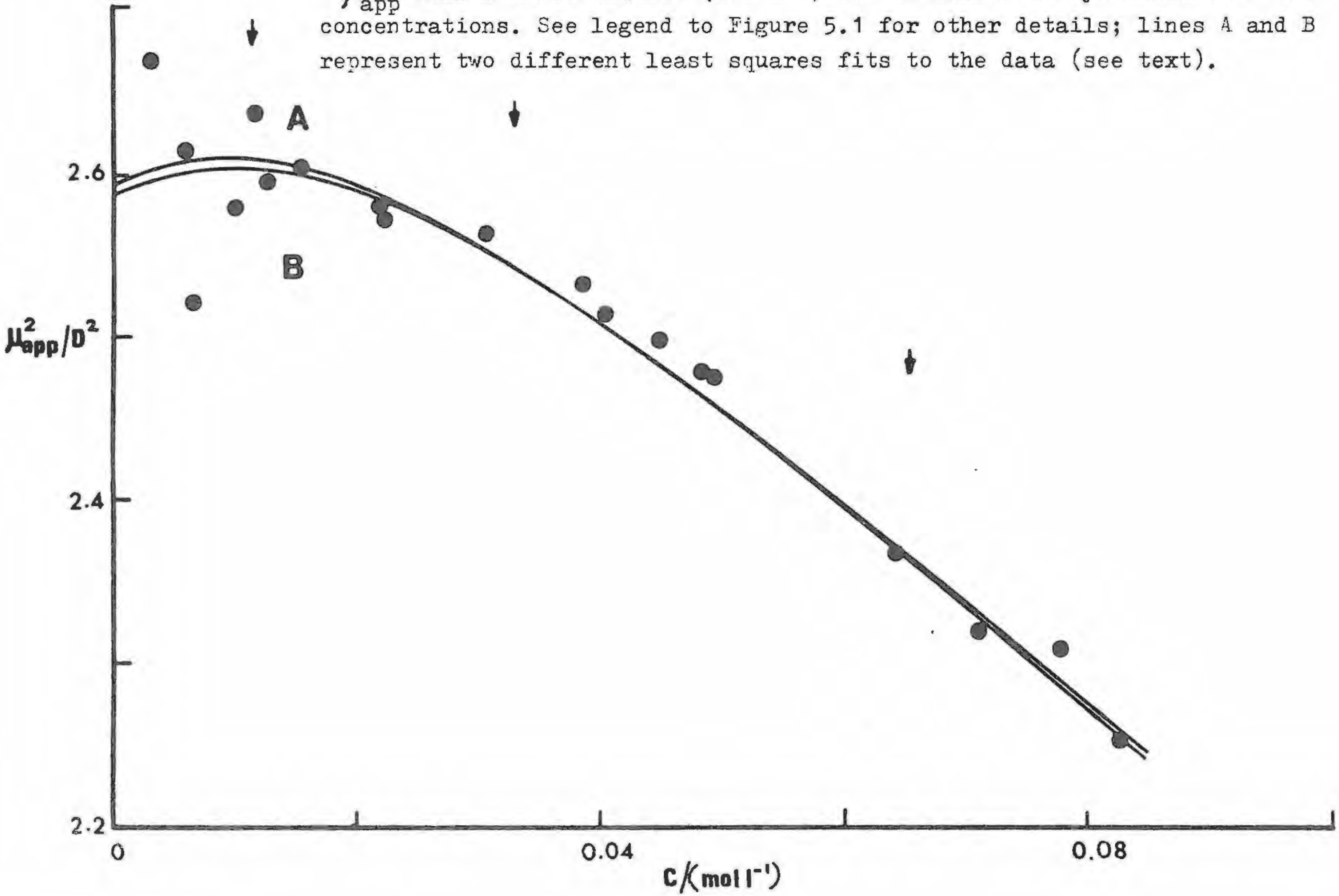


FIGURE 5.3

μ_{app}^2 versus concentration (mol l^{-1}) for 1-octanol in cyclohexane at low concentrations. See legend to Figure 5.1 for other details; lines A and B represent two different least squares fits to the data (see text).



benzene and cyclohexane solutions respectively. The values of μ^2_{app} are calculated from unsmoothed experimental values of ε, while the solid lines represent the least squares fits for the 1-2-3 models. Visual inspection of the Figures shows that the fitted curves represent the data well.

During the least squares optimisation, it became apparent that the minimum was extremely shallow, especially for cyclohexane solutions. Consequently, different sets of parameters could be found with about the same error. Experience gained during curve fitting such systems led to the finding that a unique set of parameters can be obtained if there is no error in the data i.e. fitting synthesised data. A nearly unique set of parameters is also apparently possible if the intercept at zero concentration, μ^2_1, is well defined i.e. when there is not much scatter in the low concentration data. For the data referring to cyclohexane solutions, this is clearly not true and different combinations of the parameters can be found which give approximately the same error of fit. It was found that the standard deviations of the least squares parameters (g's and K's) were large for the cyclohexane solution data, being of the order of several hundred per cent of the determined values of the parameters. Consequently, the results of the curve fitting for cyclohexane solutions are not reported.

The intercept for the carbon tetrachloride data is better defined and the intercept for benzene data is well defined; consequently, in these two cases, the minima found during the curve fitting were less shallow. Bordewijk et al.(1973) have described similar problems of non-unique parameters in fitting their data for solutions of 1-heptanol in carbon tetrachloride. To obtain consistent values for their results at different temperatures, they arbitrarily fixed μ_1^2 and g_2. While the data presented in this study extend to lower concentrations so that μ_1^2 is better defined, there is still uncertainty in this value because of the scatter of the data at low concentrations.

The values determined for benzene solutions are subject to the influence of an additional species, the high dipole moment multimer, which is clearly present in the latter part of the concentration range analysed, but which has not been allowed for in the analysis. It is not, however, physically meaningful to fit the data in the concentration range where only monomer and dimer are expected to be present since the parameters g_2 and K_2 are not then independent and only the product $g_2.K_2$ can be determined. Consequently, the equilibrium constants and correlation factor obtained from least squares fits to the data for benzene solutions are also not given.

In view of the above considerations, only the curve-fitting data for the carbon tetrachloride solutions are considered. Table 5.1 gives the best parameters obtained from the curve-fitting procedures applied to solutions of 1-, 2-, 3- and 4-octanols in carbon tetrachloride which were obtained, in each case, by iterating all four variables (μ_1^2, K_2. g_2 and K_3 with $g_3 = 0$) simultaneously. Inspection of Table 5.1 shows that, with the exception of the K_2 parameter for 1-octanol, a trend exists for the parameters K_2 and K_3 from 1- to 4-octanol : the K_2 and K_3 values decrease, as expected from the increasingly restricted environment of the -OH group. For 1-octanol the data are relatively more scattered, particularly at low concentrations. This results in an anomalous value of g_2 which

Table 5.1

Parameters from least squares fits for monomer-open dimer-closed trimer ($g_3 = 0$) model for 1-octanol, 2-octanol, 3-octanol and 4-octanol solutions in carbon tetrachloride at 25°C. The second set of parameters for 1-octanol (in parentheses) was determined with g_2 fixed at 1.5.

alcohol	$c_{max,M}^{\underline{a}}$	$\mu_{D^2}^{2}$	$K_2^{\underline{b}}$	$K_3^{\underline{b}}$	g_2	$\sigma^{\underline{c}}$
1-octanol	0.2979	2.682 ±0.018	2.013 ±1.201	16.272 ±6.468	1.92 ±0.34	0.32
		(2.677 +0.022)	(4.625 ±1.631)	(25.013 ±10.41)	1.5	0.34
2-octanol	0.7749	2.619 ±0.006	4.277 ±0.486	14.961 ±1.878	1.43 ±0.02	0.0086
3-octanol	0.8883	2.609 ±0.010	1.985 ±0.513	5.628 ±1.514	1.44 ±0.04	0.014
4-octanol	1.124	2.560 ±0.007	0.756 ±0.194	2.615 ±0.571	1.66 ±0.08	0.012

$\underline{a}$ Maximum concentration of data used in least squares fit of model

$\underline{b}$ Equilibrium constants, based on molar concentration units, for the equilibria : $nA \rightleftarrows A_n$.

$\underline{c}$ Standard deviation of fit calculated from μ_{calc}^2 and μ_{obs}^2 .

is substantially larger than that calculated for the other alcohols; because of the interactive nature of K_2 and g_2, the value for K_2 is significantly low. To confirm the trend, the value of g_2 was fixed for 1-octanol at a value of 1.5. The parameters thus calculated are enclosed in parentheses. This value is more representative of the g_2 values obtained for 2-, 3- and 4-octanols. This procedure emphasises the trend although fixing one of the parameters, in itself, has no chemical or statistical significance.

The quality of the fit through the data achieved using the 1-2-3 model is almost as good as is obtained using polynomials (up to tenth order); therefore, the fit depends on the errors of the data. The uncertainties in the calculated parameters are substantially larger for the 1-octanol data than for the data for 2-, 3- and 4-octanols because of the relatively large scatter of the data. The standard deviations of μ_1^2 are of the order of experimental uncertainty; the standard deviations of K_2 and K_3 are of the order of 20% for 2-, 3- and 4-octanol and about 50% for 1-octanol. Such errors are sufficiently large to render the calculated values unreliable. However, the order of magnitudes are a guide to the degree of association and to the effect of molecular structure on the association.

5.4.3. Analysis of Selected Models

It is recognised that the 1-2-3 model is not the only simple model which might be anticipated to fit the experimental data. Consequently a similar fitting procedure was subsequently applied for monomer-open dimer-closed tetramer (1-2-4) and monomer-open trimer-closed tetramer (1-3-4) models to the data for 1-octanol in carbon tetrachloride solutions. These results are listed in

Table 5.2. The standard deviations of the three fits are almost identical, which negates any attempts to distinguish among the models. Bordewijk et al.(1973) similarly found that 1-2-3 and 1-2-4 models each gave rise to the same error of fit.

Other models have also been proposed, notably the monomer-open trimer-cyclic octamer model, proposed by Tucker and Becker (1973), which will be discussed in Section 5.6, and the monomer-tetramer only model of Fletcher and Heller (1967). The latter model can be investigated here since it should be able to provide a reasonable fit to the concentration dependence of μ^2_{app} observed for 1-octanol solutions in cyclohexane. Assuming an arbitrary value of $\mu^2_4 = 8D^2$ for an open tetramer, and zero dipole moment for a closed tetramer with $\mu^2_1 = 2.5D^2$, selected values of the equilibrium constants for the formation of each of the assoicated species were applied to equations 4.v and vii. The curves obtained from a series of combinations of the equilibrium constants are compared with the observed behaviour of 1-octanol solutions in cyclohexane in Figure 5.4.

Depending on the relative magnitudes of K_{4open} and $K_{4cyclic}$, the curve of μ^2_{app}, calculated according to Fletcher and Heller's model, increases or decreases monotonically over the whole concentration range. Thus Fletcher and Heller's model cannot be regarded as an adequate representation of the association of alcohols, since it cannot allow for the maximum in μ^2_{app} observed at low concentrations in carbon tetrachloride and benzene solutions, nor the minimum in μ^2_{app} observed at intermediate alcohol concentrations which is a more serious limitation.

While a definitive answer may not result from this type of mathematical procedure because of the large uncertainties associated

Table 5.2

Parameters from least squares fits of different association models for 1-octanol solutions in carbon tetrachloride at 25^{o}C.

Monomer - open dimer - closed trimer (g_3 = 0) :

μ_1^2	K_2[a]	K_3[a]	g_2	σ[b]
2.682	2.013	16.272	1.92	0.032
±0.018	±1.201	±6.468	±0.34	

Monomer - open dimer - closed tetramer (g_4 = 0) :

μ_1^2	K_2[a]	K_4[a]	g_2	σ[b]
2.676	11.193	442.3	1.21	0.033
±0.023	±5.931	±342.6	±0.04	

Monomer - open trimer - closed tetramer (g_4 = 0) :

μ_1^2	K_3[a]	K_4[a]	g_3	σ[b]
2.715	65.78	883.2	1.92	0.033
±0.011	±33.61	±397.5	±0.24	

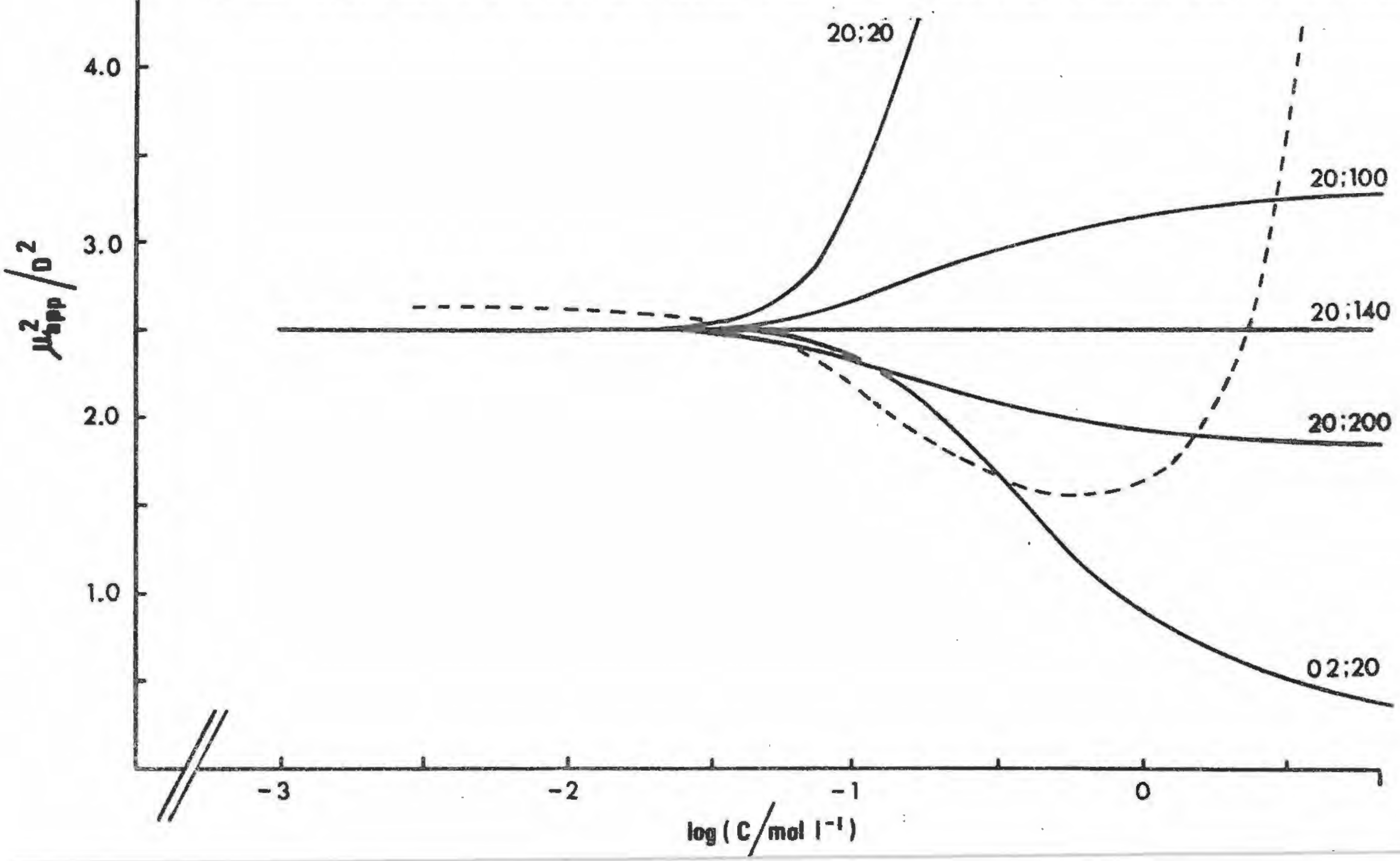
---

[a] Equilibrium constants, based on molar concentration units, for the equilibria : $nA \rightleftarrows A_n$.

[b] Standard deviation of fit calculated from μ_{calc}^2 and μ_{obs}^2 .

FIGURE 5.4

Comparison of the observed concentration dependence of μ^2_{app} (dashed line) and the behaviour predicted by the monomer-tetramer model proposed by Fletcher and Heller (1967). The curves are calculated with an arbitrary value of $\mu_1^2 = 2.5D^2$; the equilibrium constants for formation of the linear and cyclic tetramers relevant to each curve are the first and second numbers respectively printed next to the curve.



with the calculated parameters, it is useful since it does give some quantitative feeling for the relative magnitudes of the parameters involved. However, because of the large number of unknown parameters and the scatter of the data, it is difficult, or perhaps impossible, to obtain unique and physically acceptable values for both equilibrium constants and the correlation factor. There are many experiments which have the potential to yield equilibrium constants, but dielectric methods are the only ones which can yield the liquid-structure related g-value. Thus, if equilibrium constants are available from other sources, they may be used in the curve-fitting to obtain the important g-value.

5.5. Association of 2,3,4-Trimethyl-3-Pentanol.

5.5.1. Description of Permittivity and Infrared Results.

A more definitive answer regarding intermolecular association in aliphatic alcohols could possibly result from an examination of the concentration dependence of μ^2_{app} for a highly sterically hindered alcohol in which, at room temperature, the final, high dipole moment chain network is unable to form. However, studies of the association of solutions of such alcohols have not provided conclusive evidence : NMR data on solutions of 2,2,3-trimethyl-3-pentanol (2,2,3-TMP) have been explained (Biais, Lemanceau, Lussan, 1967) in terms of dimers being the only associated species. This would result in μ^2_{app} being a monotonous function of concentration, contrary to observations. The permittivity studies of Raczy *et al.* (Raczy, Constant, Lebrun, 1967) on solutions of the same alcohol suggest a maximum in g at low alcohol concentrations; the few data points do not justify a definite conclusion, however. Consequently, an investigation of the similar alcohol 2,3,4-trimethyl-3-pentanol (2,3,4-TMP) was undertaken.

The concentration dependence of μ^2_{app} in each of the solvents is shown in Figure 4.7. The shapes of the curves indicate an equilibrium among monomers, high dipole moment species and low dipole moment oligomers. No linear chains at high concentration are evident since μ^2_{app} decreases continuously, after the maximum at low concentration, to the value for the pure alcohol without passing through a further turning point. The low concentration maximum observed confirms that implied in the earlier studies of Raczy et al. while the subsequent decrease in μ^2_{app} shows that one must consider at least two associates of different size to explain the association behaviour of sterically hindered alcohols. This assumes that different, sterically hindered alcohols in which the high dipole moment species are not formed at high alcohol concentrations, exhibit qualitatively similar association behaviour.

From the shapes of the curves of Figure 4.7, we may also conclude that the influence of the solvent on the rate of formation of the associated species is similar to that observed for the straight chain octanols.

The infrared spectra depicted in Figure 4.8 show only two absorption bands, one near 3640 cm^{-1} and the other near 3500 cm^{-1}. No other bands appear as the alcohol concentration is increased. However, using a Perkin-Elmer model 180 infrared spectrophotometer (which became available only near the conclusion of these studies), the low frequency band was observed to shift from above 3500 cm^{-1} in dilute solutions to 3490 cm^{-1} in the pure alcohol. The appearance of only two bands for solutions of this alcohol is in marked contrast to the behaviour of the other alcohols studied, in which a decrease in μ^2_{app} with increasing concentration was associated with the appearance and increasing intensity of a peak near 3350 cm^{-1}.

5.5.2. Interpretation of Infrared and Permittivity Results.

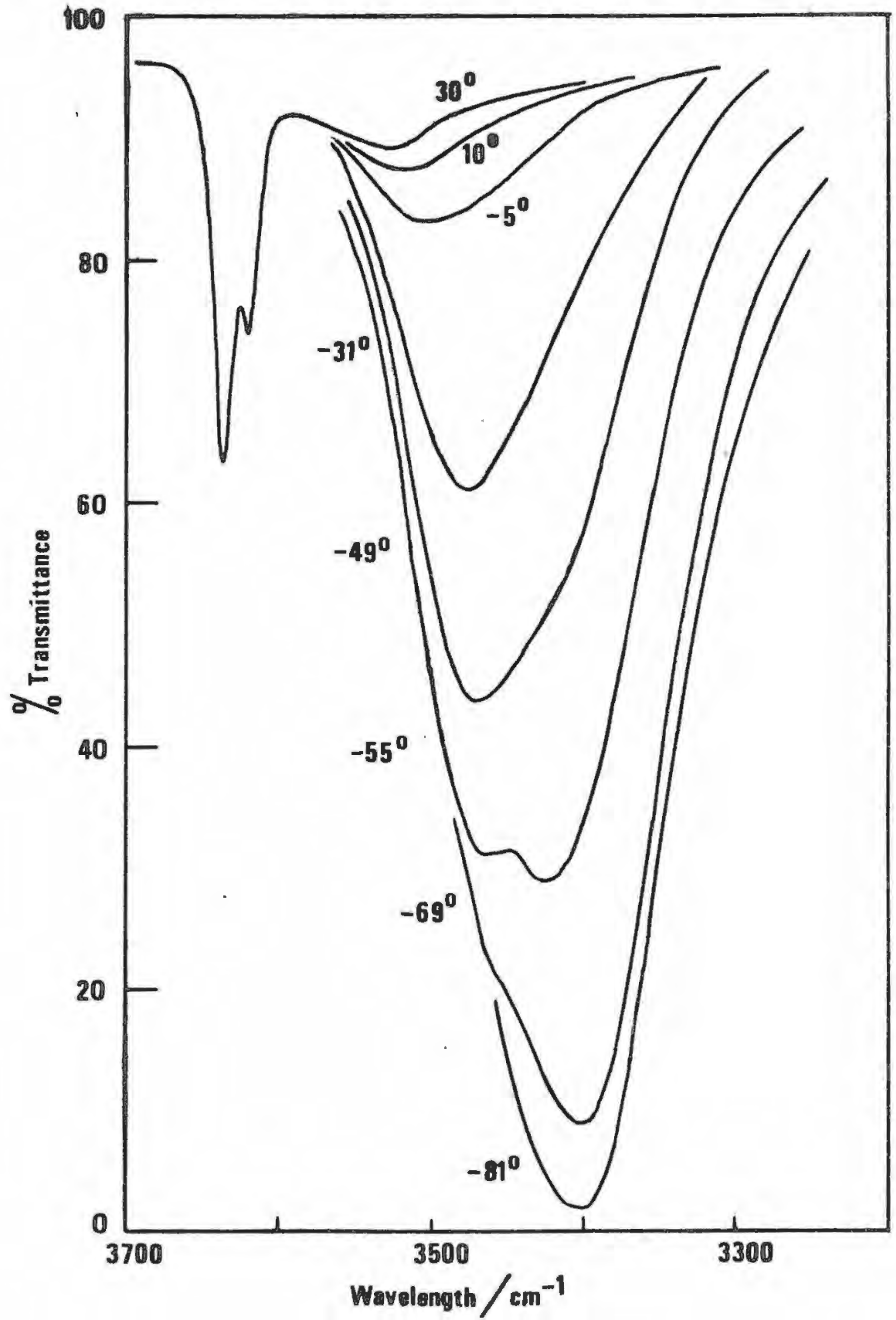
The very low concentration spectra depicted in Figure 4.8 show a peak near 3640 cm^{-1} arising from the -OH of an alcohol monomer; even at very low concentration, a shoulder, about 10 cm^{-1} lower in frequency, is evident. Using the higher resolution of the Perkin-Elmer 180 spectrophotometer, the shoulder is observed to be a peak whose intensity does not alter with concentration. A similar low frequency peak was observed by Smith and Creitz (1951), Geiseler, Fruwert and Stökel (1962) and Flynn, Werner and Graham (1959). If the absorption at this shoulder arises from the terminal -OH of an open dimer as suggested by Smith and Creitz, one would expect its intensity to be concentration dependent, contrary to observation. Flynn *et al*. observe a similar absorption for all alcohols which have the structure $R-CH_2-O$ and ascribe the absorption to Fermi resonance between the -OH and a combination band associated with a $-CH_2-O$ absorption. Although the source of the absorption may be uncertain, its characteristics indicate that it arises from a property of the alcohol geometry rather than the association behaviour of the solutions.

The spectra show the appearance, at higher concentrations, of a peak near 3500 cm^{-1} which, as before, is associated with the formation of high dipole moment species in solution. The small decrease in frequency of the band maximum with increasing concentration indicates that an overlapping band, at slightly lower frequency, is growing in intensity, presumably owing to an increase in the concentration of the species giving rise to this band. From the observed concentration dependence of μ^2_{app}, this species will have a low dipole moment. The cyclic multimers formed by sterically hindered alcohols are expected to have weaker hydrogen bonds because of the restricted environment of the -OH group. Consequently, the -OH groups of the cyclic species formed by hindered alcohols would be expected to absorb at higher frequencies than the -OH groups of similar species formed by alcohols in which the -OH group is not restricted (where the absorption is at about 3350 cm^{-1}). Such behaviour was observed by Smith and Creitz, who examined the spectra of increasingly hindered derivatives of 3-pentanol. As the alcohol becomes more hindered, the frequency maximum of the band which occurs near 3350 cm^{-1} for non-hindered alcohols moves to higher frequencies until, for 2,4-dimethyl-3-ethyl-3-pentanol (which is very similar to 2,3,4-TMP) there is overlap of the band with that near 3500 cm^{-1} (see Figure 1.3). The absorption band near 3500 cm^{-1} in 2,3,4-TMP is therefore considered to contain contributions from one band whose frequency maximum is above 3500 cm^{-1} and another, whose frequency maximum is below 3500 cm^{-1} and which is associated with low dipole moment oligomers.

Additional evidence is available to suggest the overlap of the two absorption bands. The temperature dependence of the absorption of a dilute (0.03 M at 25°C) solution of 2,3,4-TMP in n-hexane was examined and is depicted in Figure 5.5. (The solvent n-hexane was chosen because of its low freezing point.) As the temperature is lowered, both of the above absorptions shift to lower frequencies but the peak representing the cyclic species evidently moves faster. Splitting of the absorption region is observed at about -55°C and at lower temperatures the low frequency peak dominates the absorption. An alternative interpretation is that a low frequency peak develops at low temperatures independently of the overlapping peaks which occur

FIGURE 5.5

Infrared spectra of 2,3,4-trimethyl-3-pentanol in n-hexane (0.03 mol l^{-1} at $25^{o}C$) at various temperatures, recorded using a 1mm sample cell and Perkin-Elmer model 180 spectrophotometer.



at room temperature. This new peak would then represent either another cyclic, low dipole moment species or a high dipole moment species as normally occurs in non-hindered alcohols. The existence of a high dipole moment species is, however, unlikely in view of the studies of Johari and Dannhauser (1968) who have shown that the dipole moments of undiluted, sterically hindered alcohols (for example 3,4-dimethyl-3-hexanol) decrease as the temperature is lowered to -100^{o}C. By contrast, the dipole moments of most unhindered alcohols increase as the temperature decreases (Dannhauser, 1968a). We may thus conclude that the high dipole moment multimer network does not form for alcohols in which the -OH experiences a very restricted environment.

If space-filling molecular models are used to construct possible hydrogen bonded multimers for 2,3,4-TMP, it is found that linear dimers, cyclic trimers and tetramers and even linear chains are sterically possible. However, it is not possible to form bifurcated bonds which have been postulated as being necessary to stabilise the terminal -OH group of a linear chain at high concentrations. One may then postulate that the high dipole moment species do not form in solutions of sterically hindered alcohols because the terminal -OH groups of the linear chains cannot be stabilised by interaction among the chains. The cyclic species would, under these circumstances, be energetically more favourable and would be expected to dominate the solution properties at high concentration.

5.5.3. Quantisation of the Association Model.

As before, the simplest models, consistent with experimental behaviour, were considered to test the qualitative understanding of the association behaviour. Thus monomer-high dipole moment small oligomer-low dipole moment larger oligomer models were considered to represent the concentration dependence of μ^2_{app} over the whole concentration range. Two different models, 1-2-3 and 1-2-4 (using the same momenclature as in Section 5.4.), were examined for each alcohol/ solvent system and the results obtained are listed in Table 5.3. In some cases the fit did not converge and the parameters given are not necessarily the best; these parameters are enclosed in parentheses. The standard deviations of the fits are generally larger than those noted for the fits to the data for 1-, 2-, 3- and 4-octanol solutions. The uncertainties in the calculated parameters are such as to make the parameters unreliable. The standard deviations show that the 1-2-4 model fits best for carbon tetrachloride and benzene solutions, while the 1-2-3 model represents the cyclohexane data best. The relative values of the equilibrium constants reflect the qualitative understanding of the μ^2_{app} curves : association occurs readily in cyclohexane solution but increasingly less so on going to carbon tetrachloride and to benzene solutions.

5.5.4. Information Gained From NMR Experiments.

The NMR chemical shift of the -OH proton as a function of concentration for 2,3,4-TMP solutions in carbon tetrachloride (Figure 4.9) adds little extra definitive information because the observed curve is essentially featureless, being a monotonous function of concentration. The end group of the open species will have a chemical shift similar to that of the monomer; consequently little change in the chemical shift is observed at low concentrations since the only contribution to a change comes from the proton of a bonded -OH group, weighted according to its concentration. The appearance of the cyclic species at higher concentrations occasions a swifter

Table 5.3

Parameters from least squares fit for two models for 2,3,4-trimethyl-3-pentanol in solution, over the whole concentration range, at 25°C.

A. Parameters from permittivity

		Solvent	
	Cyclohexane	Carbon Tetrachloride	Benzene
		Monomer - open dimer - closed trimer ($g_3 = 0$)	
μ_1^2	2.185 ± 0.020	2.325 ± 0.018	$(2.162)^c$
K_2^a	4.292 ± 2.013	1.339 ± 0.538	$(0.0187)^c$
K_3^a	5.427 ± 3.486	1.856 ± 0.803	$(0.104)^c$
g_2	1.204 ± 0.033	1.617 ± 0.115	$(11.4)^c$
σ^b	0.027	0.0644	$(0.047)^c$
		Monomer - open dimer - closed tetramer ($g_4 = 0$)	
μ_1^2	$(2.102)^c$	2.261 ± 0.022	2.171 ± 0.012
K_2^a	$(249.9)^c$	27.59 ± 9.93	0.113 ± 0.069
K_4^a	$(14335)^c$	206.2 ± 138.0	0.0381 ± 0.018
g_2	$(1.09)^c$	1.176 ± 0.013	2.126 ± 0.475
σ^b	$(0.039)^c$	0.023	0.039

a Equilibrium constants based on molar concentration units.
b Standard deviation of fit calculated from μ^2_{calc} and μ^2_{obs}.
c Convergence not achieved.

B. Parameters from NMR data.

The following parameters were obtained for a 1-2-3 model:
$K_2 = 7.80 \pm 3.23$, $K_3 = 20.54 \pm 9.85$, $\delta_1 = 0.622 \pm 0.005$, $\delta_2 = 0.789 \pm 0.167$, $\delta_3 = 5.234 \pm 0.379$, $\sigma = 0.0089$. No convergence was achieved with a 1-2-4 model.

change in the chemical shift : the increasing concentration of this species, all of whose hydroxyl groups are involved in hydrogen bonding, results in a relatively large change in the observed chemical shift.

The chemical shift data may be quantised similarly to the dipole moment data using the Gutowsky-Saika equation (1.xxi). The relevant equation is then

$$\delta = {}^{1}/c \sum_{i} iK_i (c_1)^i \delta_i \qquad 5.iii$$

where $c = \sum_{i} iK_i (c_1)^i$ as before (equation 4.v). In addition to the previously noted 1-2-3 and 1-2-4 models, monomer-trimer (1-3) and monomer-tetramer (1-4) models, which have often been suggested (Davis and Deb, 1970), were considered. In accordance with the interpretation of the dipole moment results, the oligomer for the 1-3 and 1-4 models was assumed to have zero dipole moment.

Since the NMR experiments were conducted at 35°, the quantitative results cannot be directly compared to the corresponding dipole moment results.

The uncertainties in the calculated parameters are similar to those noted for parameters calculated from dipole moment data, being of the order of 30% of the calculated parameters themselves. Convergence could not be achieved with the 1-2-4 model, even though this was the preferred model from the dipole moment results. A good fit was obtained for the 1-2-3 model, the parameters for which are included in Table 5.3. This contrast may be a consequence of the inherent uncertainty of curve-fitting procedures or may in fact be genuine and result from a shift in equilibrium between cyclic trimers and tetramers, assuming, of course, that the equilibrium is indeed that postulated here. Least-squares fits for the 1-3 and 1-4 models gave significantly poorer fits as expected.

Since the standard deviation of the data is similar to that found for the data obtained from permittivity studies, the uncertainties in the values of K_2, K_3, δ_2 and δ_3 are substantial. This, coupled with the generally unstructured chemical shift data, limits the potential of the method.

5.6. Association of t-Butanol in Hexadecane Solutions.

Having accounted, in general terms, for many of the features of the concentration dependence of μ^2_{app} for solutions of various octanols, it remains to be seen whether the similar use of infrared and dielectric techniques can successfully explain data obtained from solutions of alcohols other than octanols. Similar thoughts motivated recent studies by Tucker and Becker (1973) who examined the equilibrium behaviour of t-butanol in hexadecane using vapour pressure, infrared and NMR techniques. They wished to ascertain whether a monomer-open trimer-cyclic octamer model, favoured for solutions of methanol in hexadecane (Tucker, Farnham and Christian, 1969) could be successfully applied to the former system. t-Butanol was selected since its steric properties are expected to modify the association behaviour noted for methanol, while hexadecane satisfied their requirements for a non-polar, inert solvent of low vapour pressure. Accordingly, the present study was undertaken to find if the combination of dielectric and infrared techniques could, by providing complementary information, extend the information provided by Tucker and Becker.

As shown by Figure 4.10, the general pattern of the concentration dependence of μ^2_{app} for t-butanol solutions in hexadecane is similar to that of 1-octanol in non-polar solvents (Figure 4.1). Similarly, the infrared spectra of t-butanol solutions in carbon tetrachloride and hexadecane (Figure 4.11) indicate qualitatively similar behaviour. The association behaviour of t-butanol may therefore be described in terms of species similar to those occuring in octanol solutions.

The most significant feature of the infrared results for hexadecane solutions is that at least two, distinct associated species (represented by the 3514 cm^{-1} and 3358 cm^{-1} bands) appear in the infrared spectra more-or-less simultaneously, i.e. the monomer never occurs in equilibrium with only a single associated species. By contrast, the spectra for solutions of t-butanol in carbon tetrachloride shown in Figure 4.11, as well as spectra recorded by Liddel and Becker (1957) on the same system, indicate that the peak near 3500 cm^{-1} has a different concentration dependence from the peak near 3350 cm^{-1}. Thus, at low concentrations (below 0.05 mol ℓ^{-1} at 25°C) in carbon tetrachloride, the peaks near 3600 cm^{-1} and 3500 cm^{-1} are present without a significant intensity of the peak near 3350 cm^{-1} (for 1 mm cell length). Similar behaviour was observed for 1-octanol in carbon tetrachloride and in benzene solutions. The considerably different concentration dependencies of the 3350 cm^{-1} absorption band of alcohols in the various solvents appears to invalidate Tucker and Becker's and Tucker, Farnham and Christian's (1969) suggestion that the two absorptions arise principally from different -OH groups in the same species if it can be assumed that the important oligomer species are the same for a given alcohol in cyclohexane, carbon tetrachloride and benzene solutions.

The results presented in this study must be compared more closely with those observed from other techniques in order to elucidate the maximum information and to clarify points of agreement and conflict. In Figure 4.10, curves (ii) and (iii) represent the results of Tucker and Becker derived from NMR chemical shift and vapour pressure studies respectively, on the same concentration axis. It will be noted that discontinuities in all three curves occur at roughly the same concentration. There is, of course, a different bias to each curve depending on the weighting attached to each oligomer as appropriate to the respective technique: the NMR chemical shift is weighted according to the number of -OH protons of each kind and their chemical shifts, the vapour pressure according to the number, alone, of each species present (i.e. it is a colligative property) and μ^2_{app} according to the number of species of each kind and their dipole moments squared.

The two straight lines in the log-log plot of the vapour pressure derived function (Figure 4.10; curve (iii)) have slopes of about 2.8 and 5 respectively. This was taken by Tucker and Becker, on the basis of the function plotted, to indicate that the first important species is a trimer, supplemented by at least a hexamer at concentrations beyond the break(at roughly 0.1 mol ℓ^{-1}) in the vapour pressure function plot. The infrared spectra show that it is necessary to consider the simultaneous formation of two polymers in this lowest portion of the concentration range, a conclusion which is reinforced by comparison with the dielectric data since the concentration at which spectrum IIa was recorded is close enough to the discontinuity in curve (i) to indicate that a significant concentration of the second, low dipole moment oligomer is already present. In terms of Tucker and Becker's analysis, this implies that the portion of the vapour pressure function plot at concentrations below the first break is already weighted by contributions from two species, suggesting that the first species is indeed a dimer (since the initial slope of curve (iii) is 2.8) which must, following the dielectric formation, be of high dipole moment and therefore an open species. This open character is in accord with Tucker and Becker's conclusion. The second oligomer species is, again from dielectric information, clearly of low dipole moment and, therefore, probably cyclic. In Tucker and Becker's model, this cyclic species is actually treated as an infinite set of cyclic species with related equilibrium constants i.e. their favoured association model is 1-3-∞. This model is favoured because it provides better correlation of both vapour pressure and NMR data than any other model considered. There would seem to be no experimental justification for invoking an infinite series of oligomers. Rather, it is considered preferable to treat the cyclic species as a discrete, stable entity on the previously stated principle of considering the simplest hypothesis compatible with experimental observations.

The monotonous curve obtained from the concentration dependence of the NMR chemical shift of the -OH proton adds little to the understanding of the association behaviour. As noted for 2,3,4-TMP solutions, the appearance of the cyclic multimeric species is associated with a swifter change in the chemical shift. This contrasts with the relatively small effect of the appearance of the cyclic species on the vapour pressure plot.

In view of the similarity of the concentration dependencies of μ^2_{app} for 1-octanol solutions and for t-butanol in hexadecane, the models applied to the former systems viz. 1-2-3, 1-2-4 and 1-3-4, were considered for the low concentration t-butanol solutions. However, the standard deviations between the calculated and observed values of μ^2_{app} for each model are, as for 1-octanol solutions in carbon tetrachloride, not significantly different. More seriously, the uncertainties in the calculated parameters (g's and K's) were found, in some cases, to be of the order of several hundred per cent of the calculated value. Consequently, the results of this curve-fitting are not given. The lack of success in obtaining statistically meaningful parameters is apparently the result of the large uncertainty of the limiting value of μ^2_{app} at zero concentration. Similar difficulties have already been noted for the data on 1-octanol solutions in cyclohexane.

From the studies discussed here, it seems that the association model developed from studies of octanol solutions may be generally applied to alcohol solutions in solvents which do not form formal hydrogen bonds, provided that the alcohol is not so hindered as to preclude the formation of chain-like networks. However, in spite of the understanding gained about the low concentration association behaviour, relatively little is understood about the associated networks proposed as existing at high concentrations. Accordingly, an investigation of concentrated alcohol solutions, for selected alcohols in the three solvents cyclohexane, carbon tetrachloride and benzene, was undertaken by means of dielectric relaxation and viscosity measurements.

5.7. Study of Molecular Association in Concentrated Alcohol Solutions.

5.7.1. Dielectric Relaxation Behaviour of Concentrated Alcohol Solutions.

As has been noted in Section 1.2, a principal feature of the Cole-Cole plots observed for relatively concentrated (> 30 mole %) solutions of most primary and secondary alcohols in non-polar solvents is the adherence of the low frequency absorption to Debye behaviour (although conditions can be created in which non-Debye behaviour is observed); i.e. the relaxation process appears to be described, within experimental error, by a single relaxation time. However, in spite of the uniformity of this behaviour, the relaxation times characterising such plots have repeatedly been shown to be influenced by the solvent, by the solute concentration and by the temperature as well as by the particular alcohol studied (Koshii et al., 1974; Sagal, 1962; van den Berg et al., 1973; Hanna and Hakim, 1971, 1972). It therefore seemed useful, in view of the limited understanding of the association behaviour in concentrated alcohol solutions, to examine the concentration dependence of and influence of solvent on the relaxation times for solutions of some straight chain alcohols in the non-polar solvents utilised for static permittivity studies.

The Cole-Cole plots observed in this study follow the expected trends : the plots exhibit the Debye semi-circle (see Figures 4, 14, 15, 16) characteristic of a single relaxation time rather than the depressed or skewed arc characteristic of distributions of relaxation times; the magnitude of the low frequency dispersion, $\varepsilon_{0,1}-\varepsilon_{\infty,1}$ decreases with decreasing alcohol concentration. The values of the relaxation time, τ, at any given concentration are observed to decrease as the proton-accepting ability of the solvent increases. This trend, which is consistent with that reported for other systems (Crossley, 1970) may probably be ascribed to a slowing down of the reorientation process of the alcohols because of increased interaction with the solvent.

As has been shown in Figure 4.17 and 18 and noted in sub-section 4.3.3, a principal feature of curves of τ against alcohol concentration, observed for these alcohol solutions, is a maximum in τ whose magnitude and position on the concentration axis are sensitive to the chain length of the alcohol and the nature of the solvent. The maximum moves out of the available concentration range with increases in the alcohol chain length (Figure 4.17) and the proton-accepting ability of the solvent (Figure 4.18) and decreases in magnitude as the proton-accepting ability of the solvent increases (Figure 4.18). In addition, Sagal's temperature studies (1962) of the relaxation characteristics of ethanol solutions in cyclohexane suggest that the maximum becomes less pronounced and shifts to higher concentrations with increasing temperature. This temperature dependence implies that the concentration dependence of the relaxation time is similarly influenced by increases in the proton-accepting ability of the solvent and the temperature of the solution. The concentration and temperature dependencies of τ, in this concentration range, are related to the break-up of the hydrogen bonded multimers formed in concentrated alcohol solutions, since the low frequency dispersion is observed only for alcohols which form such multimers (Crossley, 1970). However, the complex concentration dependence of τ as a function of the solvent and of the temperature as well as of the alcohol implies that self-association in alcohol solutions is not as simple as the monotonous increase in both the viscosity (Bamelis _et al._, 1965) and μ^2_{app} (Huyskens _et al._, 1963; Clerbaux and Zeegers - Huyskens, 1966) with increasing concentration seem to indicate.

5.7.2. Concentration Dependence of the Reduced Relaxation Time.

The concentration dependencies of the reduced relaxation time, $^{\tau}/\eta$, (Figures 4.20 and 21) were examined for solutions of selected alcohols in an attempt to facilitate an interpretation of the concentration dependence of τ. The most interesting result then observed is that each of the alcohols studied (even those of larger carbon number) exhibit qualitatively similar behaviour : for each alcohol/solvent system, a maximum in $^{\tau}/\eta$ appears with increasing concentration. In cyclohexane solutions, the maximum appears at about 50 mole % of alcohol, but shifts to higher concentrations and is slightly decreased in magnitude for solutions in which the solvent exhibits greater proton accepting ability than does cyclohexane.

This similarity of behaviours supports the assumption made in Section 4.3 that simply dividing τ by η removes at least part of the contribution of viscosity to the relaxation time. Alternatively, the ratio may be considered in terms of Kauzmann's rate theory of relaxation, which has been discussed in Section 1.2. The activation energy, which appears in the exponential, may be estimated as the sum of the energy required for hydrogen bond rupture (assuming, as will later be justified, that Dannhauser and Flueckinger's theory (1970) of the relaxation mechanism is tenable) and of that required for reorientation of the freed species in its local environment. Similarly, the viscosity may also be treated as a rate process with the corresponding activation energy being that required for reorientation. The ratio may then be considered to remove or, at least, reduce the latter contribution to the rate expression.

In his studies of the temperature dependence of the relaxation times for alcohol solutions, Sagal (1962) interpreted his results in terms of a frequency factor, ν_c^o, and an activation energy for reorientation, E_a ; the relationship between ν_c^o and E_a has been discussed in sub-section 1.2.5 (equation 1.xviii).

The frequency factor includes a "configuration" factor which measures, "...... the frequency with which a dipole finds itself in a local environment favourable for reorientation, independent of whether or not it possesses enough energy to surmount the energy barrier." Given the inverse relationship between τ and ν, the reduced relaxation time will be considered, for the purposes of this discussion, as inversely dependent on ν_c^o. This argument may be developed alternatively : describing

$$\tau = \tau_o \exp[(H + E)/RT] \ , \qquad 5.iv$$

where H is the activation energy for hydrogen bond rupture and E the activation energy for reorientation, the viscosity may be similarly expressed :

$$\eta = \eta_o \exp(E/RT) \ . \qquad 5.v$$

Then $\quad {}^{\tau}/\eta = {}^{\tau_o}/\eta_o \exp(H/RT)$; $\qquad$ 5.vi

or $\quad {}^{\eta}/\tau = {}^{\eta_o}/\tau_o \exp(-H/RT)$,

which may be compared with

$$\nu_c = \nu_c^o \exp(-E_a/RT) \ ,$$

the relationship utilised by Sagal. (It should be noted that equation 5.v represents the temperature dependence of viscosity over only a small range of temperature (Mallikarjun and Hill, 1965). However, the small temperature range to be considered justifies use of the equation).

This interpretation of the reduced relaxation time would seem to to indicate that ${}^{\tau}/\eta$ should be approximately constant for pure alcohols in which the low frequency dispersion region is observed since it is unlikely that the energy required for hydrogen bond rupture in a hydrogen bonded network would vary greatly in the series of small and medium chain-length primary and secondary alcohols. Values of $^{\tau}/\eta$ for some pure alcohols are listed in Table 5.4.

Certain details of the information in Table 5.4 should be noted : the values for ethanol, obtained from interpolation of Sagal's data, cannot be compared directly with the values for the other alcohols in view of the reported (Middelhoek and Böttcher, 1966) inaccuracies in Garg and Smyth's (1965) relaxation times. However, since these inaccuracies are systematic, a comparison within the results incorporating Garg and Smyth's data is valid. In spite of the scatter at any given temperature, part of which probably results from inaccuracies in the viscosity as well as the relaxation data, the reduced relaxation times may be assumed to be independent of the alcohol chain length since the scatter appears to be largely random. The values listed in Table 5.4 also suggest a decrease in $^{\tau}/\eta$ with increasing temperature which is expected from Debye's model in which $^{\tau}/\eta$ is inversely proportional to temperature. A table of $^{\tau T}/\eta$ should produce values which are independent of both the alcohol chain length and of temperature. Such a table (Table 5.5), however, shows a residual temperature effect. In spite of the small, not unexpected, differences between the anticipated and observed behaviours obtained from considering $^{\tau}/\eta$ as described above, the broad concurrence encourages further development of this concept towards an interpretation of the molecular rôle in the relaxation process.

In the preceding sections, non-hindered alcohol molecules have been described, from a consideration of the concentration dependence

Table 5.4

Values of $^{\tau}/\eta$ (ps. cp^{-1}) for various alcohols at three temperatures

	Ethanol	Propanol	Butanol	Pentanol	Hexanol	Heptanol	Octanol
20°C	$(170)^a$	191^a	227^b	182^b	224^c	209^b	199^b
40°C	$(143)^a$	152^a	215^b	161^b	175^c	–	–
60°C	–	143^b	152^b	144^b	137^c	–	–

Relaxation times are those reported by Garg and Smyth except for ethanol for which Sagal's data (1962) were interpolated. The value of τ_1 for propanol at 40°C reported by Garg and Smyth is rather high, possibly as a result of a typographical error. Consequently a modified value of 213ps, calculated from a plot of ε' against $\varepsilon''\omega$, was used.

a Viscosities obtained from Handbook of Chemistry and Physics, 47th edition, Chemical Rubber Company, Ohio.

b) Viscosities calculated from equations and constants listed in International Critical Tables, Vol. VII, McGraw-Hill, New York, 1930.

c) Viscosities reported by Hovorka, Lankelma and Stanford (1938).

Table 5.5

Values of $\frac{\tau . T}{\eta} \times 10^{-4}$ (ps. K cp^{-1}) for various alcohols.

	Ethanol	Propanol	Butanol	Pentanol	Hexanol	Heptanol	Octanol
20°C	4.98	5.60	6.66	5.34	6.57	6.13	5.83
40°C	4.48	4.76	6.73	5.04	5.48	-	-
60°C	-	4.76	5.06	4.80	4.56	-	-

The relaxation times and viscosities used to construct the above table are those used for Table 5.4.

of μ^2_{app}, as associating into an increasingly complex hydrogen bonded network at high concentrations. While it is feasible to associate the relaxation process with some characteristic property of this network, one cannot consider the relaxation time as being determined by motion of the multimers of the network since the size of such multimers would decrease with rising temperature, leading to a temperature dependence of the activation energy for the process. Such a dependence is not observed. The relaxation process seems, then, to require explanation in terms of movement of a discrete species existing in high concentration solutions. The theories of Dannhauser and Flueckinger (1970) and of Bordewijk et al. (1969) provide such an explanation. However, Bordewijk's concept of cooperative movement of a high dipole moment cyclic oligomer and its surroundings seems unable to account for the observed maximum in $^{\tau}/\eta$ as a function of concentration. Thus we continue with Dannhauser and Flueckinger's theory in which hydrogen bond rupture occurs, not as the rate determining step, but as a prerequisite for reorientation which then occurs as a cooperative process with a favourable disposition of the surroundings.

Being more specific about the "favourable disposition" of the surroundings, we may adopt Sagal's (1962) concept of the approach of a third oxygen favourably oriented for a "switch", causing a reduction in the energy barrier for hydrogen bond rupture. This argument implies that the rate of reorientation will be directly related to the fraction of "free" hydroxyl groups, i.e. hydroxyl groups whose oxygen atoms are not already involved in hydrogen bonding. Such hydroxyl groups are those of alcohol monomers or those at the end of hydrogen bonded chains. Making justifiable assumptions and approximations, Sagal calculated, from published data (Becker et al., 1958) the concentration dependence of the fraction, F_A, of ethanol molecules that are chain ends or monomers and produced curve (a) of Figure 5.6.

Sagal considered F_A and the alcohol mole fraction, X_A, to be directly proportional to the frequency factor :

$$\nu_c^o \propto X_A . F_A .$$

Therefore, from the concentration dependence of F_A, it is expected that the decrease in F_A as a function of concentration will more than overcome the increase in X_A leading to decreasing values of ν_c^o with rising concentration. It is reasonable to assume that concentration dependence of F_A for other straight chain alcohols is qualitatively similar to that for ethanol since, in this concentration range, many physical properties of solutions of non-hindered alcohols exhibit qualitatively similar behaviour. Therefore a decrease in ν_c^o and a rise in $^\tau/\eta$ is expected and, in fact, observed for straight chain alcohols as the alcohol concentration increases from low concentrations.

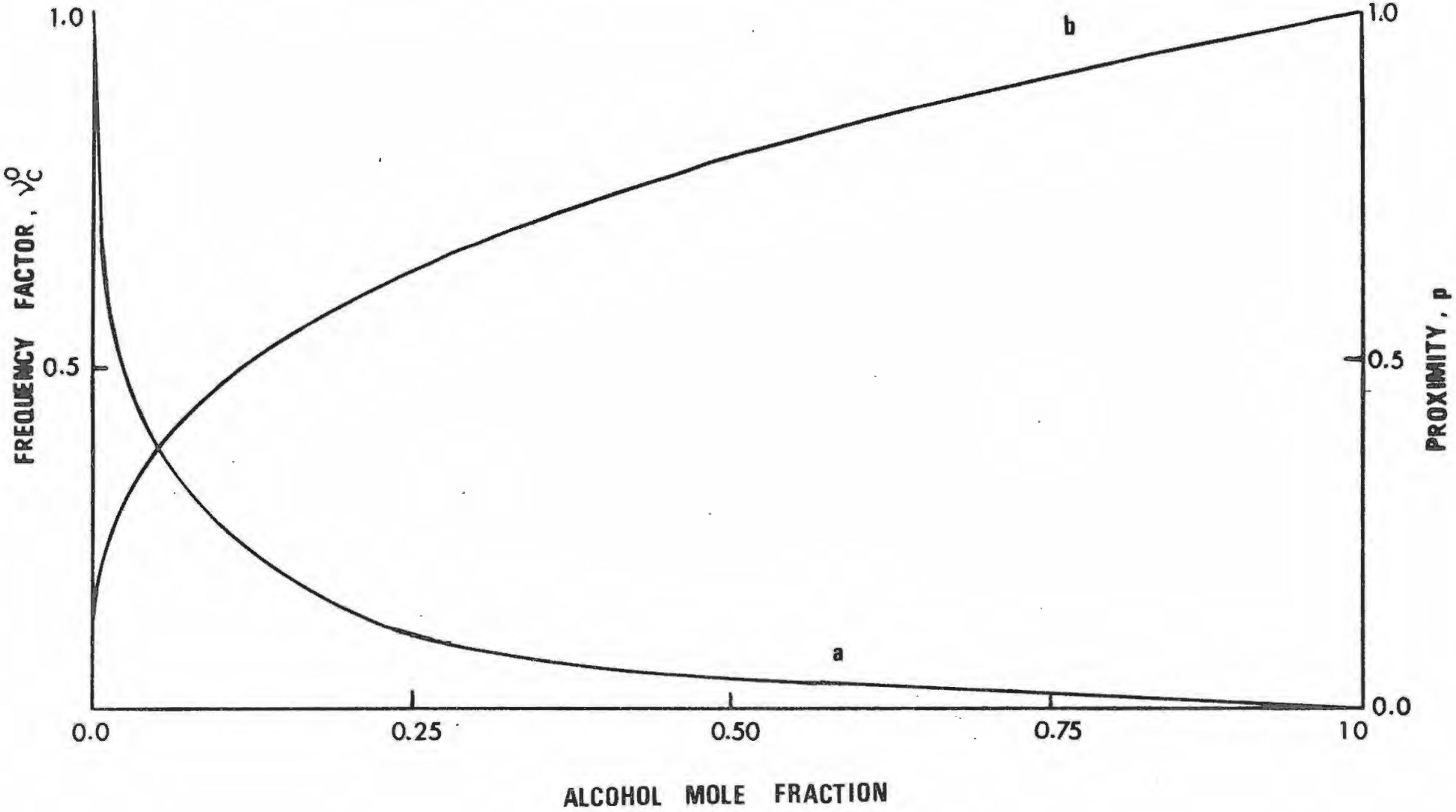
However, a second effect obviously becomes increasingly important as the alcohol concentration rises, since $^\tau/\eta$ is shown to decrease at high alcohol mole fractions : this may be termed a "proximity effect". As the hydrogen bonding in a solution becomes more extensive, the linearly associated chains will presumably become increasingly entangled. There will also be an increasing extent of network formation. The total effect is a decrease in the separation of all species or, alternatively, an increase in the proximity of species. The intermolecular distance, S, may be estimated; thus, assuming spherical particles

$$NS^3 \propto V = {}^k/X \qquad 5.viii$$

where N is the number of particles, V is the molar volume and k is

FIGURE 5.6

Comparison of the concentration dependence of the frequency factor, ν_c^o, (Sagal, 1962) curve a, and the proximity, p, (see text) curve b.



a proportionality constant. The proximity, p , may be related to S as

$$p = {}^{1}/S = \left(\frac{X.N}{k}\right)^{1/3} \qquad 5.ix$$

and a plot of p against X gives curve (b) of Figure 5.6. By this argument, the concentration dependence of the "proximity effect" will be contrary to that of F_A, giving rise to a decrease in ${}^{\tau}/\eta$ (and an increase in ν_c^o) with increasing alcohol concentrations. The detailed shape of the curve of ${}^{\tau}/\eta$ as a function of concentration will depend on the relative weightings of curves (a) and (b) of Figure 5.6; but it is not difficult, or unreasonable, to envisage a resultant curve similar to those observed for the concentration dependence of ${}^{\tau}/\eta$ for several alcohols in solutions of non-polar solvents (Figures 4.20 and 21).

5.7.3 Concentration Dependence of the Relaxation Time

While the concentration dependence of ${}^{\tau}/\eta$ may be explained by considering the ratio as the time for reorientation of the dipole with a reduced contribution from movement of the hydrocarbon part of the species, it remains to be seen whether inclusion of the latter contribution facilitates an explanation of the concentration dependence of τ. In particular, the relative importance of the contribution from hydrocarbon movement compared with the influence of the effect of proximity for the various alcohols must be examined. (The contribution from dipole reorientation is considered as similar for all alcohols in view of the similarity of hydrogen bonding expected in the linear multimers.) For short chain primary alcohols (with less than six carbon atoms in the alkyl chain), the molar concentration attains high values because of the small chain size.

This leads to the "proximity effect" having a significant influence which, coupled with the reduced hindrance to rotation resulting from the smaller, less bulky, side chains, leads to a net decrease in the relaxation time at high concentrations. As the length of the alkyl chain increases, the decrease in τ should become less marked, eventually disappearing as the second contribution, which appears in the exponential term of the relaxation expression, increasingly dominates the behaviour. Such concentration dependence of τ, as a function of alkyl chain length, is indeed observed.

Similarly, application of this model can explain the observed solvent effect and the temperature dependence of τ reported by Sagal (1962). As permittivity studies have shown, the influence of the solvent is dependent upon its ability to interact with the solute : as the proton-accepting ability of the solvent increases, solute/solvent interactions compete with solute/solute interactions, so reducing the average chain length and extent of network formation. This stabilisation of shorter chains would increase the fraction of "free" hydroxyl groups, leading to an increased probability of reorientation. Thus, as the proton-accepting ability of the solvent increases, shorter relaxation times are expected and are observed in this and other studiies (van Gemert et al., 1973; Koshii et al., 1974 a,b). Similarly, an increase in solution temperature is expected to break up the hydrogen bonded multimers, giving rise to species of shorter average chain length. Thus one finds as expected that the effect of increased temperature parallels that of increased solvent proton-accepting ability.

The model developed is thus seen to explain many of the features noted in Figures 4.18 and 20. However, it is necessary to stress the tentative nature of this model : it is merely proposed as adequately explaining, on a qualitative basis, the deceptively simple relaxation behaviour observed for a series of alcohol solutions.

5.8. Conclusions and Suggestions for Further Studies

It has been shown that important structural information on solute association at low concentration can be obtained by measuring static dielectric properties as a function of concentration. The interpretation of these results is greatly assisted by the happy combination of infrared and dielectric data. The results establish interesting differences in the behaviour of the alcohols in the three solvents studied : there is a fairly large solute/solvent interaction in benzene solution which delays association. This contrasts with the behaviour of solutions in cyclohexane which behaves as a rather inert solvent.

It is further established that, for the sterically non-hindered octanols, a general pattern of the concentration dependence of solute association is observed : monomer-small high dipole moment multimer-larger low dipole moment multimer-high dipole moment multimer network. Each of these is in turn favoured as the alcohol concentration increases. The ease of formation of the final, high dipole moment multimers is very sensitive to the steric environment of the hydroxyl group : as the hydroxyl group becomes sterically more hindered, these species form less readily until, for very restricted -OH environments, they do not form at all.

The model has been successfully applied to data on t-butanol solutions in hexadecane. A comparison of the results with those of Tucker and Becker (1973) on the same system provides evidence which seems to favour the dimer as the first associated species, rather than the trimer favoured by Tucker and Becker.

To extend the investigations of alcohol association, it would be interesting to conduct similar experiments over a wide range of temperatures; in particular, studies on alcohols with very hindered -OH groups would seem warranted since the lack of high dipole moment species at high concentrations simplifies the analysis of the concentration dependence of μ^2_{app}. Curve fitting techniques could then be applied with more confidence to estimate the thermodynamic parameters.

The application of curve fitting techniques has, however, generally been of limited value owing to the large uncertainties of the calculated parameters. To reduce these uncertainties, it would seem necessary to reduce the scatter in the data, particularly at very low concentrations. With data of better quality, it might prove possible to obtain a reliable association model which is statistically superior to all others for a range of temperatures, solvents and solutes.

It would also seem appropriate to investigate similarly the association of compounds having different functional groups capable of interacting through hydrogen bonds. Such studies would extend the understanding of molecular interactions in the liquid state and of liquid structure.

The model derived to explain the association behaviour of concentrated alcohol solutions is less definitive than that proposed for low concentration association. This is a result of the lack of understanding of the exceedingly complex molecular interactions which govern the association behaviour at high concentrations. It will therefore be necessary to obtain data from alcohol solutions in which the environment of the alcohol -OH group is systematically varied and in which the solvents exhibit a wide range of both viscosity and proton accepting ability. Investigation of the effect of temperature on the relaxation parameters observed for such systems would also be interesting, particularly if the thermodynamic parameters obtained exhibit a dependence on the solute concentration.

TDS techniques would seem particularly suited to this end because of the potential speed of data capture and the relative ease with which the appropriate relaxation parameters may be obtained. However, a refinement of the technique is required to obtain reproducible and accurate data in the important frequency range from 0.01 to 0.15 GHz. This may be assisted by computer-controlled averaging of many sets of sampled, time domain data; but a more important consideration appears to be construction of a sample cell which allows the sample to be introduced and removed without disturbing the coaxial connectors.

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APPENDIX TABLES A.I - XVIII

Supplementary Table A.I

Dielectric data at 2 MHz for 1-octanol in carbon tetrachloride at 25.0°.

$\frac{w}{10^{-2}}$	$\frac{c}{\text{mol } \ell^{-1}}$	$\frac{\rho}{\text{g cm}^{-3}}$	ε	$\frac{\mu^2}{D^2}$
0.0151	0.00184	1.58437	2.22690	2.745
0.0208	0.00253	1.58423	2.22711	2.691
0.0218	0.00265	1.58422	2.22718	2.787
0.0289	0.00352	1.58413	2.22740	2.632
0.0404	0.00491	1.58394	2.22790	2.736
0.0416	0.00506	1.58390	2.22792	2.691
0.0425	0.00517	1.58389	2.22800	2.763
0.0440	0.00535	1.58386	2.22801	2.686
0.0546	0.00664	1.58373	2.22843	2.696
0.0547	0.00665	1.58373	2.22848	2.753
0.0570	0.00693	1.58370	2.22859	2.760
0.0678	0.00824	1.58354	2.22900	2.751
0.0684	0 00832	1.58353	2.22900	2.751
0.0746	0.00907	1.58344	2.22929	2.768
0.0750	0.00912	1.58343	2.22935	2.718
0.0896	0.01089	1.5832	2.22990	2.764
0.0902	0.01097	1.5832	2.22991	2.764
0.1144	0.01390	1.5828	2.23092	2.789
0.1737	0.02110	1.5819	2.23340	2.823
0.2406	0.02921	1.5809	2.2362	2.842
0.3193	0.03873	1.5797	2.2394	2.834
0.6283	0.07598	1.5749	2.2515	2.776
0.8892	0.10726	1.5710	2.2611	2.713
1.007	0.1213	1.5687	2.2651	2.675
1.086	0.1307	1.5681	2.2680	2.666
1.468[a]	0.1761	1.5622	2.2797	2.533
2.507	0.2979	1.5472	2.3085	2.303
5.312	0.6165	1.5113	2.3773	2.035
8.207	0.9294	1.4748	2.4479	1.967
11.990	1.3166	1.4301	2.5484	1.996
18.119	1.8964	1.3630	2.7493	2.200
24.810	2.4689	1.2959	3.0368	2.544
34.412	3.2030	1.2122	3.6191	3.219
100.000	6.3127	0.8221	9.83	7.71

[a] DFL 1 cell used for solutions up to this concentration.

Supplementary Table A.II

Dielectric data at 2 MHz for 2-octanol in carbon tetrachloride at 25.0°

$\underline{w}$ / 10^{-2}	$\underline{c}$ / mol ℓ^{-1}	$\underline{\rho}$ / g cm^{-3}	ε	μ^2 / D^2
0.0258	0.00314	1.58413	2.22730	2.655
0.0286	0.00348	1.58409	2.22741	2.661
0.0445	0.00541	1.58383	2.22802	2.661
0.0517	0.00629	1.58372	2.22830	2.665
0.0638	0.00776	1.58352	2.22878	2.681
0.0643	0.00782	1.58350	2.22879	2.671
0.0723	0.00879	1.58339	2.22911	2.682
0.0863	0.01049	1.58317	2.22967	2.696
0.1009	0.01226	1.58293	2.23022	2.685
0.1148	0.01395	1.58271	2.23080	2.709
0.1229	0.01494	1.58258	2.23111	2.706
0.1395	0.01695	1.58232	2.23183	2.741
0.1587	0.01928	1.58201	2.23260	2.745
0.2137	0.02595	1.58114	2.23480	2.753
0.2287	0.02776	1.5809	2.23541	2.754
0.3300	0.04002	1.5793	2.23950	2.770
0.4379[a]	0.05305	1.5776	2.2437	2.754
0.5155	0.06240	1.5763	2.2468	2.758
0.6442	0.07788	1.5743	2.2517	2.737
0.7233	0.08737	1.5730	2.2547	2.727
0.8339	0.1006	1.5713	2.2588	2.709
1.030	0.1240	1.5681	2.2661	2.689
1.277	0.1534	1.5642	2.2747	2.643
1.441	0.1728	1.5616	2.2803	2.616
1.438	0.1726	1.5627	2.2800	2.606
3.067	0.3625	1.5394	2.3294	2.373
6.772	0.7749	1.4902	2.4200	2.073
12.056	1.3199	1.4258	2.5208	1.841
16.385	1.7339	1.3781	2.6066	1.798
25.335	2.5059	1.2881	2.8160	1.891
32.468	3.0493	1.2231	3.0136	2.039
57.000	4.5660	1.0432	4.1207	3.036
100.000	6.2727	0.8169	7.09	5.22

[a] DFL 1 cell used for solutions up to this concentration

Supplementary Table A.III

Dielectric data at 2 MHz for 3-octanol in carbon tetrachloride at 25.0^{o}

$\frac{w}{10^{-2}}$	$\frac{c}{mol\ \ell^{-1}}$	$\frac{\rho}{g\ cm^{-3}}$	ε	$\frac{\mu^2}{D^2}$
0.0264	0.00321	1,58409	2.22723	2.640
0.0363	0.00442	1.58402	2.22760	2.627
0.0613	0.00745	1.58365	2.22855	2.633
0.0655	0.00797	1.58360	2.22873	2.652
0.0790	0.00961	1.58335	2.22922	2.630
0.1011	0.01229	1.58301	2.23010	2.658
0.1776	0.02157	1.58179	2.23303	2.659
0.2636	0.03199	1.58044	2.23641	2.681
0.4199	0.05088	1.5780	2.24262	2.711
0.5429[a]	0.06570	1.5761	2.24738	2.707
0.7520	0.09082	1.5728	2.2554	2.698
0.8601	0.1038	1.5711	2.2595	2.692
1.451	0.1740	1.5620	2.2803	2.604
1.918	0.2292	1.5561	2.2948	2.505
5.168	0.5998	1.5150	2.3837	2.184
7.840	0.8883	1.4755	2.4425	2.018
11.856	1.2994	1.4273	2.5223	1.880
15.895	1.6856	1.3810	2.5980	1.811
24.866	2.4589	1.2878	2.7599	1.762
34.880	3.2188	1.2018	2.9485	1.798
48.635	4.1200	1.1032	3.2624	1.969
100.000	6.2735	0.8170	5.38	3.57

[a] DFL 1 cell used for solutions up to this concentration

Supplementary Table A.IV

Dielectric data at 2 MHz for 4-octanol in carbon tetrachloride at 25.0°

$\frac{w}{10^{-2}}$	$\frac{c}{\text{mol } \ell^{-1}}$	$\frac{\rho}{\text{g cm}^{-3}}$	ε	$\frac{\mu^2}{D^2}$
0.0280	0.00341	1.58415	2.22724	2.583
0.0394	0.00479	1.58397	2.22766	2.580
0.0603	0.00734	1.58361	2.22843	2.568
0.0640	0.00778	1.58351	2.22856	2.563
0.0714	0.00868	1.58346	2.22886	2.589
0.1004	0.01220	1.58292	2.22992	2.575
0.1741	0.02115	1.58176	2.23274	2.610
0.2580	0.03131	1.58045	2.23591	2.616
0.4079	0.04943	1.57809	2.24160	2.625
0.5715	0.06914	1.5766	2.2478	2.630
0.7333	0.08857	1.5730	2.2538	2.621
0.8976	0.1082	1.5704	2.2598	2.610
1.0936[a]	0.1316	1.5674	2.2670	2.604
1.511	0.1811	1.5610	2.2816	2.565
4.136	0.4844	1.5252	2.3536	2.197
7.635	0.8671	1.4790	2.4267	1.926
10.111	1.1240	1.4477	2.4720	1.818
17.626	1.8454	1.3635	2.5932	1.644
24.565	2.4405	1.2938	2.6939	1.578
35.364	3.2545	1.1985	2.8439	1.551
50.230	4.2092	1.0913	3.0492	1.582
100.000	6.2651	0.8159	4.35	2.54

[a] DFL 1 cell used for solutions up to this concentration

Supplementary Table A.V

Dielectric data at 2 MHz for 1-octanol in cyclohexane at 25.0°.

$\frac{w}{10^{-2}}$	$\frac{c}{\mathrm{mol}\ \ell^{-1}}$	$\frac{\rho}{\mathrm{g\ cm}^{-3}}$	ε	$\frac{\mu^2}{D^2}$
0.0513	0.00305	0.77388	2.01587	2.668
0.1201	0.00607	0.77388	2.01679	2.614
0.1124	0.00668	0.77388	2.01698	2.521
0.1699	0.01010	0.77387	2.01802	2.578
0.1978	0.01175	0.77387	2.01853	2.637
0.2130	0.01266	0.77387	2.01880	2.594
0.2619	0.01550	0.77386	2.01967	2.606
0.3689	0.02192	0.77385	2.02161	2.580
0.3779	0.02246	0.77385	2.02177	2.571
0.5146	0.03058	0.77388	2.02417	2.563
0.6492	0.03858	0.77391	2.02645	2.532
0.6848	0.04070	0.77392	2.02704	2.513
0.7562	0.04494	0.77392	2.02820	2.497
0.8138	0.04836	0.77394	2.02911	2.477
0.8316	0.04942	0.77398	2.02939	2.473
1.082	0.06431	0.77398	2.03300	2.365
1.194	0.07097	0.77404	2.03451	2.318
1.309	0.07781	0.77408	2.03631	2.307
1.389	0.08256	0.77410	2.03712	2.252
1.604	0.09535	0.77417	2.04003	2.201
1.679	0.09981	0.77418	2.04080	2.164
1.981[a]	0.1178	0.7743	2.04442	2.083
5.167	0.3074	0.7748	2.0781	1.665
10.137	0.6041	0.7761	2.1340	1.573
16.348	0.9764	0.7778	2.2167	1.634
22.845	1.3671	0.7793	2.3295	1.807
29.730	1.7841	0.7815	2.4906	2.073
45.024	2.7191	0.7865	3.1034	2.994
63.458	3.8659	0.7934	4.6592	4.748
100.000	6.3127	0.8221	9.83	7.71

[a] DFL 1 cell used for solutions up to this concentration

Supplementary Table A.VI

Dielectric data at 2 MHz for 2-octanol in cyclohexane at 25.0°.

$\frac{w}{10^{-2}}$	$\frac{c}{\mathrm{mol}\ \ell^{-1}}$	$\frac{\rho}{\mathrm{g\ cm^{-3}}}$	ε	$\frac{\mu^2}{D^2}$
0.0395	0.00235	0.77389	2.01550	2.561
0.0623	0.00370	0.77388	2.01589	2.521
0.1037	0.00616	0.77388	2.01661	2.510
0.1451	0.00862	0.77388	2.01740	2.579
0.2088	0.01241	0.77387	2.01851	2.554
0.2343	0.01392	0.77386	2.01889	2.505
0.2696	0.01602	0.77386	2.01960	2.558
0.4239	0.02519	0.77384	2.02230	2.539
0.5473	0.03252	0.77382	2.02452	2.548
0.7096	0.04216	0.77376	2.02720	2.503
0.8162	0.04849	0.77375	2.02891	2.473
1.058	0.06286	0.77380	2.03290	2.444
1.266	0.07523	0.77384	2.03594	2.379
1.477	0.08777	0.77385	2.03922	2.353
2.107[a]	0.1252	0.7739	2.04743	2.189
2.179	0.1295	0.7739	2.0475	2.116
4.803	0.2855	0.7741	2.0762	1.767
9.409	0.5599	0.7749	2.1220	1.541
14.389	0.8573	0.7759	2.1698	1.433
32.527	1.9484	0.7801	2.4106	1.567
42.868	2.5771	0.7829	2.6160	1.773
54.640	3.2990	0.7863	2.9800	2.174
100.000	6.2727	0.8169	7.09	5.22

[a] DFL 1 cell used for solutions up to this concentration

Supplementary Table A.VII

Dielectric data at 2 MHz for 3-octanol in cyclohexane at 25.0°.

$\frac{w}{10^{-2}}$	$\frac{c}{\text{mol } \ell^{-1}}$	$\frac{\rho}{\text{g cm}^{-3}}$	ε	$\frac{\mu^2}{D^2}$
0.0533	0.00317	0.77390	2.01569	2.550
0.1041	0.00619	0.77390	2.01660	2.563
0.1785	0.01061	0.77392	2.01790	2.540
0.2095	0.01245	0.77393	2.01841	2.512
0.2596	0.01543	0.77392	2.01931	2.525
0.3770	0.02240	0.77389	2.02142	2.543
0.4910	0.02918	0.77392	2.02340	2.530
0.5939	0.03529	0.77389	2.02520	2.525
0.6429	0.03820	0.77385	2.02611	2.536
0.7932	0.04714	0.77392	2.02854	2.491
1.0650[a]	0.06329	0.77386	2.03303	2.455
1.441	0.08563	0.7739	2.0390	2.401
1.905	0.1132	0.7741	2.0460	2.332
2.318	0.1378	0.7741	2.0515	2.246
5.140	0.3055	0.7741	2.0852	1.907
10.256	0.6106	0.7753	2.1381	1.634
14.973	0.8927	0.7764	2.1841	1.511
22.168	1.3247	0.7782	2.2582	1.440
30.248	1.8128	0.7805	2.3566	1.458
44.750	2.6968	0.7848	2.5705	1.558
59.566	3.6157	0.7905	2.8880	1.784
100.000	6.2735	0.8170	5.38	3.567

[a] DFL 1 cell used for solutions up to this concentration.

Supplementary Table A.VIII

Dielectric data at 2 MHz for 4-octanol in cyclohexane at 25.0°.

$\frac{w}{10^{-2}}$	$\frac{c}{\text{mol } \ell^{-1}}$	$\frac{\rho}{\text{g cm}^{-3}}$	ε	$\frac{\mu^2}{D^2}$
0.0422	0.00251	0.77389	2.01546	2.577
0.1001	0.00595	0.77389	2.01651	2.598
0.1767	0.01050	0.77390	2.01789	2.596
0.2178	0.01294	0.77392	2.01861	2.581
0.2801	0.01665	0.77393	2.01982	2.631
0.3808	0.02263	0.77389	2.02163	2.619
0.5157	0.03071	0.77389	2.02401	2.591
0.6114	0.03633	0.77388	2.02562	2.566
0.7275	0.04323	0.77389	2.02750	2.525
0.9317	0.05537	0.77390	2.03093	2.496
1.1380[a]	0.06763	0.77393	2.03424	2.457
1.440	0.08558	0.7740	2.0387	2.378
1.998	0.1188	0.7741	2.0467	2.275
2.322	0.1381	0.7743	2.0506	2.188
6.240	0.3712	0.7746	2.0921	1.709
10.047	0.5984	0.7757	2.1258	1.494
15.156	0.9043	0.7770	2.1704	1.362
22.209	1.3281	0.7788	2.2351	1.292
30.154	1.8086	0.7811	2.3092	1.248
44.247	2.6692	0.7856	2.4652	1.267
59.935	3.6418	0.7913	2.7021	1.390
100.000	6.2651	0.8159	4.39	2.58

[a] DFL 1 cell used for solutions up to this concentration

Supplementary Table A.IX

Dielectric data at 2 MHz for 1-octanol in benzene at 25.0°.

$\frac{w}{10^{-2}}$	$\frac{c}{\text{mol } \ell^{-1}}$	$\frac{\rho}{\text{g cm}^{-3}}$	ε	$\frac{\mu^2}{D^2}$
0.1062	0.00713	0.87362	2.27489	2.638
0.2777	0.01863	0.87350	2.27847	2.680
0.4326	0.02901	0.87338	2.28172	2.662
0.5963	0.04012	0.87326	2.28523	2.670
0.6736	0.04516	0.87320	2.28684	2.688
0.8861	0.05941	0.8731	2.29141	2.692
1.053	0.07057	0.8729	2.29505	2.700
1.252	0.08390	0.8727	2.29944	2.725
1.578	0.1057	0.8724	2.30682	2.749
1.983[a]	0.1328	0.8722	2.3160	2.777
2.991	0.2000	0.8710	2.3398	2.839
3.733	0.2495	0.8704	2.3572	2.859
4.819	0.3217	0.8693	2.3823	2.867
7.611	0.5068	0.8671	2.4452	2.844
10.031	0.6661	0.8648	2.4989	2.822
12.863	0.8497	0.8625	2.5601	2.788
15.783	1.0424	0.8601	2.6270	2.789
21.992	1.4447	0.8555	2.7862	2.869
29.822	1.9458	0.8497	3.0167	3.018
45.512	2.9667	0.8489	3.6982	3.593
58.531	3.7335	0.8307	4.6357	4.500
100.000	6.3127	0.8221	9.83	7.71

[a] DFL 1 cell used for solutions up to this concentration.

Supplementary Table A.X

Dielectric data at 2 MHz for 2-octanol in benzene at 25.0°.

$\underline{w}$ / 10^{-2}	$\underline{c}$ / mol ℓ^{-1}	$\underline{\rho}$ / g cm^{-3}	ε	$\underline{\mu}^2$ / D^2
0.0848	0.00569	0.87362	2.27450	2.618
0.2189	0.01468	0.87350	2.27731	2.661
0.2928	0.01964	0.87343	2.27883	2.656
0.3479	0.02333	0.87338	2.27990	2.631
0.4489	0.03010	0.87329	2.28201	2.642
0.5321	0.03568	0.87321	2.28370	2.637
0.6124	0.04106	0.87314	2.28542	2.650
0.6966	0.04670	0.87306	2.28709	2.638
0.8288	0.05555	0.87294	2.28990	2.651
1.044	0.06996	0.87274	2.29451	2.669
1.479	0.09906	0.87228	2.30400	2.702
1.584	0.1061	0.87223	2.30638	2.714
1.941[a]	0.1299	0.87194	2.31423	2.729
4.551	0.3037	0.8691	2.3708	2.741
7.291	0.4852	0.8666	2.4265	2.678
12.046	0.7974	0.8621	2.5191	2.592
22.272	1.4589	0.8531	2.7156	2.506
26.216	1.7115	0.8502	2.7933	2.496
49.769	3.1823	0.8327	3.3613	2.686
61.351	3.8847	0.8246	3.8381	3.059
100.000	6.2727	0.8169	7.09	5.22

[a] DFL 1 cell used for solution up to this concentration

Supplementary Table A.XI

Dielectric data at 2 MHz for 3-octanol in benzene at 25.0°.

$\frac{w}{10^{-2}}$	$\frac{c}{\text{mol } \ell^{-1}}$	$\frac{\rho}{\text{g cm}^{-3}}$	ε	$\frac{\mu^2}{D^2}$
0.1411	0.00947	0.87363	2.27560	2.532
0.2516	0.01688	0.87345	2.27769	2.494
0.3960	0.02656	0.87336	2.28051	2.503
0.5209	0.03493	0.87323	2.28291	2.498
0.7335	0.04917	0.87304	2.28710	2.509
0.8454	0.05667	0.87295	2.28928	2.510
1.2017	0.08052	0.87261	2.29671	2.558
1.4495[a]	0.09710	0.87241	2.30171	2.563
1.577	0.1056	0.8723	2.3043	2.566
1.956	0.1310	0.8720	2.3123	2.591
2.235	0.1496	0.8718	2.3182	2.605
4.010	0.2679	0.8699	2.3556	2.639
5.137	0.3427	0.8688	2.3802	2.666
10.010	0.6704	0.8643	2.4792	2.596
15.807	1.0430	0.8593	2.5860	2.512
22.271	1.4606	0.8541	2.7010	2.433
29.606	1.9285	0.8483	2.8259	2.363
44.944	2.8903	0.8375	3.0930	2.302
57.915	3.6871	0.8291	3.3493	2.333
100.000	6.2735	0.8170	5.38	3.57

[a] DFL 1 cell used for solutions up to this concentration

Supplementary Table A.XII

Dielectric data at 2 MHz for 4-octanol in benzene at 25.0^{o}.

$\frac{w}{10^{-2}}$	$\frac{c}{\text{mol } \ell^{-1}}$	$\frac{\rho}{\text{g cm}^{-3}}$	ε	$\frac{\mu^2}{D^2}$
0.1139	0.00764	0.87360	2.27491	2.558
0.2526	0.01694	0.87345	2.27760	2.530
0.4637	0.03109	0.87326	2.28161	2.497
0.5956	0.03993	0.87314	2.28438	2.541
0.6671	0.04472	0.87307	2.28570	2.525
0.8690	0.05825	0.87288	2.28951	2.505
0.9288	0.06225	0.87284	2.29088	2.532
1.0493	0.07032	0.87271	2.29342	2.552
1.2845[a]	0.08606	0.8725	2.29833	2.574
1.544	0.1034	0.8723	2.3037	2.587
2.340	0.1566	0.8716	2.3200	2.599
2.741	0.1834	0.8713	2.3284	2.610
4.671	0.3119	0.8696	2.3695	2.650
9.106	0.6057	0.8662	2.4556	2.560
14.665	0.9707	0.8620	2.5553	2.451
21.809	1.4353	0.8571	2.6711	2.323
29.955	1.9595	0.8519	2.7984	2.231
45.478	2.9428	0.8427	3.0264	2.110
60.841	3.8982	0.8344	3.2583	2.063
100.000	6.2651	0.8159	4.39	2.58

[a] DFL 1 cell used for solutions up to this concentration

Supplementary Table A.XIII

Dielectric data at 2 MHz for 1-octanol in n-hexene at 25°C

$\underline{w}$ / 10^{-2}	$\underline{c}$ / mol ℓ^{-1}	$\underline{\rho}$ / g cm^{-3}	ε	$\underline{\mu}^2$ / D^2
0.0630	0.00317	0.65481	1.87736	2.583
0.1257	0.00632	0.65489	1.87828	2.446
0.2141	0.01077	0.65509	1.87971	2.506
0.2545	0.01280	0.65514	1.88027	2.490
0.3287	0.01654	0.65524	1.88120	2.350
0.4459	0.02244	0.65551	1.88354	2.605
0.6177	0.03111	0.65579	1.88637	2.654
0.7525	0.03790	0.65587	1.88839	2.606
0.9707	0.04890	0.65607	1.89126	2.488
1.289	0.06499	0.65642	1.89465	2.262
1.738	0.08770	0.65712	1.90092	2.238
2.136	0.10788	0.65773	1.90527	2.124
2.311[a]	0.11678	0.65798	1.90732	2.092
3.309	0.1675	0.6592	1.9167	1.855
5.281	0.2638	0.6617	1.9359	1.666
10.367	0.5323	0.6687	1.9886	1.543
16.402	0.8531	0.6774	2.0646	1.613
22.876	1.2061	0.6866	2.1656	1.759
29.866	1.5985	0.6970	2.3109	2.004
45.187	2.5011	0.7208	2.8574	2.869
60.520	3.4668	0.7460	3.9772	4.242
100.00	6.3127	0.8221	9.83	7.71

[a] DFL 1 cell used for solutions up to this concentration

Supplementary Table XIV

Dielectric data at 2 MHz for 2,3,4-trimethyl-3-pentanol in cyclohexane at 25°.

$\frac{w}{10^{-2}}$	$\frac{c}{\text{mol } \ell^{-1}}$	$\frac{\rho}{\text{g cm}^{-3}}$	ε	$\frac{\mu^2}{D^2}$
0.0841	0.00499	0.77392	2.01612	2.211
0.0905	0.00538	0.77392	2.01620	2.175
0.1241	0.00738	0.77393	2.01680	2.271
0.1536	0.00913	0.77394	2.01718	2.173
0.1706	0.01014	0.77395	2.01748	2.205
0.2355	0.01399	0.77397	2.01861	2.275
0.2938	0.01746	0.77400	2.01947	2.230
0.2981	0.01772	0.77400	2.01951	2.216
0.5172	0.03074	0.77409	2.02296	2.209
0.5398	0.03209	0.77410	2.02337	2.224
0.7690	0.04572	0.77419	2.02717	2.253
0.8711	0.05179	0.77422	2.02871	2.234
1.045	0.06214	0.77429	2.03167	2.259
1.245	0.07402	0.77436	2.03489	2.257
1.491	0.08867	0.77446	2.03888	2.256
2.054	0.1222	0.77468	2.04803	2.257
2.988[a]	0.1778	0.77508	2.06295	2.239
3.139	0.1869	0.7754	2.0652	2.228
6.445	0.3843	0.7766	2.1130	2.081
9.828	0.5875	0.7785	2.1620	2.019
20.211	1.2169	0.7841	2.2990	1.825
30.395	1.8454	0.7907	2.4296	1.712
39.882	2.4383	0.7962	2.5435	1.616
58.997	3.6667	0.8094	2.7868	1.512
100.000	6.4885	0.845	3.3350	1.365

[a] DFL 1 cell used for solutions up to this concentration

Supplementary Table A.XV

Dielectric data at 2 MHz for 2,3,4-trimethyl-3-pentanol in carbon tetrachloride at 25°.

w 10^{-2}	c mol ℓ^{-1}	ρ g cm^{-3}	ε	$\frac{\mu^2}{D^2}$
0.0159	0.00193	1.58446	2.22681	2.296
0.0184	0.00224	1.58444	2.22690	2.322
0.0198	0.00241	1.58442	2.22694	2.297
0.0376	0.00457	1.58420	2.22754	2.311
0.0483	0.00588	1.58402	2.22790	2.314
0.0576	0.00698	1.58388	2.22824	2.355
0.0642	0.00781	1.58378	2.22847	2.353
0.0912	0.01109	1.58341	2.22944	2.390
0.1300	0.01580	1.58282	2.23082	2.409
0.1812	0.02201	1.58207	2.23271	2.447
0.2315	0.02811	1.58134	2.23452	2.455
0.3026	0.03672	1.58033	2.23715	2.478
0.3777	0.04580	1.57920	2.23770	2.465
0.5396[a]	0.06534	1.57686	2.24557	2.469
0.9699	0.1170	1.5710	2.2612	2.490
1.137	0.1364	1.5621	2.2665	2.459
3.079	0.3669	1.5520	2.3333	2.412
5.790	0.6701	1.5072	2.4168	2.329
9.710	1.0875	1.4585	2.5230	2.211
19.344	2.0111	1.3539	2.7365	2.019
29.700	2.8788	1.2623	2.8933	1.828
37.488	3.4529	1.1995	2.9881	1.735
51.997	4.3868	1.0987	3.1275	1.611
100.000	6.4885	0.845	3.3350	1.365

[a] DFL 1 cell used for solutions up to this concentration.

Supplementary Table A.XVI

Dielectric data at 2 MHz for 2,3,4-trimethyl-3-pentanol in benzene at 25°.

$\frac{w}{10^{-2}}$	$\frac{c}{\text{mol } \ell^{-1}}$	$\frac{\rho}{\text{g cm}^{-3}}$	ε	$\frac{\mu^2}{D^2}$
0.0509	0.00342	0.87369	2.27353	2.137
0.0806	0.00541	0.87368	2.27404	2.161
0.1272	0.00853	0.87364	2.27479	2.129
0.1468	0.00985	0.87360	2.27516	2.167
0.1973	0.01324	0.87360	2.27598	2.147
0.2125	0.01425	0.87358	2.27628	2.173
0.2247	0.01507	0.87358	2.27646	2.159
0.3019	0.02025	0.87354	2.27786	2.199
0.3894	0.02612	0.87346	2.27940	2.211
0.5433	0.03644	0.87339	2.28201	2.201
0.8227	0.05517	0.87325	2.28699	2.227
0.9769	0.06550	0.87316	2.28988	2.252
1.231	0.08250	0.87303	2.29404	2.221
1.435	0.09619	0.87292	2.29782	2.240
1.981[a]	0.1328	0.87264	2.30759	2.250
3.029	0.2028	0.8719	2.3276	2.308
6.557	0.4379	0.8697	2.3939	2.338
10.120	0.6744	0.8678	2.4655	2.391
19.798	1.3114	0.8623	2.6379	2.294
30.337	1.9985	0.8579	2.8097	2.188
39.100	2.5655	0.8545	2.9410	2.106
60.026	3.9155	0.8495	3.1880	1.880
100.000	6.4885	0.8450	3.335	1.365

[a] OFL 1 cell used for solutions up to this concentration.

Supplementary Table A.XVII

Dielectric data at 2 MHz for *t*-butanol in hexadecane at 25.0°.

$\underline{w}^{a}$ 10^{-2}	$\underline{c}$ mol ℓ^{-1}	$\underline{\rho}$ g cm^{-3}	ε	$\underline{\mu}^{2}$ D^{2}
0.0265	0.00275	0.76997	2.04331	2.439
0.0286	0.00300	0.76997	2.04339	2.478
0.0322	0.00334	0.76996	2.04350	2.522
0.0466	0.00484	0.76994	2.04389	2.474
0.0584	0.00607	0.76994	2.04420	2.438
0.0747	0.00776	0.76993	2.04472	2.513
0.0754	0.00783	0.76993	2.04472	2.490
0.0810	0.00841	0.76993	2.04493	2.543
0.1049	0.01090	0.76991	2.04562	2.538
0.1133	0.01177	0.76990	2.04583	2.512
0.1478	0.01535	0.76988	2.04684	2.521
0.1763	0.01831	0.76987	2.04772	2.549
0.2217	0.02303	0.76983	2.04905	2.550
0.2520	0.02617	0.76984	2.04992	2.544
0.3133	0.03254	0.76982	2.05160	2.514
0.3735	0.03879	0.76975	2.05310	2.458
0.4437	0.04608	0.76975	2.05481	2.404
0.5047	0.05241	0.76973	2.05610	2.338
0.6362	0.06606	0.76967	2.05889	2.239
0.7254 [a]	0.07532	0.76962	2.06060	2.169
1.067	0.1107	0.7691	2.0672	2.015
1.990	0.2065	0.7690	2.0816	1.712
6.875	0.7130	0.7687	2.1419	1.257
9.905	1.0271	0.7686	2.1835	1.231
19.803	2.0529	0.7683	2.3600	1.353
25.443	2.6375	0.7683	2.5051	1.505
50.124	5.[illegible]	0.7701	3.8942	2.723
100.000	10.53[illegible]	0.7812	12.47	6.51

[a] DFL 1 cell used for solution up to this concentration.

Supplementary Table A.XVIII

Proton magnetic resonance chemical shifts for the hydroxyl proton of 2,3,4-trimethyl-3-pentanol in carbon tetrachloride at 35^o relative to TMS

Mole fraction	δ/ppm
1.0000	2.257
0.9036	2.204
0.8218	2.157
0.6962	2.058
0.5870	1.927
0.4819	1.816
0.4203	1.760
0.3253	1.625
0.2971	1.552
0.2376	1.457
0.1670	1.282
0.1463	1.217
0.1068	1.089
0.03840	0.809
0.02634	0.734
0.01879	0.707
0.01343	0.679
0.00875	0.656
0.00683	0.645
0.00464	0.639
0.00247	0.634
0.00159	0.628
0.00113	0.628
0.000642	0.616
0.000524	0.628

TABLES B.I - X

Supplementary Tables B.I

ε' and ε'' at selected frequencies for solutions of 1-propanol in cyclohexane at 20°C at alcohol mole fraction, X.

	X = 0.1919		X = 0.2849		X = 0.4068	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.05	2.62	0.03	3.46	0.11	5.48	0.41
0.10	2.61	0.05	3.42	0.22	5.31	0.77
0.15	2.60	0.08	3.37	0.32	5.07	1.05
0.20	2.59	0.10	3.31	0.40	4.79	1.24
0.25	2.57	0.12	3.23	0.46	4.51	1.35
0.30	2.56	0.13	3.16	0.50	4.26	1.40
0.35	2.54	0.14	3.09	0.53	4.03	1.39
0.40	2.53	0.15	3.02	0.55	3.85	1.36
0.45	2.51	0.16	2.96	0.55	3.70	1.31
0.50	2.50	0.16	2.91	0.55	3.58	1.26
0.60	2.47	0.17	2.84	0.55	3.40	1.17
0.70	2.44	0.19	2.78	0.55	3.26	1.11
0.80	2.42	0.18	2.73	0.56	3.14	1.05
0.90	2.39	0.18	2.67	0.56	3.04	0.99
1.00	2.37	0.17	2.60	0.55	2.96	0.93
1.25	2.34	0.16	2.52	0.47	2.86	0.81
1.50	2.32	0.12	2.50	0.46	2.76	0.74
1.75	2.31	0.12	2.44	0.45	2.71	0.66
2.00	2.30	0.11	2.44	0.43	2.67	0.64
3.00	2.31	0.06	2.37	0.45	2.56	0.48
4.00	2.23	0.04	2.30	0.48	2.46	0.48
5.00	2.19	0.00	2.21	0.47	2.48	0.45

Supplementary Tables B.I

ε' and ε'' at selected frequencies for solutions of 1-propanol in cyclohexane at 20^{0}C at alcohol mole fraction, X.

	X = 0.5058		X = 0.6224		X = 0.6967	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.05	7.52	0.71	10.52	1.22	12.41	1.41
0.10	7.21	1.34	9.97	2.27	11.81	2.64
0.15	6.77	1.81	9.21	3.03	10.95	3.57
0.20	6.28	2.12	8.38	3.49	10.00	4.17
0.25	5.80	2.27	7.60	3.71	9.07	4.50
0.30	5.36	2.32	6.91	3.75	8.24	4.60
0.35	4.99	2.29	6.35	3.69	7.52	4.57
0.40	4.69	2.21	5.89	3.57	6.93	4.46
0.45	4.44	2.12	5.52	3.44	6.45	4.31
0.50	4.25	2.03	5.22	3.31	6.05	4.14
0.60	3.96	1.86	4.75	3.07	5.44	3.83
0.70	3.74	1.73	4.37	2.87	4.97	3.55
0.80	3.55	1.63	4.06	2.65	4.60	3.29
0.90	3.40	1.52	3.83	2.43	4.31	3.04
1.00	3.27	1.41	3.67	2.23	4.09	2.81
1.25	3.11	1.20	3.46	1.92	3.76	2.33
1.50	2.99	1.06	3.23	1.67	3.57	1.99
1.75	2.94	0.92	3.17	1.41	3.46	1.76
2.00	2.91	0.88	3.11	1.34	3.33	1.61
3.00	2.73	0.60	2.90	1.02	3.11	1.12
4.00	2.60	0.52	2.68	0.96	2.92	1.07
5.00	2.65	0.43	2.80	0.81	2.89	0.82

Supplementary Tables B.I

ε' and ε'' at selected frequencies for solutions of 1-propanol in cyclohexane at 20°C at alcohol mole fraction, X.

f GHz	X = 0.8097 ε'	X = 0.8097 ε''	X = 0.9078 ε'	X = 0.9078 ε''	X = 1.0 ε'	X = 1.0 ε''
0.05	15.61	1.89	18.59	2.06	20.82	2.21
0.10	14.78	3.52	17.75	3.87	19.98	4.17
0.15	13.63	4.72	16.56	5.28	18.77	5.73
0.20	12.38	5.48	15.21	6.23	17.40	6.85
0.25	11.20	5.87	13.89	6.80	16.03	7.57
0.30	10.15	6.01	12.68	7.08	14.78	7.99
0.35	9.28	5.99	11.62	7.16	13.66	8.21
0.40	8.55	5.90	10.71	7.12	12.67	8.31
0.45	7.94	5.78	9.93	7.02	11.80	8.34
0.50	7.41	5.65	9.25	6.90	11.02	8.32
0.60	6.51	5.37	8.10	6.59	9.62	8.17
0.70	5.76	5.03	7.14	6.23	8.43	7.83
0.80	5.18	4.64	6.38	5.79	7.49	7.34
0.90	4.78	4.23	5.80	5.34	6.82	6.81
1.00	4.53	3.89	5.40	4.93	6.35	6.33
1.25	4.09	3.37	4.76	4.19	5.53	5.43
1.50	3.72	2.86	4.31	3.61	4.95	4.55
1.75	3.65	2.50	4.13	3.15	4.72	3.92
2.00	3.44	2.35	3.93	2.88	4.35	3.54
3.00	3.15	1.72	3.58	2.01	3.84	2.55
4.00	2.83	1.61	3.14	1.75	3.43	2.15
5.00	2.90	1.38	3.35	1.42	3.32	1.87

Supplementary Tables B.II

ε' and ε'' at selected frequencies for solutions of 1-propanol in benzene at 20°C at alcohol mole fraction, X.

	X = 0.3790		X = 0.4698		X = 0.5669	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.05	5.80	0.24	7.58	0.44	9.38	0.62
0.10	5.72	0.46	7.43	0.83	9.20	1.20
0.15	5.62	0.65	7.22	1.15	8.93	1.71
0.20	5.49	0.79	6.98	1.39	8.60	2.13
0.25	5.37	0.91	6.75	1.57	8.24	2.47
0.30	5.26	1.00	6.55	1.70	7.88	2.73
0.35	5.16	1.08	6.36	1.81	7.52	2.93
0.40	5.07	1.15	6.19	1.92	7.18	3.08
0.45	4.99	1.22	6.03	2.03	6.86	3.18
0.50	4.89	1.30	5.85	2.13	6.56	3.25
0.60	4.68	1.43	5.46	2.30	6.02	3.32
0.70	4.45	1.51	5.05	2.35	5.55	3.32
0.80	4.23	1.52	4.70	2.29	5.12	3.27
0.90	4.04	1.49	4.44	2.19	4.75	3.16
1.00	3.90	1.45	4.25	2.10	4.43	3.00
1.25	3.62	1.36	3.85	1.94	4.00	2.68
1.50	3.40	1.23	3.55	1.71	3.67	2.33
1.75	3.26	1.10	3.37	1.56	3.45	1.97
2.00	3.15	1.01	3.18	1.40	3.32	1.79
3.00	2.84	0.71	2.88	0.92	2.94	1.12
4.00	2.57	0.56	2.62	0.66	2.56	0.84
5.00	2.57	0.34	2.49	0.49	2.48	0.66

Supplementary Tables B.II

ε' and ε'' at selected frequencies for solutions of 1-propanol in benzene at 20°C at alcohol mole fraction, X.

	X = 0.6776		X = 0.7802		X = 0.8827	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.05	11.98	0.96	14.62	1.44	16.74	1.77
0.10	11.67	1.83	14.07	2.70	16.08	3.35
0.15	11.21	2.57	13.31	3.70	15.14	4.62
0.20	10.67	3.15	12.47	4.41	14.07	5.56
0.25	10.11	3.60	11.65	4.90	12.99	6.20
0.30	9.56	3.92	10.89	5.23	11.96	6.62
0.35	9.04	4.15	10.20	5.47	11.00	6.86
0.40	8.54	4.31	9.55	5.64	10.14	6.98
0.45	8.08	4.42	8.95	5.75	9.35	7.00
0.50	7.65	4.47	8.36	5.81	8.65	6.96
0.60	6.88	4.48	7.29	5.74	7.46	6.71
0.70	6.24	4.39	6.42	5.48	6.54	6.36
0.80	5.69	4.23	5.77	5.14	5.82	5.96
0.90	5.25	4.01	5.29	4.82	5.24	5.58
1.00	4.89	3.76	4.90	4.52	4.79	5.17
1.25	4.41	3.19	4.21	3.80	4.19	4.27
1.50	4.02	2.81	3.85	3.23	3.78	3.69
1.75	3.79	2.33	3.59	2.76	3.54	3.11
2.00	3.64	2.07	3.43	2.42	3.37	2.77
3.00	3.13	1.16	2.96	1.53	2.93	1.71
4.00	2.76	0.82	2.68	1.15	2.56	1.26
5.00	2.71	0.60	2.61	0.79	2.52	0.99

Supplementary Tables B III

ε' and ε" at selected frequencies for solutions of 1-butanol in cyclohexane at 20°C at alcohol mole fraction, X.

	X = 0.3714		X = 0.4923		X = 0.6086	
f GHz	ε'	ε"	ε'	ε"	ε'	ε"
0.05	4.41	0.32	6.49	0.76	9.12	1.29
0.10	4.27	0.59	6.11	1.38	8.45	2.34
0.15	4.07	0.79	5.61	1.79	7.57	3.02
0.20	3.85	0.90	5.08	1.99	6.68	3.32
0.25	3.65	0.95	4.61	2.03	5.90	3.36
0.30	3.46	0.96	4.24	1.97	5.28	3.25
0.35	3.32	0.93	3.96	1.87	4.83	3.06
0.40	3.21	0.89	3.75	1.75	4.49	2.86
0.45	3.12	0.84	3.60	1.64	4.24	2.68
0.50	3.06	0.80	3.48	1.55	4.05	2.53
0.60	2.96	0.75	3.31	1.41	3.77	2.28
0.70	2.89	0.71	3.16	1.31	3.54	2.07
0.80	2.80	0.66	3.04	1.20	3.37	1.88
0.90	2.74	0.60	2.95	1.08	3.26	1.70
1.00	2.71	0.54	2.91	0.98	3.20	1.55
1.25	2.66	0.46	2.83	0.85	3.01	1.33
1.50	2.61	0.38	2.77	0.72	3.00	1.12
1.75	2.60	0.34	2.76	0.68	2.99	1.03
2.00	2.56	0.31	2.67	0.63	2.89	0.95
3.00	2.50	0.13	2.60	0.48	2.80	0.69
4.00	2.46	0.05	2.56	0.42	2.70	0.54
5.00	2.39	0.00	2.43	0.30	2.57	0.54

Supplementary Tables B III

ε' and ε'' at selected frequencies for solutions of 1-butanol in cyclohexane at 20°C at alcohol mole fraction, X.

	X = 0.6973		X = 0.8027		X = 0.9009	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.05	10.85	1.64	13.05	1.97	14.97	2.23
0.10	10.00	2.95	12.06	3.58	13.89	4.10
0.15	8.88	3.78	10.74	4.66	12.41	5.38
0.20	7.75	4.14	9.37	5.18	10.85	6.05
0.25	6.68	4.17	8.16	5.29	9.43	6.25
0.30	6.02	4.01	7.18	5.15	8.26	6.13
0.35	5.46	3.78	6.43	4.89	7.35	5.86
0.40	5.04	3.53	5.89	4.59	6.66	5.54
0.45	4.74	3.30	5.46	4.31	6.14	5.22
0.50	4.50	3.11	5.13	4.07	5.73	4.92
0.60	4.13	2.79	4.64	3.65	5.11	4.42
0.70	3.84	2.51	4.27	3.30	4.65	3.98
0.80	3.63	2.25	4.00	2.98	4.33	3.59
0.90	3.50	2.01	3.82	2.67	4.11	3.25
1.00	3.42	1.83	3.70	2.43	3.95	2.96
1.25	3.27	1.50	3.51	2.01	3.68	2.43
1.50	3.22	1.23	3.43	1.68	3.59	2.03
1.75	3.19	1.16	3.39	1.55	3.51	1.87
2.00	3.07	1.03	2.23	1.40	3.34	1.66
3.00	2.97	0.69	3.18	0.95	3.25	1.14
4.00	2.88	0.51	2.99	0.78	3.09	0.95
5.00	2.81	0.40	2.90	0.58	3.02	0.90

Supplementary Tables B III

ε' and ε'' at selected frequencies for 1-butanol at 20°C

f GHz	ε'	ε''
0.05	17.16	2.28
0.10	16.15	4.25
0.15	14.72	5.73
0.20	13.12	6.64
0.25	11.58	7.04
0.30	10.23	7.07
0.35	9.14	6.88
0.40	8.28	6.58
0.45	7.61	6.26
0.50	7.08	5.94
0.60	6.27	5.40
0.70	5.67	4.92
0.80	5.20	4.46
0.90	4.86	4.03
1.00	4.63	3.65
1.25	4.31	2.99
1.50	4.08	2.53
1.75	3.95	2.21
2.00	3.76	1.99
3.00	3.53	1.30
4.00	3.35	1.03
5.00	3.23	0.91

Supplementary Tables B IV

ε' and ε'' at selected frequencies for solutions of 1-butanol in carbon tetrachloride at 20°C at alcohol mole fraction, X.

	X = 0.4034		X = 0.4974		X = 0.5949	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.05	5.16	0.37	6.82	0.74	8.68	1.16
0.10	5.00	0.69	6.45	1.34	8.07	2.09
0.15	4.78	0.93	5.97	1.73	7.29	2.66
0.20	4.53	1.07	5.48	1.94	6.53	2.93
0.25	4.30	1.15	5.05	2.00	5.87	2.98
0.30	4.10	1.18	4.70	1.98	5.35	2.91
0.35	3.93	1.17	4.42	1.92	4.95	2.79
0.40	3.79	1.15	4.21	1.84	4.64	2.66
0.45	3.70	1.13	4.04	1.77	4.39	2.53
0.50	3.58	1.10	3.90	1.71	4.19	2.42
0.60	3.41	1.06	3.66	1.60	3.87	2.22
0.70	3.27	1.00	3.45	1.49	3.61	2.03
0.80	3.15	0.93	3.30	1.36	3.42	1.84
0.90	3.07	0.84	3.19	1.24	3.28	1.67
1.00	3.02	0.77	3.12	1.14	3.20	1.52
1.25	2.92	0.68	2.97	0.98	3.04	1.30
1.50	2.82	0.58	2.87	0.81	2.91	1.10
1.75	2.78	0.50	2.84	0.74	2.86	0.96
2.00	2.70	0.44	2.75	0.65	2.78	0.85
3.00	2.54	0.20	2.60	0.38	2.63	0.53
4.00	2.37	0.08	2.45	0.22	2.52	0.35
5.00	2.30	*	*	0.04	2.30	0.17

* Data obtained are not physically meaningful

Supplementary Tables B IV

ε' and ε'' at selected frequencies for solutions of 1-butanol in carbon tetrachloride at 20°C at alcohol mole fraction, X.

	X = 0.6957		X = 0.7986		X = 0.8989	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.05	10.65	1.63	13.05	2.06	14.76	2.54
0.10	9.75	2.89	11.95	3.66	13.38	4.50
0.15	8.64	3.61	10.56	4.63	11.67	5.65
0.20	7.59	3.88	9.21	5.05	10.05	6.12
0.25	6.73	3.88	8.08	5.10	8.70	6.15
0.30	6.07	3.74	7.17	4.95	7.64	5.97
0.35	5.57	3.56	6.48	4.71	6.83	5.70
0.40	5.20	3.37	5.95	4.45	6.21	5.42
0.45	4.90	3.21	5.53	4.20	5.72	5.14
0.50	4.65	3.07	5.20	3.97	5.31	4.89
0.60	4.23	2.81	4.70	3.56	4.69	4.43
0.70	3.89	2.54	4.33	3.22	4.23	4.02
0.80	3.65	2.27	4.04	2.91	3.89	3.64
0.90	3.51	2.02	3.82	2.63	3.66	3.30
1.00	3.42	1.83	3.67	2.38	3.51	3.01
1.25	3.23	1.53	3.46	1.91	3.28	2.49
1.50	3.09	1.22	3.29	1.60	3.12	2.13
1.75	3.04	1.06	3.21	1.33	3.01	1.85
2.00	2.91	0.90	3.12	1.18	2.91	1.62
3.00	2.73	0.43	2.92	0.62	2.71	1.08
4.00	2.52	0.17	2.65	0.35	2.46	0.86
5.00	2.31	*	*	0.14	2.38	0.67

* Data obtained are not physically meaningful

Supplementary Tables B V

ε' and ε'' at selected frequencies for solutions of 1-butanol in benzene at 20^{o}C at alcohol mole fraction, X.

	X = 0.3425		X = 0.4502		X = 0.5587	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.05	4.79	0.16	6.50	0.37	8.50	0.71
0.10	4.74	0.31	6.37	0.70	8.21	1.32
0.15	4.67	0.44	6.19	0.97	7.82	1.78
0.20	4.58	0.54	5.99	1.17	7.40	2.10
0.25	4.50	0.62	5.78	1.32	7.00	2.30
0.30	4.43	0.68	5.59	1.44	6.65	2.43
0.35	4.36	0.74	5.41	1.52	6.33	2.52
0.40	4.29	0.79	5.24	1.60	6.05	2.60
0.45	4.22	0.85	5.08	1.66	5.78	2.65
0.50	4.15	0.90	4.91	1.71	5.51	2.70
0.60	3.98	0.98	4.58	1.77	4.98	2.70
0.70	3.80	1.00	4.27	1.73	4.52	2.56
0.80	3.65	0.97	4.02	1.64	4.19	2.35
0.90	3.54	0.93	3.85	1.53	3.98	2.15
1.00	3.47	0.89	3.73	1.45	3.84	2.00
1.25	3.29	0.84	3.47	1.29	3.52	1.76
1.50	3.15	0.73	3.28	1.12	3.31	1.47
1.75	3.05	0.67	3.13	0.99	3.17	1.32
2.00	2.95	0.57	3.04	0.85	3.03	1.12
3.00	2.72	0.33	2.75	0.49	2.77	0.66
4.00	2.51	0.19	2.58	0.26	2.58	0.38
5.00	2.39	0.02	2.40	0.05	2.37	0.19

Supplementary Tables B V

ε' and ε" at selected frequencies for solutions of 1-butanol in benzene at 20°C at alcohol mole fraction, X.

	X = 0.6567		X = 0.7591		X = 0.8705	
f GHz	ε'	ε"	ε'	ε"	ε'	ε"
0.05	10.43	1.06	12.49	1.49	14.68	2.13
0.10	9.97	1.97	11.82	2.74	13.58	3.81
0.15	9.35	2.63	10.92	3.63	12.20	4.87
0.20	8.70	3.06	9.97	4.18	10.86	5.39
0.25	8.08	3.31	9.09	4.47	9.72	5.55
0.30	7.53	3.45	8.32	4.59	8.79	5.54
0.35	7.06	3.52	7.65	4.62	8.03	5.45
0.40	6.64	3.55	7.07	4.58	7.41	5.33
0.45	6.25	3.57	6.56	4.50	6.85	5.20
0.50	5.88	3.55	6.11	4.39	6.35	5.06
0.60	5.20	3.42	5.35	4.09	5.47	4.69
0.70	4.67	3.17	4.79	3.72	4.81	4.20
0.80	4.29	2.88	4.41	3.37	4.40	3.72
0.90	4.05	2.62	4.15	3.07	4.16	3.32
1.00	3.88	2.42	3.95	2.82	4.00	3.04
1.25	3.51	2.06	3.57	2.32	3.58	2.53
1.50	3.28	1.73	3.38	1.95	3.40	2.04
1.75	3.13	1.51	3.21	1.70	3.29	1.83
2.00	3.04	1.29	3.10	1.46	3.13	1.54
3.00	2.80	0.80	2.86	0.84	2.93	0.89
4.00	2.58	0.44	2.61	0.44	2.62	0.42
5.00	2.35	0.22	2.43	0.23	2.37	0.20

Supplementary Tables B VI

ε' and ε" at selected frequencies for solutions of 1-hexanol in cyclohexane at 20^{0}C at alcohol mole fraction, X.

	X = 0.4144		X = 0.5158		X = 0.6255	
f GHz	ε'	ε"	ε'	ε"	ε'	ε"
0.01	*	*	*	*	*	*
0.02	*	*	*	*	8.36	0.13
0.03	*	*	*	*	8.18	0.60
0.04	*	*	6.14	0.22	8.01	0.96
0.05	*	*	6.01	0.52	7.83	1.27
0.06	4.73	0.14	5.90	0.72	7.62	1.53
0.07	4.67	0.29	5.79	0.93	7.40	1.74
0.08	4.56	0.40	5.63	1.08	7.17	1.91
0.09	4.47	0.44	5.50	1.16	6.95	2.04
0.10	4.43	0.48	5.43	1.24	6.75	2.16
0.11	4.40	0.57	5.32	1.35	6.53	2.26
0.12	4.32	0.64	5.19	1.41	6.30	2.34
0.13	4.25	0.69	5.08	1.46	6.09	2.37
0.14	4.19	0.74	4.97	1.51	5.92	2.39
0.15	4.11	0.79	4.85	1.53	5.73	2.43
0.17	3.97	0.82	4.62	1.54	5.37	2.37
0.19	3.86	0.84	4.45	1.48	5.12	2.33
0.21	3.78	0.83	4.28	1.44	4.90	2.25
0.23	3.73	0.84	4.18	1.40	4.70	2.17
0.25	3.67	0.85	4.07	1.38	4.56	2.10
0.27	3.60	0.83	3.92	1.34	4.40	2.02
0.30	3.50	0.80	3.74	1.27	4.17	1.86
0.33	3.41	0.74	3.64	1.23	4.00	1.70
0.36	3.36	0.70	3.57	1.18	3.89	1.56
0.40	3.28	0.68	3.49	1.11	3.72	1.41

* Data obtained are not physically meaningful

Supplementary Tables B VI

ε' and ε'' at selected frequencies for solutions of 1-hexanol in cyclohexane at 20°C at alcohol mole fraction, X.

	X = 0.7181		X = 0.8054		X = 0.8701	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.01	*	*	10.95	0.65	11.73	0.37
0.02	9.43	0.57	10.83	1.08	11.42	1.15
0.03	9.23	1.05	10.64	1.50	11.20	1.74
0.04	9.02	1.49	10.39	1.92	10.95	2.33
0.05	8.74	1.86	10.06	2.28	10.59	2.83
0.06	8.45	2.15	9.71	2.58	10.22	3.21
0.07	8.16	2.42	9.34	2.85	9.87	3.56
0.08	7.81	2.62	8.93	3.05	9.44	3.85
0.09	7.50	2.72	8.55	3.16	9.05	4.00
0.10	7.25	2.83	8.22	3.28	8.74	4.16
0.11	6.96	2.95	7.85	3.40	8.35	4.33
0.12	6.66	3.00	7.48	3.44	7.95	4.36
0.13	6.40	3.02	7.17	3.45	7.65	4.35
0.14	6.15	3.04	6.87	3.45	7.33	4.37
0.15	5.92	3.01	6.59	3.41	7.01	4.31
0.17	5.54	2.95	6.14	3.36	6.53	4.18
0.19	5.22	2.84	5.75	3.25	6.10	3.97
0.21	4.97	2.74	5.43	3.08	5.71	3.82
0.23	4.75	2.67	5.21	2.98	5.40	3.64
0.25	4.55	2.51	4.99	2.78	5.08	3.50
0.27	4.42	2.38	4.83	2.60	4.80	3.27
0.30	4.17	2.22	4.57	2.34	4.48	3.14
0.33	4.02	2.04	4.35	2.06	4.26	2.98
0.36	3.88	1.83	4.17	1.81	4.14	2.84
0.40	3.71	1.61	3.87	1.48	4.02	2.68

* Data obtained are not physically meaningful

Supplementary Tables B VI

ε' and ε'' at selected frequencies for 1-hexanol at 20°C.

f GHz	ε'	ε''
0.01	13.26	1.33
0.02	13.14	1.91
0.03	12.85	2.51
0.04	12.49	3.11
0.05	12.01	3.65
0.06	11.51	4.06
0.07	11.01	4.43
0.08	10.44	4.72
0.09	9.89	4.85
0.10	9.45	4.95
0.11	8.98	5.06
0.12	8.49	5.07
0.13	8.09	5.02
0.14	7.71	4.96
0.15	7.38	4.86
0.17	6.79	4.69
0.19	6.34	4.46
0.21	5.84	4.20
0.23	5.54	3.98
0.25	5.24	3.71
0.27	4.99	3.44
0.30	4.67	3.18
0.33	4.38	2.94
0.36	4.23	2.65
0.40	4.06	2.29

Supplementary Tables B VII

ε' and ε'' selected frequencies for solutions of 1-octanol in cyclohexane at 20°C at alcohol mole fraction, X.

	X = 0.3951		X = 0.4958		X = 0.5979	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.01	*	*	*	*	*	*
0.02	*	*	*	*	*	*
0.03	*	*	*	*	*	*
0.04	*	*	*	*	*	*
0.05	*	*	*	*	5.11	0.31
0.06	*	*	4.28	0.05	5.01	0.50
0.07	*	*	4.21	0.19	4.94	0.69
0.08	*	*	4.12	0.30	4.82	0.85
0.09	*	*	4.03	0.34	4.72	0.91
0.10	*	*	4.01	0.37	4.69	0.98
0.11	3.39	0.05	3.99	0.44	4.62	1.09
0.12	3.37	0.11	3.94	0.50	4.52	1.14
0.13	3.36	0.14	3.89	0.55	4.46	1.17
0.14	3.34	0.18	3.85	0.60	4.38	1.21
0.15	3.31	0.21	3.78	0.64	4.29	1.21
0.17	3.26	0.23	3.68	0.67	4.16	1.20
0.19	3.21	0.22	3.61	0.67	4.05	1.16
0.21	3.18	0.21	3.56	0.67	3.93	1.12
0.23	3.17	0.21	3.53	0.67	3.86	1.10
0.25	3.14	0.21	3.51	0.70	3.77	1.08
0.27	3.08	0.22	3.42	0.69	3.65	1.07
0.30	3.02	0.21	3.35	0.67	3.53	1.07
0.33	2.97	0.18	3.30	0.61	3.46	1.05
0.36	2.95	0.17	3.27	0.62	3.46	1.08
0.40	2.90	0.20	3.22	0.64	3.45	1.11

* Data obtained are not physically meaningful

Supplementary Tables B VII

ε' and ε'' at selected frequencies for solutions of 1-octanol in cyclohexane at 20°C at alcohol mole fraction, X.

	X = 0.5881		X = 0.7833		X = 0.8887	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.01	*	*	*	*	*	*
0.02	*	*	*	*	8.56	0.35
0.03	6.43	0.04	7.19	0.36	8.35	0.85
0.04	6.35	0.43	7.04	0.82	8.18	1.37
0.05	6.14	0.74	6.83	1.20	7.85	1.79
0.06	5.96	0.91	6.60	1.46	7.54	2.03
0.07	5.83	1.09	6.39	1.67	7.29	2.26
0.08	5.61	1.26	6.17	1.84	6.96	2.47
0.09	5.41	1.30	5.95	1.93	6.67	2.52
0.10	5.30	1.35	5.79	1.99	6.46	2.60
0.11	5.15	1.44	5.62	2.06	6.20	2.68
0.12	5.00	1.46	5.45	2.09	5.97	2.65
0.13	4.90	1.49	5.32	2.10	5.82	2.67
0.14	4.77	1.55	5.19	2.13	5.60	2.71
0.15	4.62	1.55	5.02	2.12	5.41	2.63
0.17	4.44	1.54	4.78	2.04	5.11	2.61
0.19	4.27	1.48	4.58	1.95	4.89	2.42
0.21	4.17	1.44	4.43	1.86	4.66	2.33
0.23	4.06	1.43	4.29	1.79	4.52	2.29
0.25	4.01	1.37	4.17	1.73	4.39	2.16
0.27	3.87	1.34	4.02	1.67	4.18	2.09
0.30	3.76	1.24	3.88	1.60	4.02	1.99
0.33	3.63	1.12	3.77	1.49	3.89	1.88
0.36	3.58	1.08	3.72	1.49	3.80	1.81
0.40	3.44	1.02	3.67	1.44	3.73	1.72

*Data obtained are not physically meaningful

Supplementary Table B VII

ε' and ε'' at selected frequencies for 1-octanol at 20°C.

f	ε'	ε''
0.01	10.07	0.22
0.02	9.75	0.90
0.03	9.48	1.40
0.04	9.19	1.84
0.05	8.82	2.20
0.06	8.45	2.47
0.07	8.08	2.69
0.08	7.68	2.85
0.09	7.31	2.92
0.10	7.01	2.98
0.11	6.70	3.04
0.12	6.41	3.04
0.13	6.17	3.03
0.14	5.93	3.03
0.15	5.70	2.99
0.17	5.37	2.92
0.19	5.07	2.82
0.21	4.88	2.72
0.23	4.66	2.61
0.25	4.59	2.49
0.27	4.41	2.35
0.30	4.25	2.22
0.33	4.15	2.01
0.36	3.97	1.86
0.40	3.80	1.69

Supplementary Tables B VIII

ε' and ε" at selected frequencies for solutions of 1-octanol in carbon tetrachloride at 20°C at alcohol mole fraction, X.

	X = 0.3954		X = 0.4812		X = 0.5879	
f GHz	ε'	ε"	ε'	ε"	ε'	ε"
0.01	*	*	*	*	*	*
0.02	*	*	*	*	*	*
0.03	*	*	*	*	*	*
0.04	*	*	*	*	*	*
0.05	*	*	*	*	5.41	0.21
0.06	*	*	*	*	5.33	0.40
0.07	*	*	4.43	0.11	5.27	0.58
0.08	3.75	0.02	4.37	0.23	5.16	0.74
0.09	3.71	0.07	4.30	0.29	5.06	0.82
0.10	3.73	0.10	4.30	0.35	5.02	0.89
0.11	3.77	0.16	4.27	0.44	4.96	0.99
0.12	3.76	0.23	4.21	0.49	4.86	1.05
0.13	3.75	0.26	4.19	0.53	4.80	1.08
0.14	3.76	0.31	4.16	0.60	4.75	1.15
0.15	3.73	0.36	4.09	0.64	4.64	1.20
0.17	3.68	0.35	4.02	0.68	4.50	1.19
0.19	3.62	0.37	3.91	0.69	4.36	1.20
0.21	3.60	0.36	3.87	0.70	4.23	1.17
0.23	3.56	0.35	3.84	0.71	4.17	1.16
0.25	3.53	0.40	3.78	0.74	4.05	1.16
0.27	3.48	0.43	3.73	0.78	3.98	1.20
0.30	3.41	0.46	3.65	0.76	3.84	1.16
0.33	3.37	0.49	3.60	0.78	3.76	1.18
0.36	3.39	0.54	3.60	0.79	3.74	1.23
0.40	3.39	0.60	3.53	0.84	3.68	1.24

* Data obtained are not physically meaningful

Supplementary Tables B VIII

ε' and ε" at selected frequencies for solutions of 1-octanol in carbon tetrachloride at 20°C at alcohol mole fraction, X.

	X = 0.6986		X = 0.7907		X = 0.8629	
f GHz	ε'	ε"	ε'	ε"	ε'	ε"
0.01	*	*	*	*	*	*
0.02	*	*	*	*	8.58	0.21
0.03	6.75	0.05	7.60	0.42	8.37	0.75
0.04	6.62	0.41	7.43	0.83	8.17	1.21
0.05	6.46	0.70	7.22	1.17	7.89	1.59
0.06	6.30	0.91	7.00	1.40	7.60	1.83
0.07	6.14	1.08	6.79	1.60	7.35	2.03
0.08	5.98	1.22	6.58	1.76	7.09	2.22
0.09	5.83	1.33	6.36	1.86	6.81	2.33
0.10	5.68	1.42	6.18	1.95	6.58	2.40
0.11	5.53	1.49	5.98	2.02	6.34	2.47
0.12	5.39	1.53	5.79	2.04	6.10	2.49
0.13	5.28	1.58	5.65	2.07	5.93	2.48
0.14	5.15	1.64	5.49	2.12	5.75	2.52
0.15	4.99	1.66	5.28	2.11	5.53	2.51
0.17	4.79	1.63	5.06	2.03	5.27	2.43
0.19	4.60	1.62	4.79	1.97	4.96	2.32
0.21	4.45	1.58	4.63	1.89	4.78	2.25
0.23	4.34	1.51	4.48	1.79	4.60	2.12
0.25	4.24	1.48	4.36	1.73	4.44	2.04
0.27	4.13	1.44	4.23	1.71	4.32	2.00
0.30	4.02	1.35	4.07	1.58	4.15	1.85
0.33	3.89	1.27	3.95	1.49	4.02	1.75
0.36	3.82	1.23	3.83	1.42	3.89	1.65
0.40	3.67	1.14	3.69	1.29	3.70	1.53

* Data obtained are not physically meaningful.

Supplementary Tables B IX

ε' and ε'' at selected frequencies for solutions of 1-octanol in benzene at 20^{o}C at alcohol mole fraction, X.

	X = 0.3498		X = 0.4439		X = 0.5382	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.01	*	*	*	*	*	*
0.02	*	*	*	*	*	*
0.03	*	*	*	*	*	*
0.04	*	*	*	*	*	*
0.05	*	*	*	*	5.57	0.01
0.06	*	*	*	*	5.52	0.18
0.07	*	*	4.72	0.03	5.45	0.32
0.08	*	*	4.66	0.11	5.38	0.41
0.09	*	*	4.62	0.16	5.33	0.47
0.10	*	*	4.62	0.19	5.30	0.53
0.11	*	*	4.63	0.26	5.29	0.63
0.12	3.99	0.06	4.60	0.36	5.22	0.72
0.13	3.97	0.09	4.55	0.41	5.15	0.77
0.14	3.97	0.13	4.53	0.45	5.11	0.83
0.15	3.94	0.18	4.50	0.51	5.04	0.91
0.17	3.87	0.20	4.39	0.56	4.86	0.92
0.19	3.84	0.21	4.33	0.62	4.75	0.96
0.21	3.82	0.22	4.30	0.63	4.67	0.96
0.23	3.81	0.24	4.28	0.68	4.60	0.98
0.25	3.79	0.27	4.22	0.75	4.48	1.03
0.27	3.77	0.31	4.18	0.80	4.41	1.06
0.30	3.69	0.33	4.09	0.80	4.24	1.05
0.33	3.66	0.31	4.06	0.79	4.14	1.03
0.36	3.63	0.36	4.03	0.83	4.05	1.02
0.40	3.58	0.41	3.97	0.92	3.90	1.03

* Data obtained are not physically meaningful

Supplementary Tables B IX

ε' and ε'' at selected frequencies for solutions of 1-octanol in benzene at 20°C at alcohol mole fraction, X.

	X = 0.6530		X = 0.7564		X = 0.8818	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.01	*	*	*	*	*	*
0.02	*	*	*	*	8.72	0.11
0.03	*	*	7.62	0.30	8.52	0.73
0.04	6.53	0.16	7.50	0.63	8.31	1.20
0.05	6.44	0.47	7.36	0.91	8.10	1.58
0.06	6.35	0.69	7.21	1.14	7.88	1.90
0.07	6.28	0.89	7.04	1.35	7.63	2.16
0.08	6.18	1.06	6.85	1.51	7.37	2.34
0.09	6.08	1.17	6.68	1.62	7.14	2.48
0.10	6.03	1.27	6.53	1.73	6.92	2.58
0.11	5.97	1.41	6.38	1.84	6.71	2.67
0.12	5.86	1.52	6.20	1.94	6.49	2.73
0.13	5.75	1.58	6.02	2.01	6.27	2.74
0.14	5.65	1.63	5.86	2.04	6.10	2.73
0.15	5.55	1.68	5.71	2.09	5.92	2.74
0.17	5.33	1.70	5.40	2.09	5.55	2.63
0.19	5.17	1.70	5.20	2.08	5.30	2.53
0.21	4.99	1.70	5.02	2.04	5.06	2.39
0.23	4.87	1.71	4.86	2.05	4.87	2.34
0.25	4.70	1.74	4.71	1.98	4.63	2.23
0.27	4.53	1.77	4.58	1.99	4.47	2.21
0.30	4.31	1.76	4.36	1.87	4.20	2.11
0.33	4.26	1.77	4.24	1.75	4.09	1.95
0.36	4.11	1.85	4.13	1.66	3.94	1.95
0.40	4.09	1.92	3.91	1.59	3.81	1.88

* Data obtained are not physically meaningful

Supplementary Tables B X

ε' and ε'' at selected frequencies for solutions of 1-decanol in cyclohexane at 20°C at alcohol mole fraction, X.

	X = 0.5912		X = 0.6903		X = 0.8120	
f GHz	ε'	ε''	ε'	ε''	ε'	ε''
0.01	*	*	*	*	*	*
0.02	*	*	*	*	*	*
0.03	*	*	*	*	5.91	0.15
0.04	*	*	5.39	0.34	5.69	0.63
0.05	4.54	0.20	5.20	0.63	5.44	0.98
0.06	4.41	0.35	5.02	0.82	5.21	1.19
0.07	4.29	0.47	4.85	0.97	5.02	1.36
0.08	4.13	0.56	4.66	1.07	4.80	1.46
0.09	4.00	0.58	4.50	1.09	4.62	1.47
0.10	3.93	0.59	4.40	1.11	4.53	1.48
0.11	3.86	0.63	4.31	1.15	4.42	1.51
0.12	3.78	0.66	4.20	1.16	4.29	1.49
0.13	3.71	0.68	4.11	1.16	4.22	1.45
0.14	3.64	0.71	4.04	1.16	4.14	1.44
0.15	3.56	0.73	3.94	1.16	4.05	1.41
0.17	3.44	0.70	3.79	1.09	3.89	1.30
0.19	3.36	0.69	3.67	1.03	3.77	1.18
0.21	3.31	0.66	3.59	0.95	3.66	1.05
0.23	3.27	0.64	3.53	0.90	3.60	0.97
0.25	3.25	0.62	3.47	0.87	3.50	0.93
0.27	3.20	0.60	3.40	0.83	3.39	0.88
0.30	3.15	0.55	3.30	0.78	3.28	0.84
0.33	3.09	0.48	3.23	0.73	3.21	0.81
0.36	3.06	0.43	3.21	0.72	3.21	0.77
0.40	2.99	0.42	3.17	0.70	3.22	0.77

* Data obtained are not physically meaningful.

Supplementary Tables B X

ε' and ε'' at selected frequencies for solution of 1-decanol in cyclohexane at 20°C at alcohol mole fraction, X.

	X = 0.9085		X = 1.0	
f GHz	ε'	ε''	ε'	ε''
0.01	*	*	*	*
0.02	*	*	*	*
0.03	6.40	0.68	6.72	0.68
0.04	6.05	1.16	6.36	1.18
0.05	5.69	1.48	6.04	1.51
0.06	5.37	1.66	5.73	1.75
0.07	5.10	1.78	5.42	1.90
0.08	4.82	1.84	5.16	1.95
0.09	4.60	1.80	4.96	1.95
0.10	4.46	1.76	4.80	1.94
0.11	4.34	1.74	4.65	1.94
0.12	4.21	1.71	4.51	1.90
0.13	4.12	1.66	4.40	1.85
0.14	4.02	1.62	4.31	1.81
0.15	3.91	1.56	4.20	1.77
0.17	3.77	1.42	4.03	1.63
0.19	3.65	1.29	3.88	1.49
0.21	3.56	1.16	3.78	1.35
0.23	3.50	1.07	3.70	1.27
0.25	3.42	1.01	3.58	1.19
0.27	3.33	0.97	3.51	1.16
0.30	3.22	0.90	3.38	1.08
0.33	3.19	0.83	3.30	1.05
0.36	3.14	0.81	3.29	1.02
0.40	3.13	0.77	3.28	0.99

* Data obtained are not physically meaningful.

COMPUTER PROGRAMS USED IN THIS STUDY

PROGRAM DATA

This program corrects the sampled time domain data for time jitter (Nicolson, 1968) and voltage drift. The time jitter is calculated from reference voltages (see subsection 3.3.2) measured simultaneously with the time domain data. Corresponding times are added algebraically to the assumed time for each discretely measured point. To correct for voltage drift, all measured voltages are referred to the reference voltage on the horizontal portion of the time domain signal.

```
      MASTER DATA
      REAL IMEET, NUNUL
      DIMENSION VOLT(256), C(256), B(256), HORIZ(256), PT(5), AHORIZ(5),
     1R(256),W(256),A(5),P(530),IMEET(256),T(256),HEAD(10), HOUSE(2)
      IBEGIN = 1
      INDEX = 1
C
C     ITRACE=1 READS DATA FILE BUT DOES NO CALCULATIONS;OTHERWISE
C     PROCEEDS WITH CALCULATIONS
C     IREAD DEFINES INPUT CHANNEL ; 4 IMPLIES MAG TAPE ; 5 IMPLIES CARD
C     READER
C     IPRINT=1 SUPRESSES OUTPUT OF DATA LIST ; OTHERWISE DATA LISTED
C     INDEX=1 IMPLIES INCIDENT SIGNAL DATA ;=2 REFLECTED DATA ;
C     OTHERWISE TERMINATES PROGRAM
C
111   READ(5,39) ITRACE,IREAD,IPRINT,INDEX
39    FORMAT(4I1)
      IF (INDEX .GT. 2) GO TO 999
      READ(5,59) (HEAD(J),J=1,10)
59    FORMAT(10A8)
C
C     N IS NUMBER OF DATA POINTS
C     TAU IS THE TIME INTERVAL PER POINT
C
100   READ(5,9) N,TAU
9     FORMAT(I5,1F0.0)
      IEIND = IBEGIN+N-1
      DO 1 I=1,IEIND
1     HORIZ(I),VOLT(I),IMEET(I) =0
      IEH = IEIND/2
      DO 2 I=1,IEH
      C(I),B(I) =0.0
2     CONTINUE
C    VOLT IS DIGITISED VOLTAGE SIGNAL
C    C IS REFERENCE POINT ON FLAT SECTION OF WAVEFORM
C    B IS REFERENCE POINT ON SLOPING SECTION OF WAVEFORM
      IF (IREAD .EQ. 5) GO TO 5
      IF (IREAD .EQ. 9) GO TO 4
      READ(4,29) DATE,SAMPLE,CONDITIONS,HOUSE(1),HOUSE(2),NCOUNT,
     1(C(I),VOLT(I),B(I),VOLT(I+1),I=1,IEIND,2)
      GO TO 6
4     READ(4,29) DATE,SAMPLE,CONDITIONS,HOUSE(1),HOUSE(2),NCOUNT,
```

```
     1(VOLT(I),I=1,IEIND)
20    FORMAT(A6,A8,A5,A8,A4,I4,9X,64F5.0/(44X,64F5.0))
6     IF (ITRACE .EQ. 1) GO TO 111
      GO TO 7
5     READ(5,19) (C(I),VOLT(I),B(I),VOLT(I+1),I=1,IEIND,2)
19    FORMAT(1024F0.0)
7     CONTINUE
      WRITE(6,70) (HEAD(J),J=1,10)
70    FORMAT(1H1,30X,10A8)
C
C     CALCULATION TO FIND INTERSECTION POINT OF LINES DRAWN FROM SLOPING
C      AND INITIAL HORIZONTAL REGIONS
C      DIST IS THE NUMBER OF TAU STEPS TO INTERSECTION POINT
C      GRAD IS THE GRADIENT OF SLOPING PORTION OF WAVEFORM
C
      K1 = 1
      K2 = 10
      K3 = K2-K1+1
      L1 = 0
      Y1 = 0.
      L2 = 0
      Y9 = 0.
      DO 25 I=K1,K2
      L1 = L1+I
      Y1 = Y1+VOLT(I)
      L2 = L2+I*I
25    Y9 = Y9+I*VOLT(I)
      LL = K3*L2-L1*L1
      A1 = (K3*Y9-L1*Y1)/LL
      B1 = (Y1*L2-L1*Y9)/LL
      WRITE(6,80) A1
80    FORMAT(1H0,45X,29HSLOPE OF HORIZONTAL SECTION =, F8.3)
      G2 = 0.
      JJ = 0
      K4 = K2+1
      DO 26 M=K4,IEIND
      G1 = VOLT(M)-VOLT(M-1)
      IF (G1 .GT. G2) GO TO 26
      G2 = G1
      JJ = M
26    CONTINUE
      W0 = VOLT(JJ-2)-VOLT(JJ-3)
      W1 = VOLT(JJ-1)-VOLT(JJ-2)
      W2 = VOLT(JJ)-VOLT(JJ-1)
      W3 = VOLT(JJ+1)-VOLT(JJ)
      W4 = VOLT(JJ+2)-VOLT(JJ+1)
      AN1 = 3.*W0+W1-W2-3.*W3
      AN2 = W0-W1-W2+W3
      X5 = AN1/(AN2*5.)-0.5
      A2 = W2+X5*(W3-W2)+X5*(X5-1.)*(W4-W3-W2+W1)/4.
      B2 = VOLT(JJ)-A2*JJ
      B9 = VOLT(JJ-1)-W2*(JJ-1)
      Z9 = (B9-B1)/(A1-W2)
      DIST = (B2-B1)/(A1-A2)
      IF (ABS(DIST-Z9) .LT. 0.5) GO TO 87
      DIST = Z9
87    RJ = FLOAT(JJ)-0.5
      WRITE(6,90) VOLT(JJ),RJ
90    FORMAT(1H0,35X,30HINFLECTION VOLTAGE AND TAU ARE ,F8.2,2X,3HAND,
     1F8.2)
      WRITE(6,91) W2,Z9
```

```
91     FORMAT(1H0,40X,30HDIFFERENCE APPROX. TO SLOPE IS,F8.2,/,49X,
      114HAPPROX. TREF = ,F8.5 )
       WRITE(6,92) A2,DIST,TAU
92     FORMAT(1H0,44X,8HSLOPE   =,F8.3,/,45X,8HDIST    =,F8.3,/,45X,
      18HTAU     =,F11.6)
       TREFZ = DIST*TAU
C
C      CALCULATION OF GRAD
C
       DO 28 I=1,IEIND
       IF (B(1) .GT. VOLT(I) .AND. B(1) .LT. VOLT(I-1)) K = I
28     CONTINUE
       GRAD = (VOLT(K-2)-VOLT(K+1))/(3.*TAU)
       WRITE(6,93) GRAD
93     FORMAT(1H0,35X,40HGRADIENT FOR TIME CORRECTION PROCEDURE = ,F8.2)
       IF (IPRINT .EQ. 1) GO TO 23
       IF (INDEX .EQ. 1) WRITE (6,10)
10     FORMAT(1H0,51X,18HINCIDENT WAVE DATA )
       IF (INDEX .EQ. 2) WRITE(6,20)
20     FORMAT(1H0,50X,20HREFLECTION WAVE DATA  )
       WRITE (6,30)
30     FORMAT (1H0, 2X, 17HMEASURED TIME(NS), 3X, 16HMEASURED VOLTAGE,
      14X, 17HADJUSTED TIME(NS), 3X, 16HADJUSTED VOLTAGE,///)
23     IE1 = IEIND-1
       IE2 = IEIND-2
       IE3 = IEIND-3
       IE4 = IEIND-4
C
C      CALCULATION OF VOLTAGES, CORRECTED FOR TIME JITTER AND DRIFT
C
       DO 14 I=1,IE3,2
       IMEFT(I) = VOLT(I)-C(I)
14     IMEFT(I+1) = VOLT(I+1)-((C(I)+C(I+2))/2.)
       IMEFT(IE1) = VOLT(IE1)-C(IE1)
       IMEFT(IEIND) = VOLT(IEIND)-C(IE1)
       FUN = C(1)-B(1)
       DO 15 I=1,IEIND,2
15     HORIZ(I) = (C(I)-B(I)-FUN)/GRAD
       DO 11 I=1,IEH
       C(I) = HORIZ(2*I-1)
11     B(I) = 2*I-1.
       P(1) = -1.0
       P(3) = 0.
       P(4) = 0.
       P(5) = 0.
       IMAX = 15+2*IEH
C
C      SMOOTHING OF B VOLTAGES TO A QUADRATIC
C
       DO 12 M=1,3
12     CALL F4CFORPL(IEH, 4, IMAX, B  , C, R, W, A, P)
       DO 21 I=1,IEH
       U = I
       CALL F4CALFUN(U, V, IMAX, P)
21     C(I) = V
       DO 22 K=1,IEH
22     HORIZ(2*K-1) = C(K)-C(1)
       DO 16 I = 1,IE3,2
16     HORIZ(I+1) = (HORIZ(I)+HORIZ(I+2))/2.
       HORIZ(IEIND) = HORIZ(IE1)
       DO 17 I=1,IEIND
```

```
      T(I) = I*TAU-TREFZ
17    HORIZ(I) = T(I)+HORIZ(I)
      IF (IPRINT .EQ. 1) GO TO 24
      DO 18 M=1,2
      HORIZ(M) = T(M)
      WRITE (6,40) HORIZ(M), VOLT(M), T(M), IMEET(M)
40    FORMAT( 6X, F8.5, 12X, F8.2, 12X, F8.5, 12X, F8.2,6X)
18    CONTINUE
24    DO 99 J=1,IE4
      P(1) = -1.0
      P(3) = 0.
      P(4) = 0.
      P(5) = 0.
      DO 3 K=1,5
      L = J+K-1
      PT(K) = IMEET(L)
3     AHORIZ(K) = HORIZ(L)
C
C     INTERPOLATION OF VOLTAGE AT REQUIRED VALUE OF TIME
C
      DO 13 M=1,5
13    CALL F4CFORPL(5,5,28,AHORIZ,PT,R,W,A,P)
      L=J+2
      U=T(L)
      CALL F4CALFUN(U,V,28,P)
      IF (IPRINT .EQ. 1) GO TO 99
      WRITE(6,40) HORIZ(L), VOLT(L), T(L), IMEET(L)
99    CONTINUE
      WRITE(7,50) (IMEET(K),K=1,IE2)
50    FORMAT(10F8.2)
      GO TO 111
999   CONTINUE
      ENDFILE 7
      STOP
      END
```

PROGRAM SHANTDR

This program, considerably developed from a program of the same name presented by van Gemert (1972), calculates the Fourier transform of the time domain data using the Samulon (1951) modification of the Shannon (1949) sampling theorem. It also allows the calculation of a reference spectrum , as suggested by Glasser (1975), for total reflection studies.

```
      MASTER SHANTDR
      COMPLEX CE,CEHLF,CRHO,CDEC,CSHANE,CSHANH,CSHAN,CR,CSHORT
      DIMENSION HEAD(15),HHEAD(15),KONST(1),LL(1),AMP(51),PHI(51),ANU(51
     1),CSHANE(51),CSHANH(51),VOLT(1024),HOUSE(2),AMPD(51),PHID(51)
      CALL USEFILE(11,2HED,12HCHCC-TRNSFM ,0,0)
      PI = 3.14159265
C
C     INDEX=1 IMPLIES INCIDENT SIGNAL DATA ;=2 REFLECTED DATA ;
C     OTHERWISE END OF CALCULATIONS AT THE CURRENT FREQUENCY RANGE
C
100   READ(5,79) INDEX
      IF (INDEX .GT. 2) GO TO 999
C
C     N IS NUMBER OF DATA POINTS
C     ITOT IS NUMBER OF FREQUENCY ITERATIONS
C     SCALE IS VOLTAGE MULTIPLICATION FACTOR (FROM SCREEN )
C     ANUNUL IS FREQUENCY INCREMENT
C     TAU IS TIME INTERVAL PER POINT
C     FREQBEG IS STARTING FREQUENCY - FREQ INCREMENT
C
1     READ(5,9) KONST,(HEAD(J),J=1,15)
9     FORMAT(I5,15A5)
C
C    TITLE CARDS
C
      READ(5,19) N,ITOT,SCALE,ANUNUL,TAU,FREQBEG
19    FORMAT(2I5,4F0.0)
C
C     IREAD DEFINES INPUT CHANNEL ; 3 IS MAG TAPE ; 4 IS FROM OUTPUT
C     FILE OF PROGRAM DATA ; 5 IS FROM CARDS
C     ICHECK = 0 HAS NO EFFECT ; = 1 FOR DATA FROM REFERENCE LIQUID FOR
C     TOTAL REFLECTION METHOD
C
      READ(5,29) IREAD,ICHECK
29    FORMAT(2I2)
      WRITE(6,10) KONST,(HEAD(J),J=1,15)
10    FORMAT(1H1,I5,15A5)
      IF (IREAD .NE. 3) GO TO 5
      READ(3,49) DATE,SAMPLE,CONDITIONS,HOUSE(1),HOUSE(2),NCOUNT,(VOLT(
     1),I=1,N)
49    FORMAT(A6,A8,A5,A8,A4,I4,9X,64F5.0/(44X,64F5.0))
      GO TO 5
```

```
3     N = N-2
      READ(IREAD,39) (VOLT(I),I=1,N)
39    FORMAT(10F8.2)
5     CONTINUE
      IF (ICHECK .EQ. 10) GO TO 100
C
C    CALCULATION TO FIND INTERSECTION POINT OF LINES DRAWN FROM SLOPING
C     AND INITIAL HORIZONTAL REGIONS
C
      K1 = 1
      K2 = 10
      K3 = K2-K1+1
      L1 = 0
      Y1 = 0.
      L2 = 0
      Y9 = 0.
      DO 25 I=K1,K2
      L1 = L1+I
      Y1 = Y1+VOLT(I)
      L2 = L2+I*I
25    Y9 = Y9+I*VOLT(I)
      LJ = K3*L2-L1*L1
      A1 = (K3*Y9-L1*Y1)/LJ
      B1 = (Y1*L2-L1*Y9)/LJ
      WRITE(6,81) A1
81    FORMAT(1H0,45X,29HSLOPE OF HORIZONTAL SECTION =, F8.3)
      G2 = 0.
      JJ = 0
      K4 = K2+1
      DO 26 M=K4,N
      G1 = VOLT(M)-VOLT(M-1)
      IF (G1 .GT. G2) GO TO 26
      G2 = G1
      JJ = M
26    CONTINUE
      W0 = VOLT(JJ-2)-VOLT(JJ-3)
      W1 = VOLT(JJ-1)-VOLT(JJ-2)
      W2 = VOLT(JJ)-VOLT(JJ-1)
      W3 = VOLT(JJ+1)-VOLT(JJ)
      W4 = VOLT(JJ+2)-VOLT(JJ+1)
      AN1 = 3.*W0+W1-W2-3.*W3
      AN2 = W0-W1-W2+W3
      X5 = AN1/(AN2*5.)-0.5
      A2 = W2+X5*(W3-W2)+X5*(X5-1.)*(W4-W3-W2+W1)/4.
      B2 = VOLT(JJ)-A2*JJ
      B9 = VOLT(JJ-1)-W2*(JJ-1)
      Z9 = (B9-B1)/(A1-W2)
      DIST = (B2-B1)/(A1-A2)
      IF (ABS(DIST-Z9) .LT. 0.5) GO TO 87
      DIST = Z9
87    RJ = FLOAT(JJ)-0.5
      WRITE(6,88) VOLT(JJ),RJ
88    FORMAT(1H0,35X,30HINFLECTION VOLTAGE AND TAU ARE ,F8.2,2X,3HAND,
     1F8.2)
      WRITE(6,91) W2,Z9
91    FORMAT(1H0,40X,30HDIFFERENCE APPROX. TO SLOPE IS,F8.2,/,49X,
     114HAPPROX. TREF = ,F10.5)
      WRITE(6,92) A2,DIST,TAU
92    FORMAT(1H0,44X,8HSLOPE  = ,F12.5,/,45X,8HDIST   = ,F12.5,/,45X,
     18HTAU    = ,F12.5)
      TREFZ = DIST*TAU
```

```
      DO 4 I=1,N
4     VOLT(I) = VOLT(I)/SCALE
      IF (IREAD .EQ. 4) GO TO 112
      IF (INDEX .EQ. 1) WRITE(6,20)
20    FORMAT(1H0,51X,18HINCIDENT WAVE DATA  )
      IF (INDEX .EQ. 2) WRITE(6,30)
30    FORMAT(1H0,51X,19HREFLECTED WAVE DATA  )
      WRITE(6,40)
40    FORMAT(1H0,7X,1H1,6X,7HVOLT(I) ,6X,9HVOLT(I+1) ,4X,9HVOLT(I+2) ,
     14X,9HVOLT(I+3) ,4X,9HVOLT(I+4) ;4X,9HVOLT(I+5) ,4X,9HVOLT(I+6) ,
     24X,9HVOLT(I+7)//)
      WRITE(6,50) (I,(VOLT(J),J=I,I+7),I=1,N,8)
50    FORMAT((5X,I5,8(3X,F10.4)))
112   CONTINUE
      IF (INDEX .EQ. 2) GO TO 113
      WRITE(6,70)
70    FORMAT(1H1,40X,41HFOURIER TRANSFORM OF INCIDENT SIGNAL DATA  //)
      GO TO 114
113   WRITE(6,80)
80    FORMAT(1H1,39X,42HFOURIER TRANSFORM OF REFLECTED SIGNAL DATA //)
114   WRITE(6,90)
90    FORMAT(30X,4HREAL,11X,4HIMAG,11X,3HAMP,11X,5HPHASE,11X,4HFREQ,/)
C
C     CALCULATION OF FOURIER TRANSFORM
C
      DO 116 J=1,ITOT
      ANU(J) =(ANUNUL*J)+FREQBEG
      OMEGA = 2.*PI*ANU(J)
      CRL = COS(-OMEGA*TAU)
      CIM = SIN(-OMEGA*TAU)
      CGR = (1-CRL)/(2.*(1.-CRL))
      CGIM = CIM/(2.*(1.-CRL))
      SUMR = 0.
      SUMIM = 0.
      N1 = N-1
      DO 117 I=1,N1
      T = FLOAT(I+1)*TAU-TREFZ
      SUMR = SUMR+(VOLT(I+1)-VOLT(I))*COS(-OMEGA*T)
117   SUMIM = SUMIM+(VOLT(I+1)-VOLT(I))*SIN(-OMEGA*T)
      SHANR = TAU*(CGR*SUMR-CGIM*SUMIM)
      SHANIM = TAU*(CGIM*SUMR+SUMIM*CGR)
      AMP(J) = SQRT(SHANR*SHANR+SHANIM*SHANIM)
      PHI(J) = ATAN(SHANIM/SHANR)
      IF (ICHECK .EQ. 0) GO TO 116
      CSHAN = CMPLX(SHANR,SHANIM)
      IF (ICHECK .EQ. 1) GO TO 121
      CSHANE(J) = CSHAN
      GO TO 116
121   CSHANH(J) = CSHAN
116   WRITE(6,110) SHANR,SHANIM,AMP(J),PHI(J),ANU(J)
110   FORMAT(20X,5(F15.5))
C
C     IFILE DEFINES OUTPUT CHANNEL ; = 10 TO DISC FILE ; = 11 TO D.A.[illegible]
C     PROCEDURE
C
      READ(5,79) IFILE
79    FORMAT(I2)
      IF (ICHECK .NE. 1)GO TO 126
C
C     EZ AND EINF ARE LOW AND HIGH FREQUENCY LIMITS OF PERMITTIVITY
C    FOR REFERENCE LIQUID ; TRELAX IS THE CORRESPONDING RELAXATION TIME
```

```
C
      READ(5,89) EZ,EINF,TRELAX
89    FORMAT(3F0.0)
C
C     LENGTH OF SAMPLE CELL ASSUMED AS 10 CM
C
      V = 3.123
      AL = V/0.3123
      B = 0.41919*AL
C
C     CALCULATION OF INCIDENT SPECTRUM FROM REFERENCE LIQUID DATA
C
      DO 800 J = 1,ITOT
      OMEGA = 2.*PI*ANU(J)
      CE = EINF+(EZ-EINF)/CMPLX(1.,OMEGA*TRELAX)
      CEHLF = CSQRT(CE)
      CRHO = (1.-CEHLF)/(1.+CEHLF)
      CDEC = CEXP(CMPLX(ANU(J)*B*AIMAG(CEHLF),-ANU(J)*B*REAL(CEHLF)))
      CR = CRHO*(1.-CDEC)/(1.-CRHO*CRHO*CDEC)
      AMPD(J) = CABS(CR)
      PHID(J) = ATAN(AIMAG(CR)/REAL(CR))
      CSHORT = CSHANH(J)/CR
      AMP(J) = CABS(CSHORT)
      PHI(J) = ATAN(AIMAG(CSHORT)/REAL(CSHORT))
800   CONTINUE
      WRITE(6,140)
140   FORMAT(1H1,32X,55HRESULTS CALCULATED FROM DEBYE ANALYSIS OF HEPTAN
     1OL DATA   )
      WRITE(6,160) EZ,EINF,TRELAX
160   FORMAT(1H0,15X,4HE0 = ,F6.2,14X,6HEINF = ,F5.2,14X,13HRELAXN TIME
     1= ,F5.2,2HNS,//,39X,5HSHORT,39X,8HHEPTANOL,/,38X,7H-------,37X,
     210H----------,//,9X,5HANU,17X,3HAMP,17X,3HPHI,27X,3HAMP,17X,3HPHI/
     3/)
      WRITE(6,150) (ANU(N),AMP(N),PHI(N),AMPD(N),PHID(N),N=1,ITOT)
150   FORMAT((5X,F11.5,2(9X,F11.5),10X,2(9X,F11.5)))
126   IF (IFILE .EQ. 11) GO TO 118
      WRITE(10,120) KONST,(HEAD(J),J=1,15)
120   FORMAT(I5,15A5)
      WRITE(10,130) (ANU(I),AMP(I),PHI(I),I=1,ITOT)
130   FORMAT(29E17.11)
      GO TO 100
118   K=((3*ITOT+16)*(KONST(1)-1))+1
      CALL PUTARRAY(11,K,KONST)
      CALL PUTARRAY(11,K,HEAD)
      CALL PUTPART(11,K,ANU,ANU(1),ANU(ITOT))
      CALL PUTPART(11,K,AMP,AMP(1),AMP(ITOT))
      CALL PUTPART(11,K,PHI,PHI(1),PHI(ITOT))
      GO TO 100
999   CONTINUE
C
     IREPEAT = 1 ALLOWS RE-CALCULATION OF SAME DATA AT DIFFERENT FREQS
C     OTHERWISE TERMINATES PROGRAM
C
      READ(5,79) IREPEAT
      IF (IREPEAT .EQ. 1) REWIND IREAD
      IF (IREPEAT .EQ. 1) GO TO 100
      ENDFILE 10
      STOP
      END
```

PROGRAM EPSILON

This program calculates the complex permittivity from the frequency domain results produced by the program SHANTDR. For single reflection experiments, the program requires spectral data for a reference liquid (see sub-section 2.3.1). Subroutine PLOT provides a rough graphical output of the final results on the line printer.

```
      MASTER EPSILON
      COMPLEX CIB,CI,CPRODB,CFACTB,CPROD,CPRODUN,CORFAC,CEPSUN,CEPS,CR,
     1CF,CENEW,CEHLF,CFEPS,CFEPSD,CDEC,CFA,CFB,CRE,CER,CERHLF,CUN,CFIN,
     2CSHORT
      DIMENSION KONST(1),HEAD(15),AMPE(51),PHIE(51),AMPS(51),PHIS(51),
     1AMP(51),PHI(51),ANU(51),EPSR(53),EPSIM(53),QUOT(51),PHASE(51),
     2AMPB(51),PHIB(51),QUOTB(51),PHASEB(51),RELAX(51)
      CALL USEFILE(11,2HED,12HCHCC-TRNSFM ,0,0)
      PI = 3.14159265
C
C     ITOT IS NUMBER OF FREQUENCY ITERATIONS
C
      READ(5,9) ITOT
9     FORMAT(I5)
      ITOT2 = ITOT+2
C
C     IFILE DEFINES INPUT FILE ; = 4 FROM DISC FILE ; OTHERWISE FROM
C     D.A.B.S. PROCEDURE
C     KK GIVES POSITION IN DABS FILE OF REQUIRED ARRAY
C     INDEX = 1 IMPLIES INCIDENT SIGNAL DATA ; = 2 REFERENCE DATA
C     ICORRECT = 1 CALCULATES GIESE CORRECTIONS FROM REFERENCE SPECTRUM
C     OTHERWISE CORRECTIONS ASSUMED TO HAVE BEEN ALREADY CALCULATED
C     NB   ICORRECT NEED BE DEFINED ONLY FOR SINGLE REFLECTION DATA
C     IPLOT = 0 PRODUCES NO GRAPHS ; = 2 GIVES COLE-COLE PLOTS
C     IMETHOD = 1 IS SINGLE REFLECTION DATA ; = 99 FOR TOTAL REFL. DATA
C
1     READ(5,19) IFILE,KK,INDEX,ICORRECT,IPLOT,IMETHOD
19    FORMAT(6I2)
      IF (INDEX .GT. 2) STOP
      IF (IFILE .EQ. 4) GO TO 111
      K=((3*ITOT+16)*(KK-1))+1
      CALL GETARRAY(11,K,KONST)
      CALL GETARRAY(11,K,HEAD)
      CALL GETPART(11,K,ANU,ANU(1),ANU(ITOT))
      CALL GETPART(11,K,AMP,AMP(1),AMP(ITOT))
      CALL GETPART(11,K,PHI,PHI(1),PHI(ITOT))
C
C     ANU1,AMP1,PHI1 ARE FIRST MEMBERS OF CORRESPONDING ARRAYS OUTPUT
C     BY SHANTDR
C
      READ(5,29) ANU1,AMP1,PHI1
29    FORMAT(3F0.0)
      C = 0.0001
      X = ABS(ANU1-ANU(1))
```

```
      Y = ABS(AMP1-AMP(1))
      Z = ABS(PHI1-PHI(1))
      IF (X .GT. C .OR. Y .GT. C .OR. Z .GT. C) GO TO 222
      GO TO 112
111   READ(4,39) KONST,(HEAD(J),J=1,15)
39    FORMAT(I5,15A5)
      READ(4,59) (ANU(I),AMP(I),PHI(I),I=1,ITOT)
59    FORMAT(29E17.11)
112   CONTINUE
      IF (INDEX .EQ. 2) GO TO 114
      DO 113 I=1,ITOT
      AMPE(I) = AMP(I)
113   PHIE(I) = PHI(I)
      GO TO 116
C
C     LL IS NUMBER OF TIME SHIFTS TO BE PERFORMED
C      BEG IS STARTING TIME OF THE SHIFTS
C     DEL IS TIME INCREMENT OF THE SHIFTS
C
114   READ(5,49) LL,BEG,DEL
49    FORMAT(I2,2F0.0)
      BEG = BEG-DEL
      IZERO = NINT((LL+0.5)/2.)
      DO 115 I=1,ITOT
      AMPS(I) = AMP(I)
115   PHIS(I) = PHI(I)+2.*PI*BEG*ANU(I)
116   WRITE(6,10) KONST,(HEAD(J),J=1,15)
10    FORMAT(1H1,I5,15A5)
      IF (IMETHOD .EQ. 99) GO TO 117
      IF (ICORRECT .GT. 1) GO TO 117
C
C     NN IS POSITION OF REFERENCE DATA IN DABS FILE
C     SHIFT IS TIME SHIFT OF REFERENCE DATA ( FROM 0 )
C     CROOT = (1-ROOT(EPSILON))/(1+ROOT(EPSILON))
C
      READ(5,69) NN,SHIFT,CROOT
69    FORMAT(1I2,2F0.0)
      L = ((3*ITOT+16)*(NN-1))+57
      CALL GETPART (11,L,AMPB,AMPB(1),AMPB(ITOT))
      CALL GETPART (11,L,PHIB,PHIB(1),PHIB(ITOT))
C
C     AMPB1 AND PHIB1 ARE FIRST MEMBERS OF CORRESPONDING ARRAYS FOR
C      REFERENCE SPECTRUM AS OUTPUT BY SHANTDR
C
      READ(5,79) AMPB1,PHIB1
79    FORMAT(2F0.0)
      X1 = ABS(AMPB1-AMPB(1))
      Y1 = ABS(PHIB1-PHIB(1))
      IF (X1 .GT. C .OR. Y1 .GT. C) GO TO 221
C
C     CALCULATION OF CORRECTION FACTORS FROM REFERENCE DATA
C
      DO 124 N=1,ITOT
      QUOTB(N) = AMPB(N)/AMPE(N)
124   PHASEB(N) = (PHIB(N)+2.*PI*SHIFT*ANU(N))-PHIE(N)
117   IF (INDEX .EQ. 1) GO TO 1
500   DO 121 M=1,LL
      BEG = BEG+DEL
      IF (M .GT. 1) WRITE(6,20)
20    FORMAT(1H1)
      WRITE(6,30) BEG
```

```
30     FORMAT(1H0,45X,17HSHIFT OF ORIGIN =  ,F8.5,4H  NS )
       IF (IMETHOD .EQ. 99) GO TO 501
       WRITE(6,40)
40     FORMAT(1H0,29X,18HUNCORRECTED VALUES,27X,16HCORRECTED VALUES,6X,
      122HLINEAR RELAXN. PARAMS.,/,29X,20H------------------- ,25X,18H-
      2---------------- ,4X,24H----------------------- ,/,7X,4HFREQ,8X,
      34HQUOT,8X,5HPHASE,7X,5HEPSR ,8X,5HEPSIM,13X,4HEPSR,8X,5HEPSIM,8X,
      43HTAU,9X,2HE0,/)
C
C      CALCULATION OF REAL AND IMAGINARY PARTS OF PERMITTIVITY FOR
C      SINGLE REFLECTION EXPERIMENTS
C
       DO 122 I=1,ITOT
       PHIS(I) = PHIS(I)+2.*PI*DEL*ANU(I)
       QUOT(I) = AMPS(I)/AMPE(I)
       PHASE(I) = PHIS(I)-PHIE(I)
       CIB = CMPLX(0.,PHASEB(I))
       CI = CMPLX(0.,PHASE(I))
       CPRODB = QUOTB(I)*CEXP(-CIB)
       CFACTB = (CPRODB+CROOT)/(CROOT*(CPRODB-1.))
       CPROD = QUOT(I)*CEXP(-CI)
       CPRODUN = -QUOT(I)*CEXP(-CI)
       CORFAC = CPROD/(CFACTB*(CPROD-1.)-1.)
       CEPSUN = ((1.-CPRODUN)/(1.+CPRODUN))*((1.-CPRODUN)/(1.+CPRODUN))
       CEPS =    ((1.-CORFAC)/(1.+CORFAC))*((1.-CORFAC)/(1.+CORFAC))
       EPSRUN = REAL(CEPSUN)
       EPSIMUN =  AIMAG(CEPSUN)
C
C      LEAST SQUARES PROCEDURE TO OBTAIN TAU AND E0
C
       EPSR(I+1) = REAL(CEPS)
       EPSIM(I+1) = AIMAG(CEPS)
       RELAX(I) = EPSIM(I+1)*2.*PI*ANU(I)
       IF (I .EQ. 1) GO TO 125
       SIGX = SIGX+RELAX(I)
       SIGY = SIGY+EPSR(I+1)
       SIGXSQ = SIGXSQ+(RELAX(I)*RELAX(I))
       SIGXY = SIGXY+RELAX(I)*EPSR(I+1)
       DENOM = I*SIGXSQ-(SIGX*SIGX)
       SLOPE =-((I*SIGXY-SIGX*SIGY)/DENOM)*1000.
       RCEPT = (SIGY*SIGXSQ-SIGX*SIGXY)/DENOM
       GO TO 126
125    SIGX = RELAX(1)
       SIGY = EPSR(2)
       SIGXSQ = RELAX(1)*RELAX(1)
       SIGXY = RELAX(1)*EPSR(2)
       SLOPE = 0.
       RCEPT = 0.
126    PHASE(I) = PHASE(I)*(180./PI)
122    WRITE(6,50) ANU(I),QUOT(I),PHASE(I),EPSRUN,EPSIMUN,EPSR(I+1),
      1EPSIM(I+1),SLOPE,RCEPT
50     FORMAT(3X,5(F12.5),6X,4(F12.5))
       IF (IMETHOD .NE. 99) GO TO 502
C
   C      CALCULATION OF REAL AND IMAGINARY PARTS OF PERMITTIVITY FOR
C        TOTAL REFLECTION EXPERIMENTS
C
501    EREA = 10.
       EIMA = 0.
       CENEW = CMPLX(EREA,-EIMA)
       WRITE(6,130)
```

```
130    FORMAT(1H0,6X,4HITER,12X,4HFREQ,10X,4HQUOT,11X,5HPHASE,11X,4HEPSR
      110X,5HEPSIM,10X,3HTAU,14X,2HE0,//)
       V = 3.125
       AL = V/0.3125
       B = 0.41919*AL
       JJ=-2
       JK = IABS(JJ)+1
       DO 888 J=1,ITOT
       MM = 0
       K = 0
       JJ = JJ+1
135    CONTINUE
       CSHORT = CMPLX(AMPE(J)*COS(PHIE(J)),AMPE(J)*SIN(PHIE(J)))
       CUN = CMPLX(AMPS(J)*COS(PHIS(J)),AMPS(J)*SIN(PHIS(J)))
       CFIN = CUN/CSHORT
       QUOT(J) = -CABS(CFIN)
       PHASE(J) = ATAN(AIMAG(CFIN)/REAL(CFIN))
       CR = CMPLX(QUOT(J)*COS(PHASE(J)),QUOT(J)*SIN(PHASE(J)))
61     K = K+1
       CE = CENEW
       CEHLF = CSQRT(CE)
       CDEC = CEXP(CMPLX(ANU(J)*B*AIMAG(CEHLF),-ANU(J)*B*REAL(CEHLF)))
       CRE = 2.*CR*CEHLF
       CER = CE*(CR+1.)
       CFB = CDEC*(CR-1.-CRE+CER)
       CFEPS = CR-1.+CRE+CER-CFB
       CERHLF = CEHLF*(CR+1.)
       CFA = CERHLF+CR+CDEC*(CR-CERHLF)
       CFEPSD = (CFA+0.209596*ANU(J)*AL*(CMPLX(-AIMAG(CFB),REAL(CFB))))/
      1CEHLF
       CENEW = CE-CFEPS/CFEPSD
       IF (CABS((CENEW-CE)/CENEW) .LT. 0.001) GO TO 91
       IF (K .LT. 16) GO TO 61
       MM = 1
91     CE = CENEW
C
C      LEAST SQUARES PROCEDURE TO OBTAIN TAU AND E0
C
       EPSR(J+1) = REAL(CE)
       EPSIM(J+1) =-AIMAG(CE)
       RELAX(J) = EPSIM(J+1)*2.*PI*ANU(J)
       IF (MM .EQ. 1) GO TO 132
       IF (J .LT. JK) GO TO 128
       IF (J .EQ. JK) GO TO 131
       SIGX = SIGX+RELAX(J)
       SIGY = SIGY+EPSR(J+1)
       SIGXSQ = SIGXSQ+RELAX(J)*RELAX(J)
       SIGXY = SIGXY+RELAX(J)*EPSR(J+1)
       DENOM = JJ*SIGXSQ-(SIGX*SIGX)
       SLOPE = -((JJ*SIGXY-SIGX*SIGY)/DENOM)*1000.
       RCEPT = (SIGY*SIGXSQ-SIGX*SIGXY)/DENOM
       GO TO 132
131    SIGX = RELAX(J)
       SIGY = EPSR(J+1)
       SIGXSQ = RELAX(J)*RELAX(J)
       SIGXY = RELAX(J)*EPSR(J+1)
128    SLOPE = 0.
       RCEPT = 0.
132    PHASE(J) = PHASE(J)*(180./PI)
       IF (MM .EQ. 1) GO TO 92
       WRITE(6,140) K,ANU(J),QUOT(J),PHASE(J),EPSR(J+1),EPSIM(J+1),SLOPE,
```

```
     1RCEPT
140   FORMAT(7X,I2,13X,F5.3,7X,F8.4,7X,F9.3,6X,F9.3,6X,F8.3,8X,F7.2,9X,
     1F6.3)
      GO TO 888
92    JJ = JJ-1
      WRITE(6,150) ANU(J),QUOT(J),PHASE(J),EPSR(J+1),EPSIM(J+1)
150   FORMAT(5X,6H******,11X,F5.3,7X,F8.4,7X,F9.3,6X,F9.3,6X,F8.3,8X,7H
     1******,9X,6H******)
      CENEW = CMPLX(EREA,-EIMA)
888   CONTINUE
502   EPSR(1) = 2.
      EPSR(ITOT2) = ANINT(EPSR(2))+1.
      EPSIM(1) = 0.
      EPSIM(ITOT2) = 0.833*(EPSR(ITOT2)-EPSR(1))
      IF (IPLOT .EQ. 0) GO TO 121
      IF (IPLOT .EQ. 2) GO TO 345
      IF (M .NE. IZERO) GO TO 123
      CALL PLOT(ANU,QUOT,1,ITOT,2,0)
      WRITE(6,60)
60    FORMAT(1H0,8X,25HPLOT OF QUOT AGAINST FREQ   )
      CALL PLOT(ANU,PHASE,1,ITOT,1,0)
      WRITE(6,70)
70    FORMAT(1H0,8X,26HPLOT OF PHASE AGAINST FREQ   )
345   CALL PLOT(RELAX,EPSR,2,ITOT,0,0)
      WRITE(6,110)
110   FORMAT(1H0,8X,50HLINEAR RELAXATION PLOT : EPSR AGAINST EPSIM*OMEGA
     1   )
123   CONTINUE
      IF (IPLOT .EQ. 0)GO TO 121
      CALL PLOT(EPSR,EPSIM,1,ITOT2,0,0)
      WRITE(6,80)
80    FORMAT(1H0,8X,14HCOLE-COLE PLOT   )
121   CONTINUE
      GO TO 1
221   WRITE(6,120) AMPB(1),PHIB(1)
120   FORMAT(1H1,20X,2(F8.5))
      STOP 88
222   WRITE(6,100) KONST,ANU(1),AMP(1),PHI(1)
100   FORMAT(1H1,I5,10X,3(F8.5,5X),18HWRONG FILE ENTERED   )
      STOP 99
      END
```

PROGRAM NEWT

This program , which was developed by Dr. G. Brink, calculates equilibrium parameters by means of the Newton-Raphson procedure. The permittivity and NMR data discussed in this study were analysed using this program. As listed, the program provides parameters for a 1-2-4 model; however, parameters for any other model can be obtained by suitably altering Subroutines Equation and Derivative.

```
      MASTER NEWT
C    **
C     NEWTON-RAPHSON NON-LINEAR CURVE FITING
C     CONTAINS ERROR DETERMINATIONS
C     THE SUBROUTINES EQUATION AND DERIVATIVE MUST BE GIVEN
C    **
      DIMENSION  C(400),F(21),DB(20),W(6)
      DIMENSION CC(400),FF(20),CDIAG(20),BB(20)
      DIMENSION HEAD(10)
      COMMON X(200),Y(200),B(20),Z(20),XX(50)
1     READ(5,10) (HEAD(J),J=1,10)
10    FORMAT(10A8)
      WRITE(6,11) (HEAD(J),J=1,10)
11    FORMAT(1H1,10A8,//)
C    **
C     M IS NO. OF UNKNOWNS
C     N IS NO. OF DATA POINTS
C     TOL IS FINAL SIGMA(DB/B)
C     ITER IS MAX. NO. OF ITERATIONS
C    **
      READ(5,12) N,M,TOL,ITER
12    FORMAT(2I0,G0.0,I0)
      IF(N.LT.0) STOP
C    **
C     B ARE THE INITIAL VALUES OF THE UNKNOWNS
C    **
      READ(5,14) (B(J),J=1,M)
14    FORMAT(20G0.0)
      WRITE(6,15) (B(J),J=1,M)
15    FORMAT(5(1H ,4G14.5/))
      DO 19 J=1,N
19    READ(5,13) X(J),Y(J)
13    FORMAT(2G0.0)
      SSE=0.
      NITER=0
      NCOUNT=1
      P=0.1
      DO 16 K=1,N
      CALL EQUATION(N,M,PHI,S,K,NITER)
      NITER=1
16    SSE=SSE+S*S
      CALL PFIND(P,SSE,F(1),M,NCOUNT)
      WRITE(6,17) SSE
17    FORMAT(5H SSE=,F14.8)
      NITER=0
18    NITER=NITER+1
      SSE1=SSE
      CALL FMOVE(B(1),BB(1),M)
      F(1)=0.
      MM=M-1
      CALL FMOVE(F(1),F(2),MM)
```

```
      C(1)=0.
      MM=M*M-1
      CALL FMOVE(C(1),C(2),MM)
      DO 6 K=1,N
      CALL DERIVATIVE(N,M,PHI,S,K,NITER)
      DO 6 I=1,M
      F(I)=F(I)+S*Z(I)
      DO 6 J=I,M
      L=J+M*I-M
      C(L)=C(L)+Z(I)*Z(J)
6     C(I+M*J-M)=C(L)
      MM=M*M
      CALL FMOVE(C(1),CC(1),MM)
      CALL FMOVE(F(1),FF(1),M)
      DO 4 J=1,M
4     CDIAG(J)=C(J*M-M+J)
      CALL PFIND(P,SSE,F(1),M,NCOUNT)
2     DO 5 J=1,M
      L=J*M-M+J
5     C(L)=C(L)+P*CDIAG(J)
C    **
C     FPMGESOL IS A LIBRARY SUBROUTINE FOR SOVING SIMUL. LIN. EQUAS.
C    **
      CALL FPMGESOL(M,1,1.0E-20,C(1),F(1),W(1),D,IR,NR)
C    **
C    **
C      DETERMINE SIGN OF INCREMENTS
C    **
       DT=0.0
      DO 50 J=1,M
50    DT=DT+F(J)*FF(J)
      IF(DT) 51,52,52
51    DO 53 J=1,M
53    F(J)=-F(J)
52    DO 54 J=1,M
54    B(J)=B(J)+F(J)
C    **
      SSE=0.
      DO 25 K=1,N
      CALL EQUATION(N,M,PHI,S,K,NITER)
25    SSE=SSE+S*S
      CALL PFIND(P,SSE,F(1),M,NCOUNT)
      CALL FMOVE(BB(1),B(1),M)
      IF(NCOUNT.EQ.0) GO TO 22
      CALL FMOVE(CC(1),C(1),MM)
      CALL FMOVE(FF(1),F(1),M)
      GO TO 2
22    DO 24 J=1,M
24    B(J)=B(J)+F(J)
      NCOUNT=2
C    **
C     TESTING COVERGENCE
C    **
      CONV=0.
      DO 32 J=1,M
```

```
32     CONV=CONV+ABS(F(J)/B(J))
       IF(TOL.GE.CONV) WRITE(6,33)
33     FORMAT(13H FINAL VALUES,/)
       IF(NITER.GT.ITER) WRITE(6,34)
34     FORMAT(29H MAX. NO. ITERATIONS EXCEEDED,/)
       WRITE(6,15) (B(J),J=1,M)
       WRITE(6,17) SSE
       IF(SSE.LE.SSE1) GO TO 38
       WRITE(6,40)
40     FORMAT(36H NOT CONVERGING - PROGRAM TERMINATED,/)
       GO TO 35
38     CONTINUE
       IF(TOL.GE.CONV.OR.NITER.GT.ITER) GO TO 35
       GO TO 18
35     CONTINUE
       FN=N
       STDEV=SQRT(SSE/(FN-M))
       WRITE(6,39) STDEV,CONV,NITER
39     FORMAT(7H0STDEV=,E14.8,/,6H0CONV=,E14.8,/,16H0NO. ITERATIONS=,I3,/
      1//)
C     ****
C     DETERMINATION OF ERRORS
C      STANDARD DEVIATIONS OF ESTIMATES
C     ****
C     DET IS THE DETERMINENT OF THE MATRIX OF SLOPES (C)
C     DDET IS THIS DETERMINENT WITH COL AND ROW J TAKEN OUT
C     ****
       CALL FMOVE(CC(1),C(1),MM)
       CALL F4DET(CC,M,MM,D,ID,F,IT)
       DET=D*2.**ID
       MN=M-1
       MMN=MN*MN
       WRITE(6,64)
64     FORMAT(1H ,32HSTANDARD DEVIATIONS OF ESTIMATES,/)
       DO 61 KK=1,M
       II=1
       DO 59 I=1,MM
       DO 60 L=1,M
       M2=(L-1)*M+KK
       IF(I.EQ.M2) GOTO 59
       M1=(KK-1)*M+L
       IF(I.EQ.M1) GOTO 59
60     CONTINUE
       CC(II)=C(I)
       II=II+1
59     CONTINUE
       CALL F4DET(CC,MN,MMN,D,ID,F,IT)
       DDET=D*2.**ID
       ER=STDEV*SQRT(DDET/DET)
61     WRITE(6,62) ER
62     FORMAT(1H ,E16.4)
       WRITE(6,63)
63     FORMAT(1H ,//)
       NITER=999
       DO 36 K=1,N
```

```
      CALL EQUATION(N,M,PHI,S,K,NITER)
36    WRITE(6,37) X(K),Y(K),PHI,S
37    FORMAT(1H ,4E16.5)
      GO TO 1
      END
      SUBROUTINE PFIND(P,SSE,F,M,NCOUNT)
      DIMENSION S(4),PP(4),F2(20),F3(20),F4(20),F1(20),F(20)
      GO TO (1,2,3,4,5,6,7), NCOUNT
1     S(1)=SSE
      PP(1)=1.E+20
      NCOUNT=2
      J=M-1
      F1(1)=0.
      CALL FMOVE(F1(1),F1(2),J)
      RETURN
2     SLOPE=0.
      DO 21 J=1,M
21    SLOPE=SLOPE+F(J)*F(J)
      NCOUNT=3
      RETURN
3     PP(2)=P
      S(2)=SSE
      CALL FMOVE(F(1),F2(1),M)
      IF(SSE.LT.S(1)) GO TO 30
      P=P*1000.
      NCOUNT=4
      RETURN
30    P=P*0.01
      NCOUNT=4
      RETURN
4     S(3)=SSE
      PP(3)=P
      CALL FMOVE(F(1),F3(1),M)
      P=PP(2)*0.5
      NCOUNT=5
      RETURN
5     S(4)=SSE
      PP(4)=P
      CALL FMOVE(F(1),F4(1),M)
      P=PP(3)*0.5
      NCOUNT=6
      RETURN
6     IF(SSE.GT.S(4)) GO TO 60
      S(4)=SSE
      PP(4)=P
      CALL FMOVE(F(1),F4(1),M)
60    I=2
      BEST=S(2)
      DO 63 J=3,4
      IF(S(J).GT.BEST) GO TO 63
      BEST=S(J)
      I=J
63    CONTINUE
      IF(I.EQ.2) GO TO 67
      TEMP=S(2)
      S(2)=BEST
      S(I)=TEMP
```

```
      TEMP=PP(2)
      PP(2)=PP(I)
      PP(I)=TEMP
      CALL FMOVE(F2(1),F(1),M)
      I=I-2
      GO TO (65,66),I
65    CALL FMOVE(F3(1),F2(1),M)
      CALL FMOVE(F(1),F3(1),M)
      GO TO 67
66    CALL FMOVE(F4(1),F2(1),M)
      CALL FMOVE(F(1),F4(1),M)
67    CONTINUE
      IF(S(3).LT.S(4)) GO TO 64
      S(3)=S(4)
      PP(3)=PP(4)
      CALL FMOVE(F4(1),F3(1),M)
64    CONTINUE
      P2=1./PP(2)
      P3=1./PP(3)
      D=-2.*SLOPE
      AA=P2*P2-P3*P3
      BB=P2*P2*P2-P3*P3*P3
      EE=P2*P2+P3*P3
      FF=P2*P2*P2+P3*P3*P3
      CC=S(2)-S(3)-D*(P2-P3)
      DD=S(2)+S(3)-2.*S(1)-D*(P2+P3)
      GG=BB*EE-AA*FF
      A2=(BB*DD-FF*CC)/GG
      A3=(EE*CC-AA*DD)/GG
      AB=A2*A2-3.*D*A3
      IF(AB.LE.0.) GO TO 7
      P=3.*A3/(-A2*SQRT(AB))
      NCOUNT=7
      RETURN
7     DO 76 J=1,3
      IF(S(J).GE.SSE) GO TO 76
      SSE=S(J)
      P=PP(J)
      GO TO (71,72,73), J
71    CALL FMOVE(F1(1),F(1),M)
      GO TO 76
72    CALL FMOVE(F2(1),F(1),M)
      GO TO 76
73    CALL FMOVE(F3(1),F(1),M)
76    CONTINUE
      NCOUNT=0
      S(1)=SSE
      RETURN
      END
      SUBROUTINE EQUATION(N,M,PHI,S,K,NITER)
      COMMON X(200),Y(200),B(20),Z(20)
      COMMON/B/C1
      C1=.9*X(K)
      DO 3 J=1,200
      DIF=(4.*B(2)*C1*C1*C1*C1+2.*B(1)*C1*C1+C1-X(K))/
     1(16.*B(2)*C1*C1*C1+4.*B(1)*C1+1.)
```

```
      C1=C1-DIF
      IF(1.E-12.GE.DIF*DIF) GO TO 2
3     CONTINUE
      WRITE(6,200)
200   FORMAT(15H ROOT NOT FOUND)
      STOP
2     CONTINUE
      PHI=(C1*B(3)+B(1)*B(4)*B(3)*C1*C1*2.)/X(K)
      S=Y(K)-PHI
      RETURN
      END
      SUBROUTINE DERIVATIVE(N,M,PHI,S,K,NITER)
      COMMON X(200),Y(200),B(20),Z(20)
      COMMON/B/C1
      CALL EQUATION(N,M,PHI,S,K,NITER)
      CC=C1
      C2=C1*C1
      P=PHI
      SS=S
      C3=C2*C1
      Z(4)=(2.*B(1)*C2*B(3))/X(K)
      Z(3)=(CC+2.*B(1)*C2*B(4))/X(K)
      BB=B(1)
      B(1)=B(1)+0.0001*B(1)
      CALL EQUATION(N,M,PHI,S,K,NITER)
      DB=(C1-CC)/(0.0001*BB)
      B(1)=BB
      Z(1)=(DB*B(3)+2.*C2*B(4)*B(3)+4.*B(1)*CC*DB*B(4)*B(3))/X(K)
      BB=B(2)
      B(2)=B(2)+0.0001*B(2)
      CALL EQUATION(N,M,PHI,S,K,NITER)
      DB=(C1-CC)/(0.0001*BB)
      B(2)=BB
      Z(2)=(DB*B(3)+4.*B(1)*CC*DB*B(4)*B(3))/X(K)
      S=SS
      PHI=P
      RETURN
      END
```