DIELECTRIC RELAXATION
OF ALIPHATIC COMPOUNDS

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ABSTRACT

Dielectric constants and losses have been measured at 25°C for dilute solutions of aliphatic bromides and amines at microwave frequencies from 1 – 145 GHz using an interferometer method, a bridge technique and a coaxial line apparatus. The data were analyzed for mean relaxation times and Cole-Cole distribution parameters. In some cases where two discrete relaxation processes, molecular and intramolecular, might be anticipated, analyses in terms of a Budó distribution were also carried out. Analyses for a distribution of relaxation times in terms of two limiting values were used to assist the interpretation of the results for bromoalkanes.

It may be anticipated that the intramolecular rotation of a variety of segments, including the -CH_2Br end group, contribute to the absorption of the bromoalkanes. This has been shown to be true from the present study. The relaxation times for the shorter molecules increase non-linearly with increased chain length, but are essentially the same for C_{16} and C_{18} bromides where coiling of the chain probably occurs. The location of the dipole has a significant effect on the distribution parameters of the bromooctanes, but not on their relaxation times. The distribution parameter is much smaller for 1,10-dibromodecane than for n-bromodecane although their relaxation times are similar. Their data are adequately represented by a symmetrical

distribution and skewed-arc behaviour is not indicated.

Primary n-alkyl amines in cyclohexane are characterized by short relaxation times which are almost independent of the size of the alkyl group and the location of the $-NH_2$ group. Considerably longer values are obtained for the secondary and tertiary amines. A fast intramolecular relaxation process dominates the absorption of primary n-alkyl amines but its contribution decreases significantly with increased number and size of N-alkyl groups. Steric restriction of intramolecular rotation about C-N bonds of the secondary and tertiary n-octylamines has been considered. Analyses for relaxation parameters in terms of a Budó distribution may be significant for the secondary and tertiary n-octylamines. The relaxation times for the α, ω-diaminoalkanes and the analogous normal primary amines are very similar. The increase in relaxation times for these amines in p-dioxane is probably due to solute-solvent interactions; however, $-NH_2$ group rotation remains the predominant process.

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Chapter I. Dielectric Relaxation Studies of Aliphatic Compounds

1.1 Introduction

The majority of aliphatic polar molecules are generally considered to be non-rigid. However, a number of methane derivatives (CH_3X, CH_2X_2, CHX_3, CX_4), where X may be a halogen or other polar unit (NO_2, CN, etc.,), can be regarded as rigid polar molecules, i.e., dipole reorientation involves the whole molecule. The dielectric relaxation of such simple rigid polar molecules has been studied in some detail and correlated with temperature, internal field, viscosity, molecular size and shape, the orientation of the dipole in the molecule and the nature of solvent.[1] These variables are expected to have a similar effect upon the relaxation of non-rigid polar molecules. In the more flexible molecules, however, a range of intramolecular relaxation processes may also be possible.

Dielectric relaxation studies have been reported for aliphatic polar compounds in the solid, supercooled liquid and pure liquid states as well as in a variety of non-polar solvents. Aliphatic bromides and alcohols have received the most attention, the former group have generally been considered to be representative polar liquids without special complications of molecular structure or intermolecular forces. The following sections present a brief review of the dielectric relaxation studies of acyclic aliphatic polar molecules.

2.1 Solids[2-7]

(1) Site-Model Theory

Hoffman et. al.[8, 9, 10] considered that the distribution of relaxation times found for a number of crystals consisting of rigid polar molecules may be assoicated with a single-axis polar rotator which may occupy several sites where the energies, as well as the intervening barriers, are all different as it rotates about the axis. (Fig. 1.1) With the single-jump hypothesis, which assumed that rotational jumps are allowed only to an adjacent site, Hoffman was able to calculate the relaxation times in terms of the probabilities of transitions from one site to another for many models. A single relaxation time appeared for any model where the activation barriers between the sites are of exactly equal magnitude or the sites are all equivalent. The theory predicted that a change of width of a dielectric loss region is to be expected as the temperature changes. Indeed, several examples where a definite narrowing of the loss peak appears with rising temperature have been observed in long-chain esters.[11] Hoffman's "site" model can readily give either broadened, bimodal, or Debye-type loss curves, depending on the temperature and the nature of the barrier system. The ideal type of material for application of the site-model approach is one where all the neighbours of a dipole are fixed, as in a clathrate or urea addition compound.[12] Here the molecules are independent in the statistical mechanical sense, and not subject to co-operative

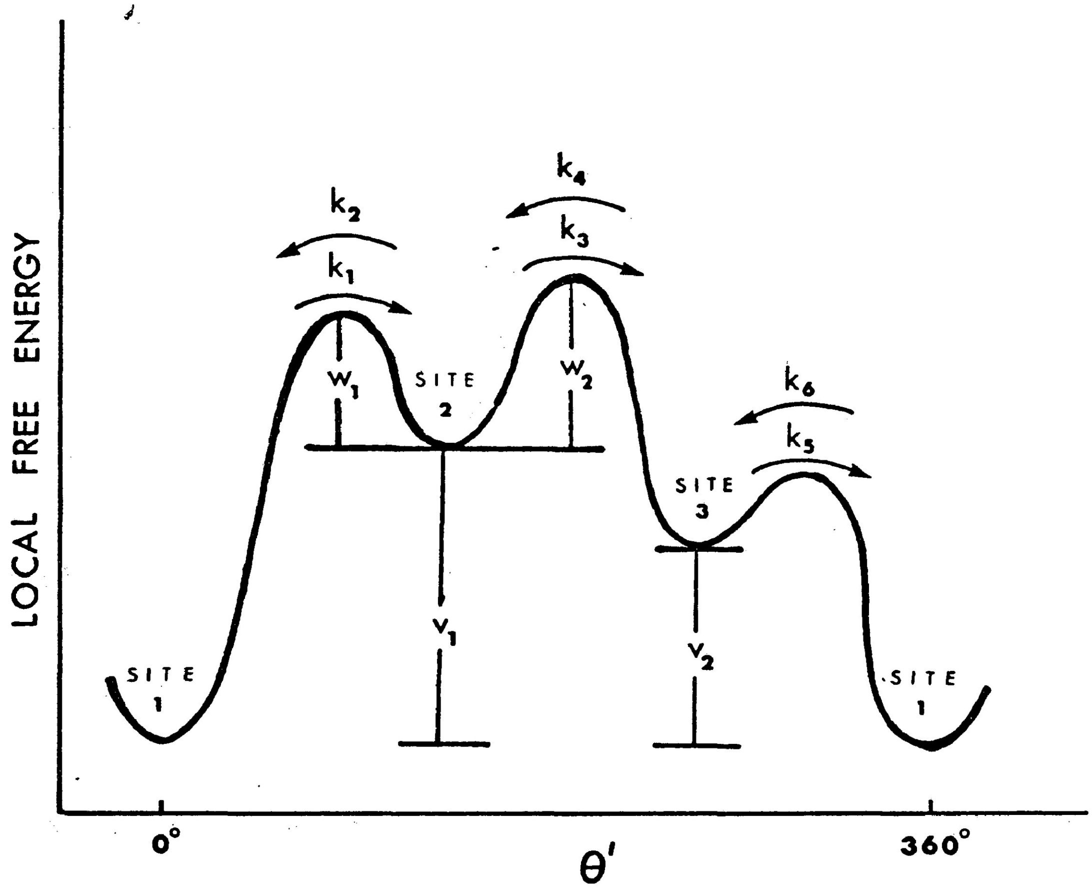


Fig.1.1. Local free energy as a function of rotational position for the general three-position single-axis rotator. Each k represents the probability that a dipole will turn to an adjacent site in the direction specified by the arrows.

$k_1 = B \exp[(w_1 + v_1)/kT]$ and so on, where B is a frequency factor. (after Hoffman, ref.9).

interaction. For the two systems, hentriacontan-16-one and 12-bromotricosane, studied in urea[12] the variation of potential energy with molecular rotational angle of C=O dipole and that of C-Br dipole calculated using the energy function of the "site" model, and that deduced from dielectric data seem to agree fairly well. The agreement persists through the changes in the dielectric loss curves with temperature. The quantitative success of the "site" model provides one of the most satisfactory molecular representatives in the dielectrics field. Nevertheless, the simple site-model theory could probably be applied only at low temperature in co-operative systems such as pure long chain polar molecules where the local energy field for one molecules varies radically with the proportion of neighbouring molecules already rotating.[10]

(2) Spheroidal Molecules -- tetrasubstituted methanes

The high dielectric constants of many tetrasubstituted methanes suggest that they have some rotational freedom in the solid state.[13 - 18] The rotational behaviour of some tetrahalogenated methanes has been examined[19] as a function of the lengths of the carbon-halogen radii C-X calculated as the sum of the two bond radii plus the Van der Waals radius of the halogen, i.e., the distance from the carbon nucleus to the hypothetical surface of the halogen atom. When the four C-X values differ by no more than 9%, molecular rotational freedom is observed in the solid in the temperature region between the freezing point and a rotational transition point. This intermediate phase is known as a solid rotator phase. Recent work on spheroidal substituted methanes by Clemett and Davies,[20] William and Smyth,[21] and Mansingh and McLay,[22] indicates that molecular rotation is generally as complete and as little hindered in the solid rotator phase as it is in the liquid. Various attempts have been made to correlate the presence of a solid rotator phase with physical properties.[20,23,24]

(3) Long-chain Molecules

Many molecules of the general formula $CH_3(CH_2)_nX$ show rotation in the solid state when n is large. When n is small, melting commonly occurs before the molecules acquire sufficient rotational energy. For the n-alkyl bromides, rotation has been detected in the solid state when n = 21 and 29,[8, 25, 26] but not when n = 17 or less.[27] The straight-chain alcohols show no rotation when n = 8, 10 or 12, but rotation and proton transfer above a monotropic transition when n = 14, 16, 18 or 22.[28 - 33] Several long-chain esters,[11, 26, 33-37] carboxylic acids,[38,39] ketones,[37, 40] ethers[37, 41] and amines[42, 43] also show a solid rotator phase.

Many long-chain compounds have two or more crystalline forms, a waxy, translucent form first obtained on solidification of the melt, ususlly termed the α - phase, and a white opaque, β - phase, formed by direct crystallization or by transition from the α - phase on standing or by lowering the temperature.[6] The α - phase consists of relatively disordered material of low specific gravity.[44] In some cases, different forms of the α - phase are known for a particular compound, e.g., n-butyl stearate shows three different α - phases.[45] The β - phase of several long-chain compounds, e.g., ketones[44, 46] esters,[47] and ethers,[44] has no significant dielectric absorption at radio-frequencies. Conversely, a number have a dielectric absorption at both radio and microwave frequencies.[26, 36, 48, 49] The low frequency relaxation times of methyl and ethyl esters (RCOOR') of behenic ($R = C_{21}$), stearic ($R = C_{17}$) and palmitic ($R = C_{15}$) acids[36] lengthen with increasing chain length which suggests that the process involves the rotatory motion of the entire molecule. The short relaxation time is relatively independent of the chain length, which together with the evidence that the short relaxation time diminishes as the dipole is removed from the chain end, as in butyl stearate and cetyl palmitate,[36] suggests that the high frequency absorption is due to the orientation of the polar groups by intramolecular motion.[6, 50] The radio frequency absorption of the β - phase is usually small compared to the total dipole concentration[6] and decreases with decreasing temperature.[36]. The relative values of ε''_{max} at different temperatures are approximately the same for methyl and ethyl esters.[36]

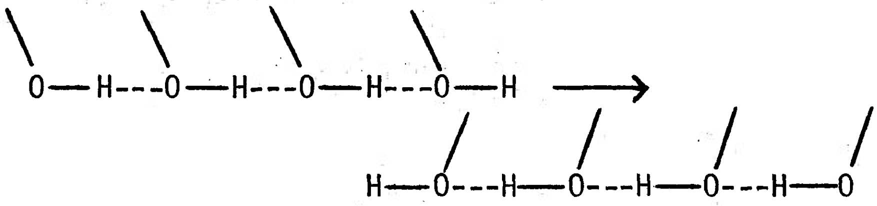
The α - phase absorption may consist of two or more maxima at audio, radio, or microwave frequencies.[6] The total dielectric absorption in the α- phase of the long-chain compounds is much larger than that in the β- phase and is proportional to the reciprocal of the absolute temperature,[6] indicating that the positions of equilibrium are of equal energy[45, 46] whereas they differ by about 2Kcal per mole in the β - phase.[36] In the α - phase, the acetate esters, the ethyl esters, and the methyl ethers show a linear increase in the free energy of activation, ΔG, for the slow relaxation process with increase in molecular chain length at room temperature. The increment in the free energy per link of the chain is approximately the same in the three series.[6] However, Cook and Meakins[44] found no apparent relationship between the molecular chain length and ΔE and ΔS, even within a particular series. They thought this was probably partly due to different forms of the α - phase in different compounds. Recent crystallographic studies[52, 53] of both methyl and ethyl esters of long-chain aliphatic acids has revealed that they have essentially the same side-by-side packing of chains, but differ in end packing. The activation energies for the radiofrequency absorptions have been determined[50] over the range from room temperature down to -70°C, which probably covers both α - and β - phases. A plot of ΔE against chain length reveals a single straight line with a slope of 0.5 Kcal per mole per chain atom for the two series of esters. The identity of slope for the two series is compatible with the general similarity of chain packing. The fact that both series lie on the same line suggests that end packing has little effect on the barrier height. This result conforms with Meakins' previous conclusion[6] that, in the α - phase, every dipole must contriubte to the absorption and that the combined absorption mechanisms involve complete rotation of the dipoles. Dryden and Welsh[54 - 56] concluded that the radiofrequency absorption is due to the coordinated rotation of groups of molecules rather than individual molecular rotation.

In the β - phase, molecular rotation at radiofrequencies has been shown to be due to the presence of imperfections in the crystal lattice[36, 44, 54]. Evidence comes from the fact that cold working or addition of impurities can increase the radiofreqency absorption in some β - phase long-chain compounds, and the absorption gradually decreases on annealing. It has been suggested that these imperfections affect the inter-layer packing of the molecules, reducing the end-to-end interaction and hence reducing the energy difference between the equilibrium positions.[36, 37, 54] On the contrary, the total absorption in α - phase long-chain compounds has a definite value at any particular temperature.[6] Cold-working may just bring about some interchange in magnitude between the different absorption regions.[45]

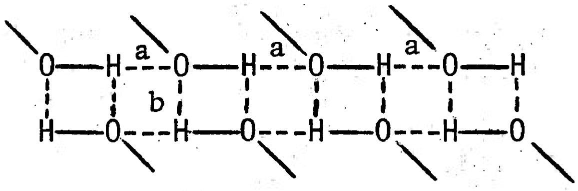
The dielectric properties of polar long-chain compounds in dilute solid solutions with long-chain hydrocarbons have been examined.[37] The magnitude of the radiofrequency absorption increases linearly with molecular chain length and also with decreasing temperature. Measurements have been made with a 5% solid solution in which the two components have the same chain length,(di-n-undecyl ketone $C_{11}H_{23}COC_{11}H_{23}$ in n-tricosane $C_{23}H_{48}$). This system shows no significant dielectric loss, which indicates a large energy difference between the equilibrium positions. This can be accounted for by a model in which the polar molecules cannot move longitudinally without encountering considerable interaction with the ends of the molecules in the next layer.

(4) Hydrogen-bonded long-chain molecules

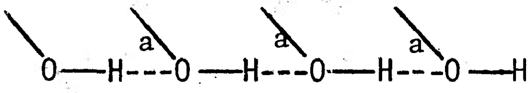
The long-chain alcohols, both primary[28, 33, 57 - 59] and secondary[29, 31, 32] show pronounced absorptions in the solid phase, usually below 1 MHz. The crystalline alcohol shows a larger permittivity than the liquid at the freezing point, which indicates that the chain-association of hydroxyl groups already present in the liquid is further extended by alignment in the solid. Sack[60] proposed that the strong dipolar absorption is the result of a reversal of such a giant dipole by rotation of the individual hydroxyl groups about the C-O bonds, accompanied by the breaking and reforming of the hydrogen bonds, and without appreciable movement of the rest of the molecules:



The dependence of the absorption upon the length of the ---O—H--- chain has been assessed.[61] The absorption is, in its major aspects, independent of the length of the individual alcohol molecules, but there is a marked difference between the primary and secondary alcohols. The former have an activation energy of about 15 Kcal/mole, the latter about 6 Kcal/mole.[6] This may well result from the head-to-head layer lattice of the primary alcohols,[62] which provides the hydroxyl groups with additional bonding sites, i.e., (a) and (b):



In the secondary alcohols only the one sequence (a) of hydroxyl-group interaction is present.



This feature may account for the larger d.c. conductivity in the primary alcohols, since inter-layer bonding would facilitate the transfer of protons through the material.[63, 64]

Daniel[65, 66] has proposed a more detailed mechanism of polarization of the ---O——H--- chains in an attempt to explain the anomalously high permittivities of the high temperature form of many long-chain secondary alcohols crystallized from the melt, which decrease with time. She stated that the dielectric properties of the long-chain secondary alcohols were due to the presence of chains of hydrogen bonds in conjunction with some kind of structural flaws.

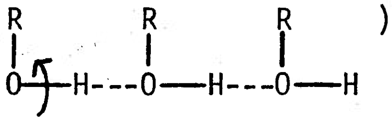
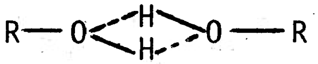
A series of long-chain aliphatic primary amines, viz., n-octyl, n-dodecyl, n-tetradecyl, n-hexadecyl and n-octadecyl, have been examined;[42] a solid rotator phase was detected only for the first two and attributed to proton transfer. The absence of any rotational transitions for the longer members may be due to the different degree of hydrogen bonding in the amines as compared with the alcohols. Garg and Kadaba[43] investigated several simple primary and secondary alkyl amines at 10, 3, 2, and 1 cm. wavelengths over a range of temperatures below 0°C into the solid state. The dielectric constant-temperature curves indicated a solid rotator phase for the primary amines only.

1.3 Liquids and Solutions

(1) Alcohols[67]

The alcohols have been more extensively studied than any other group of liquids although a molecular model capable of satisfactorily explaining the results is as yet unavailable. However, it is reasonably well established that the dielectric dispersion of primary aliphatic alcohols in the pure liquid form, over a wide temperature range, may be characterized by three relaxation regions with the low-frequency processs dominating.[68 - 74] The high-frequency processes (τ_2 and τ_3), which provide relatively small contributions in the pure liquids, become increasingly important, or alternatively the contribution from the low-frequency process (τ_1) decreases, on dilution with an inert non-polar sovent.[75 - 77] For alcohols with a sterically hindered OH group the low-frequency process is either very small or completely absent in the pure liquid[78 - 80], and in an inert solvent the absorption may be represented by the τ_2 and τ_3 processes only.[77, 81]

The highest frequency process ($\tau_3 \simeq 3$ ps at 25°C) is only slightly dependent on molecular size[68, 77] and alcohol concentration[77] and is of the same magnitude as that found for -OH group rotation in phenols[82, 83]. The fact that this process largely dominates the absorption of alcohols at very low concentrations[77] suggests that the dipole orientation of alcohol monomers occurs primarily by -OH group rotation about the C-O bond in monomers rather than by whole molecule rotation.

The intermediate relaxation time τ_2 has been accounted for by monomer or -OR group (as in  $\overset{R}{O}-H\cdots\overset{R}{O}-H\cdots\overset{R}{O}-H$) rotations[68, 73]. Dannhauser[78] examined eight liquid isomeric octanols in a wide temperature range from -90° to 130° C and proposed a model based on hydrogen-bond associative equilibrium involving both ring dimers ( $R-O\begin{smallmatrix}H\\H\end{smallmatrix}O-R$) and linear chain n-mers. He found that the magnitude and relative contribution of τ_2 are dependent upon the temperature and the steric environment of the OH group. At relatively high temperatures those species whose -OH group is most sterically blocked prefer to form nonpolar ring dimers, while those alcohols with a relatively accessible OH group tend to form open chains. The dielectric constants of the latter group increase monotonically with decreasing temperature while those of the former group go through a maximum with decreasing temperature; the reversal occurs near 70°C. At much lower temperatures, in the neighbourhood of -90°C for 5-methyl-3-heptanol, there is another reversal of the temperature dependence of dielectric constant. Dannhauser and Johari[84] also pointed out that the introduction of additional methyl groups in the neighbourhood of the -OH group does not significantly affect the dielectric properties. They also studied the pressure dependence of the relaxation processes.[85]

Crossley et. al.[77] suggested that ring-dimer formation may account for the initial decrease in the apparent dipole moment with increasing alcohol concentration in an inert solvent. However, they considered that for dilute solutions of alcohols with a sterically hindered -OH group, τ_2 is due only to the monomer rotation. In view of the increase in τ_2 and its relative contribution C_2 with increased alcohol concentration they suggested that these quantities are no longer descriptive of monomeric molecules alone, but are weighted averages of the values for the monomer and one or more polymers.

The Debye-like[68] long relaxation process (τ_1) is undoubtedly due to a mechanism which is sensitive to the steric environment of the hydroxyl group since it is not evident for the more hindered octanols[77, 80]. The molecular size dependence of τ_1 and its magnitude[68] suggest that rotation of associated molecular units might be responsible. However, if association is into linear chains the great distribution of sizes for such species would give rise to a distribution of relaxation times conflicting with the Debye-like nature of this dispersion.[67] For many years, the dielectric relaxation of alcohols has been interpreted in terms of hydrogen bond rupture followed by rotation of monomers, where the former is the rate-determining step, the required energy being interpreted as the activation enthalpy for dielectric relaxation.[70, 79, 86]

Recently in a study of 6-, 4-, and 2-methyl-1-heptanol Dannhauser and Flueckinger[87] proposed that in dielectric relaxation hydrogen bond rupture is a prerequisite rather than a rate-determining step. A particular hydrogen bond will break and reform many times without the reorientation of either the donor or acceptor molecule. Because the local liquid alcohol structure remains, on average, chain associative, the dipolar reorientation is necessarily co-operative and occurs relatively seldom. When it does occur, the rate of reorientation depends on the size and shape of the entire molecule insofar as this determines the interaction of a specific molecule with its surroundings and also because the structure of the molecule determines the nature of the surroundings. The more highly branched the alkyl group and the more sterically hindered the OH group, the greater the required degree of co-operation.

A highly polar cyclic tetramer[88] has satisfactorily accounted for the dependence of τ_1 upon molecular size, the absence of any distribution of relaxation times, the large polarization,[78] and if steric effects prevent the association of monomers into multimer other than dimers, the absence of a low-frequency process[77, 78], and the small polarization for the hindered octanols.[78] Malecki[89] proposed another model of association into a mixture of dimers, trimers, tetramers and pentamers. He was able to determine the concentration of each species for t-butanol in cyclohexane, and he concluded that trimers are cyclic while tetramers and pentamers are present as open bonded units.

In contrast to the multiple relaxation processes of primary aliphatic alcohols in dilute benzene[90] and n-heptane[77] solutions, the dielectric absorption of the same alcohols in p-dioxane solution shows a symmetrical distribution of relaxation times with a short mean relaxation time attributable to strong solute-solvent complex formation.[90] Crossley[91] examined the dielectric relaxation of the four isomeric butanols and 1-decanol in dilute p-xylene solution and 1-butanol and 1-decanol in dilute cyclohexane and mesitylene solution at 25°C over the range 1 — 35 GHz. The most dilute p-xylene solutions, about 0.02 mole fraction, show a symmetrical distribution of relaxation times. The data for the more concentrated solutions separated into two dispersion regions and were analyzed in terms of two relaxation times, both of which are sensitive to the nature of the solvent and solute and their concentration. Crossley attributed the relaxation times to molecular and -OH group relaxation processes, and found that their magnitudes and weight factors are dependent upon the relative importance of solute-solute and solute-solvent interactions.

(2) Amides

The exceptionally large dielectric constants of liquid N-monosubstituted amides have been attributed to intermolecular association into essentially linear chains by CO---HN hydrogen bonds. Dannhauser and co-workers[92, 93] measured three isomeric N-butyl acetamides, three isomeric N-methyl valeramides and N-ethyl acetamide at 0.5 — 200 MHz and 255 — 341°K and found that their dispersion loci follow the Debye equation. The relaxation times show a specific dependence on the size and shape of the alkyl group, but not on whether it is in the acid or the amine positon. They also examined the equilibrium dielectric constants of these amides as a function of temperature and observed that the association of the liquids into linear chains is independent of the size and shape of the alkyl group in either position. Meanwhile they proposed a planar, trans hydrogen-bonded polymeric structure with free rotation feasible about the C=O---N-H bond. Cole and co-workers[94] found that the dielectric absorption of N,N-dimethyl formamide, formamide, N-methyl formamide, N-methyl acetamide and N-methyl propionamide over their liquid temperature range at 1 —— 250MHz all show Debye behaviour and proposed a similar model of hydrogen bonding.

N,N-Dimethyl amides of straight-chain aliphatic monocarboxylic acids and higher N,N-dialkyl amides of formic acid and acetic acid have been studied.[95] The lower homologs show an exponential decrease in their dielectric constants with increased chain length owing to the corresponding decrease in the number of molecular dipoles. The formamides have been found to display a special behaviour which is presumably caused by associated forms effected by participation of the formyl H-atom. Consequently the existence of different rates and forms of association has been proposed.

(3) Bromoalkanes and other aliphatic liquids

The n-alkyl bromides[97 - 107] are the only class of non-associated liquids whose dielectric absorption has been studied in any detail. However, some conflict has arisen regarding the nature of their distribution function and the interpretation of the results at the molecular level. The interpretation and comparison of relaxation data for these and other classes of aliphatic liquids[43, 109 - 112] is complicated by uncertainties regarding the effects of viscosity, internal field and molecular interaction. In dilute solution these factors are minimized, but relatively few studies have been reported.[114 - 116]

(i) Alkyl Halides

Smyth and co-workers[117, 118] studied liquid i-butyl chloride, i-butyl bromide and i-amyl bromide at 0.5, 5 and 50 KHz and detected dielectric dispersion at low temperatures. In 1948, they reported[97 - 99] the results of dielectric measurements at 1.27, 3.22 and 9.72 cm wavelengths from 1 to 55°C for 27 liquid organic halides, mostly n-alkyl bromides, of different sizes, shapes and rigidities. The mean relaxation times and Cole-Cole distribution parameters increased with increased chain length, and decreased with increased temperature. A large number of alkyl bromides show Debye-like behaviour at 55°C, which may be due to an increase in the uniformity of the rotational potential barriers throughout the liquid. Smyth et. al. considered that the large distribution parameters for the long chain alkyl bromides result from segmental reorientations about C-C bonds, with a maximum rotating unit rarely larger than the segment of a chain extending ten to twelve carbon atoms from the dipole. They also noticed a close parallelism between the processes of dielectric relaxation and viscous flow. Exceptions were only observed for short molecules such as i-propyl and t-butyl bromides for which the decrease in the relaxation time brought about by chain branching is not accompanied by a consistent decrease in the viscosity of the liquid. This is not unreasonable since dipole orientation occurs merely by rotation and is facilitated by an approach to sphericity. Translational motion which in addition to rotation is required for viscous flow may be hindered by the increase in the smallest molecular dimension caused by branching of the chain. The increase in the polarizability of the rotating group with consequent increase in the van der Waals attractive forces between the molecules was considered responsible for the increase in the viscosity and the relaxation time from chloride to bromide to iodide as well as from n-propyl bromide to ethylene bromide.

Ethyl bromide, t-butyl chloride and n-octyl bromide have been measured in several nonpolar solvents (n-heptane, benzene, cyclohexane and n-hexadecane) at microwave frequencies between 0 and 60°C[114]. The relaxation times for the pure liquids are longer than those for any of the solutions even though the viscosities are sometimes smaller. Whiffen and Thompson[119] had reported earlier that in a very viscous solvent such as Nujol, the relaxation time of long-chain unsymmetrical molecules would become longer than that of the pure solute. However Smyth and co-workers[120, 121] showed that, while the long-chain flexible molecule of n-tetradecyl bromide shows a relaxation time of ∿100 ps in Nujol at 20°C which is longer than those in n-heptane ($\eta=1/260\ \eta_{Nujol}$) and in the pure liquid ($\eta=1/20\ \eta_{Nujol}$) at the same temperature, the relaxation time of t-butyl chloride is only 2/3 greater in Nujol than in n-heptane and is even smaller than that of pure t-butyl chloride. They attributed the result to the near sphericity of the t-butyl chloride molecule which can rotate without any considerable displacement of the neighbouring molecules while the rotation of an unsymmetrical molecule around one or more axes would involve the translational displacement of some of its neighbours with consequent viscosity dependence of the relaxation time. This viscosity dependence becomes less important with increasing chain length in long, flexible molecules, which is consistent with the idea that dipole orientation may involve only a small segment of the molecular chain.

Denney[103] studied i-butyl chloride, i-butyl bromide and i-amyl bromide at low temperatures (c.a. 100°K) in the frequency range 0.05 KHz to 2MHz and obtained Cole-Cole complex plane loci in an unexpected skewed-arc form[71] with small deviations at very high frequencies. This dielectric behaviour is similar to that of polyhydroxyl alcohols[71] but differs from that of monohydroxyl alcohols.[71, 72] Further investigation of these halides in the supercooled liquid state[122] established a close parallelism between the viscous flow and dielectric relaxation process as observed previously by Smyth and co-workers[117, 118] for several organic halides in the normal liquid state. In a study of i-amyl bromide and its solutions in 2-methylpentane in the ranges of 50 Hz — 300 KHz and 10^2 — 10^7 poises and room temperature to -151°C, Denney and Ring[123] observed only a single dielectric dispersion region at all concentrations, with the distribution width showing a maximum at a certain intermediate concentration which suggests the importance of environmental heterogeneity. Meanwhile they again noticed the similarity between the concentration and temperature dependence of dielectric relaxation and shear viscosity and proposed that a large molecular region is involved in the relaxation process so that individual molecular interactions tend to be averaged.

Glarum[104] reviewed both Smyth's[97 - 100] and Denney's[103] studies on alkyl halides and pointed out that, for i-butyl bromide, the parameter β occurring in the skewed-arc function varies from a low-temperature value of 0.5 to nearly unity at room temperature in which case Smyth's data are described by a circular-arc locus with a very small distribution parameter. In order to obtain some insight into the skewed-arc function for non-associated liquids Glarum examined i-amyl bromide at 1, 3, and 9 GHz between -75° and +25°C. He found that on a reduced complex plane plot the points at all temperatures fell reasonably close to a single curve which could be described by an asymmetric skewed-arc distribution function with $\beta \simeq 0.7$, although a circular-arc plot gave a better representation of the high-frequency data. In proposing a model, the defect diffusion model, to explain the dielectric behavior of this system he supposed that skewed-arc behaviour arises from a co-operative relaxation process, i.e., molecules do not relax independently of one another and the motion of a particular molecule depends to some degree on that of its neighbours. This model implies that the relaxation of a molecule is most probable immediately after one of its neighbours has relaxed.

Higasi, Bergmann and Smyth[101] represented the previously measured dielectric data for the n-alkyl bromides[99] in terms of a distribution of relaxation times, similar to that discussed by Fröhlich,[124] between two limiting values calculated from the mean relaxation time and the distribution parameter α obtained from the Cole-Cole arc plot. The lower limit was taken as the relaxation time for the rotational orientation of the $-CH_2Br$ group about its bond to the rest of the molecule. The upper limit was considered to represent the relaxation time of the largest orienting unit, usually the molecule as a whole. They claimed that the numerical values obtained for the two limits, one small and increasing slowly with molecular size, and the other large and increasing rapidly with molecular size, are consistent with this physical picture of the relaxation process, indicating the approximate correctness of the distribution function.

Vaughan et. al.[102] further investigated the dispersion of several alkyl halides at millimeter wavelengths between 1 and 25°C in order to obtain improved accuracy in the relaxation times for $-CH_2Br$ group orientation. They examined the results together with the previously measured lower frequency data and obtained asymmetric reduced complex plane plots. The losses at 2.2-mm wavelength are unexpectedly high and the curves range from left to right skews. In discussing the observed dielectric behaviour they stated that the distribution of relaxation times decreases with increasing temperature owing to a narrowing of the spread between the limiting values, and that the decrease with decreasing chain length is due to both the removal of the relaxation mechanisms with the longest relaxation times and the decreased viscosity.[99] With this evidence in support of the concept of a distribution between the limiting values they put forward a more general form of a distribution function, which is similar to Macdonald's[125] expression for a relaxation process in terms of a distribution of activitation energy barriers between limits. Meanwhile they explained the extra loss at 2.2-mm wavelength by a relaxation mechanism similar to that proposed by Whiffen.[126] In addition, they suggested that the ease of rotational orientation of the $-CH_2Br$ group is such that it contributes more strongly to the loss at 2.2-mm wavelength than is indicated by the distribution function they proposed. Winslow et. al.[127] had suggested that the Cole-Davidson behaviour is not restricted to low temperatures. Vaughan et. al. accordingly compared the exactness of the Cole-Davidson and the 'Higasi-Smyth' distribution functions as a representation of the experimental data. They concluded that, whereas the relaxation mechanism which leads to Cole-Davidson behaviour may be neglected for the normal long chain alkyl bromides, this mechanism may persist in i-butyl bromide and i-amyl bromide at room temperature and above though the unique representation for these two bromides was questioned.

Mopsik and Cole[106] examined the dielectric absorption of n-octyl iodide at audio frequencies and 12 frequencies from 10 MHz to 9 GHz between -40° and +40°C. The frequency dependence of the loss was found to only deviate slightly from a Cole-Davidson skewed-arc function, and this behaviour changes very little with temperature over the 80 degree range. They concluded that previous measurements on alkyl halides believed to show symmetrical[97 - 101, 114] or left-skewed[102] complex dielectric constant loci would be consistent with the Cole-Davidson skewed-arc representation if certain data notably those at 10 cm wavelength[100] were experimentally in error. As a consequence, the skewed-arc behaviour can be attributed either to a finite distribution of simple exponential decay processes for loss of dipole correlation as proposed by Smyth and associates,[101, 102] or to a diffusion-like mechanism for which the decay function is not exponential and is only formally expressed as a continuous distribution of exponentials. The Brown workers[104, 106, 128] have emphasized the latter viewpoint, in which the broader range of frequencies or times of significant relaxation effects is considered to result from the intermolecular co-operative nature of interactions involving any given molecule and its neighbours. Mopsik and Cole[106] also pointed out that if the observed relaxation in n-octyl iodide can be explained as a superimposition of four or five skewed-arc functions, each with $\beta = 0.7$, and times differing by a factor 5 from maximum to maximum, the intramolecular mechanism proposed by Smyth and associates[101, 102] may still act to modify the broadening produced by the co-operative processes though it is not the primary origin of the broadening.

Berberian and Cole[107] extended the previous studies of Glarum[104] and Denney[103] to supercooled i-amyl bromide from 122°K down to the glass-transition temperature, 107°K, by steady-state a.c. measurements from 10^5 to 10^{-2} Hz and by transient measurements at times from 2 to 700 seconds. They found that, except for small deviation at high frequencies probably due to minor changes in dipole moment by internal rearrangements of neighbouring bonds, the a.c. data can be described by a skewed-arc relaxation function with β in the range of 0.57 — 0.50, and the transient data by the incomplete γ function with the corresponding values of β approaching 0.5 at the glass-transition temperature. In view of the work done on i-amyl bromide they have drawn two striking features for its relaxation behaviour. First, the temperature dependence of the mean relaxation time is well described by the following empirical equation which is valid from 145°K down to its glass-transition temperature,

$$\log \beta\tau_0 = A + B/(T - T_\infty) \qquad (1.1)$$

where $A = 7.1 \times 10^{-17}$ sec., $B = 620^{\circ}K$, and $T = 74^{\circ}K$. A similar equation successfully fits Denney's data for the viscosity of isoamyl bromide[122] in the range 10^{2} — 10^{9} poises at temperatures from 137° down to $113^{\circ}K$. Secondly, the change in the frequency or time dependence of the relaxation gives strong indications of a limiting low-temperature behaviour characterized by the value of the distribution parameter $\beta = 0.5$ They have also discussed the implications of the behaviour of i-amyl bromide in relation to the molecular relaxation theories of Glarum,[104] Adam and Gibbs,[129] and Anderson and Ullman,[130] all of which have the common feature that they invoke co-operative interaction effects. So far, Cole and associates[107] have realized that, with the existing theories, the physical interpretation of the skewed-arc function is still far from being satisfactory and complete.

(ii) Esters

Smyth and co-workers[109] examined ethyl, i-amyl, cetyl and octadecyl acetates, tetradecyl palmitate, decyl, tetradecyl and cetyl stearates, tristearin, distearin, and monostearin, and ethylene dimyistate, dipalmitate and distearate at 1.25, 3.22 and 10.0 cm between 3° and $90^{\circ}C$. The mean relaxation times lengthen with molecular chain length and with viscosity as observed previously for alkyl bromides.[97 - 101, 114] However, the relaxation times for the esters are only about half as long as those of analogous alkyl bromides despite their similar viscosities. No significant change in relaxation time is detectable when the location of the molecular dipole is moved away from the chain end. It was suggested that the orientation of polar molecular segments occurs by rotation around the carbon-carbon bonds for all locations of the polar group.

(iii) Ketones and Aldehydes

Smyth and co-workers[110, 111] measured acetone, 2-heptanone, 4-heptanone, 8-pentadecanone and 9-heptadecanone at 1.25, 3.22, and 10.0 cm wavelengths from 1 to 60°C (Table 1.1). The relaxation time for 2-heptanone is slightly longer than that for i-amyl acetate,[109] a molecule of similar size and viscosity. In constrast to the alkyl esters,[109] these ketones have about the same rate of increase in relaxation time with viscosity as the alkyl bromide.[97, 99] However, unlike both long-chain alkyl bromides[101] and esters,[109] the two long-chain symmetrical ketones have very small distribution parameters ($\alpha \simeq 0.1$). This behaviour indicates that these ketones may possess a mode of intramolecular reorientation (probably twisting around the R-C and R'-C bonds) different from the segmental rotation proposed for alkyl bromides.[101] The slightly longer relaxation time for 4- than 2-heptanone may indicate that segmental rotation becomes more difficult as the dipole is removed from chain end. The ratio τ_0/η for these two heptanones decreases with increased absolute temperature in agreement with the expression,[143]

Table 1.1. Relaxation Parameters, Viscosities and Dipole Moments of Several Aliphatic Ketones. (from refs. 110 and 111)

Ketone	$t^{o}C$	α	λm (cm)	η (cp)	$\lambda m/\eta$	τ_o^* (ps)	τ_o/η	μ (D)
$(CH_3)_2CO$	1	0.03	0.75	0.397	1.9	3.98	10.0	3.04
	20	0.0	0.63	0.325	1.9	3.34	10.3	3.06
	40	0.0	0.52	0.268	1.9	2.76	10.3	3.08
$C_5H_{11}COCH_3$	1	0.12	2.88	1.10	2.6	15.3	13.9	2.96
	20	0.07	2.04	0.807	2.5	10.8	13.4	2.97
	40	0.06	1.55	0.624	2.5	8.2	13.1	2.99
	50	0.0	1.47	0.56	2.6	7.8	13.9	
	60	0.05	1.15	0.50	2.3	6.1	12.2	3.0
$C_3H_7COC_3H_7$	1	0.09	3.26	0.98	3.3	17.3	17.7	3.06
	20	0.07	2.35	0.736	3.2	12.5	17.0	3.07
	40	0.08	1.67	0.571	2.9	8.9	15.6	3.08
	60	0.10	1.35	0.460	2.9	7.2	15.7	3.09
$(C_7H_{15})_2CO$	50	0.11	6.2	1.85	3.4	32.9	17.8	
$(C_8H_{17})_2CO$	50	0.09	6.6	2.5	2.6	35.0	14.0	

* Calculated from $\lambda_m = (6\pi \times 10^{10})\tau_o$

$$\tau_o = \frac{4\pi a^3\eta}{kT} \tag{1.2}$$

where a is the molecular radius, despite the constancy shown by acetone. Smyth and co-workers also found that the τ_o/η ratio is greater for the heptanones than for acetone, but much less than the 2 to 1 relationship predicted from the ratio of molar volumes. They explained this by considering that the rotation of the heptanone molecules as extended rods around their axes may be the dominating process.

Johari et. al.[116] reported a larger distribution for 2-octanone in dilute n-heptane solution at 25°C than those for acetone, 2-heptanone and 4-heptanone as pure liquids.[111] They compared the mean relaxation time of the 2-octanone, τ_o = 4 ps, with those of several other similar molecules at similar temperature, viz., 2-heptanone,[111] ∿10 ps; acetyl group rotation for aromatic molecules in nonpolar solvent,[131, 132] ∿7 ps; acetone in benzene,[119, 113] ∿3.2 ps. Apparently, the acetone molecule rotates about the axis perpendicular to the C=O bond and sweeps out a volume similar to that swept out by the acetyl group in 2-octanone, and the comparable mean relaxation times indicate that acetyl group rotation is the dominating process in dilute solution of 2-octanone. They also measured n-octyl aldehyde in n-heptane at 25°C[116] and analyzed the data in terms of two relaxation times, $\tau_1 \simeq 18$ ps and $\tau_2 \simeq 1.9$ ps, the latter was attributed to -CHO group rotation. Lal[134] found that the relaxation times for aliphatic aldehydes increase with chain length.

(iv) Ethers and Sulfides

Smyth and co-workers[110] found that the dielectric absorptions of ethyl ether and n-decyl ether at 1.25, 3.22, and 10.0 cm wavelengths between 4^{o} and $85^{o}C$ may be characterized by single relaxation times, $\tau_0(C_4) \approx 2.3$ ps and $\tau_0(C_{20}) \approx 30$ ps. The difference is less than that required by the Debye equation, Eq. 1.2, and has been attributed to a molecular structure of zig-zag chains forming close-packed cylinders in n-decyl ether so that the molecular relaxation time should be proportional only to the internal or microscopic viscosity which is much smaller than the macroscopic viscosity. The ratio of the viscosity of ethyl ether to those of the more viscous liquids, n-butyl bromide[99] and ethyl acetate,[109] all three having a comparable molecular volume, are similar to the ratios of the mean relaxation times.

Dasgupta et. al.[115] studied several long-chain alkyl ethers, ethyl ether and didodecyl sulfide in dilute n-heptane solutions from 6^{o} to $50^{o}C$ at microwave frequencies and were able to analyze their data in terms of two relaxation times. (Table 1.2) The resultant moment associated with the over-all molecular orientation of ethers and sulfides bisects the C-O-C or the C-S-C angle, and reversal of this dipole may occur by a high-frequency, intramolecular process which involves twisting or partial rotation

Table 1.2. Relaxation Parameters for Several Alkyl Ethers and a Sulfide in n-Heptane. (from ref. 115)

t^oC	τ_o(ps)	α	τ_1(ps)	τ_2(ps)	C_2
		Ethyl ether (f_2 = 0.1505)			
6	1.9	0.03			
25	1.3	0.06			
		Dihexyl ether (f_2 = 0.1508)			
12	18.6	0.14	42.5	8.0	0.70
30	14.8	0.11	30.7	7.1	0.75
50	5.9	0.01			
		Didodecyl ether (f_2 = 0.1412)			
12	42.4	0.35	204	9.3	0.49
30	28.6	0.25	119	7.7	0.59
50	10.6	0.12	41	6.2	0.75
		Didodecyl sulfide (f_2 = 0.1187)			
20	45.1	0.35	213	11.9	0.53
35	29.2	0.26	122	10.3	0.59
50	13.3	0.13	47.7	8.5	0.72
		Dodecyl methyl ether (f_2 = 0.1523)			
12	9.5	0.34	46.4	4.4	0.63
30	7.0	0.25	36.1	3.7	0.71
50	5.5	0.18	28.4	3.2	0.80

around the C-O or C-S bond.

Johari et. al.[116] examined di-butyl ether in n-heptane at 25°C in the same frequency range. The τ_2 value of 3.4 ps is smaller than would be expected for $-OC_4H_9$ rotation about the O-C bond and is smaller than that found for the $-OCH_3$ group rotation in n-dodecyl methyl ether.[115, 116] It was considered that twisting around C-O bonds was the dominant mode of dipole orientation for symmetrical ethers, as proposed earlier.[115] The τ_1 value of $\sim$16 ps is consistent with those of other molecules having the same number of carbon atoms, i.e. n-octyl aldehyde[116] and n-octyl amine.[116] Srivastava et. al.[135, 136] also measured di-butyl ether as pure liquid at 30°C and in benzene at 25°C at 9.72 and 31.82 GHz and obtained τ_o values of 5.0 and 6.3 ps respectively.

(v) Amines

The relaxation times of some simple pure liquid alkyl amines at 20°C have been obtained from measurements at 9.5 GHz[137] (Table 1.3). For primary, secondary and tertiary amines the relaxation times lengthen with the chain length and the degree of branching. Garg and Kadaba[43] found that the mean relaxation times for pure liquid primary amines with 2 to 5 carbon atoms are almost independent of the alkyl group whereas the values for three symmetrical secondary amines (di-ethyl, di-n-propyl and di-n-butyl) lengthen with molecular size. These few examples can however hardly establish any general trend of relaxation behaviour. Johari et. al.[116] were able to detect a separation into two absorption regions in the microwave frequency range for n-octyl amine in n-heptane at 25°C. Their τ_2 value, $\sim$2 ps, is slightly longer than those obtained for the aromatic amines aniline and N,N-dimethylaniline[138 - 140] for which inversion of the nitrogen atom has been considered as a possible relaxation mechanism. Kadaba and co-workers[141] have indicated the possibility of two relaxation processes for some primary alkyl amines.

Table 1.3. Relaxation Times (ps) for Some Alkylamines (from ref.137)

	τ_o
n-Butylamine	3.8
n-Hexylamine	4.6
Di-isopropyl amine	10.4
Di-n-butyl amine	13.7
Di-isobutyl amine	16.2
Tri-ethyl amine	9.2
Tri-n-butyl amine	18.1

Chapter II. Basic Theory

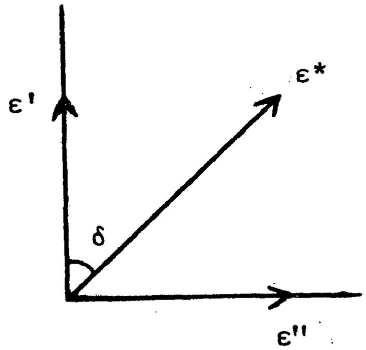
The dielectric constant or permittivity, ε, is a frequency-dependent quantity which is characteristic of the medium between two charges. It may be defined as the ratio of the field strength in vacuum to that in the material for the same distribution of charge. It is also given by the ratio of the capacitance of a condenser with material between the parallel conducting plates to the capacitance of the same condenser when the material is replaced by a vacuum. As the frequency of an applied electric field is continuously increased, for a dipolar material, from a static field up to the microwave region, the reorientation of dipoles in the field will, at some stage, lag behind the voltage oscillations. The resulting phase displacement (δ) leads to a dissipation of energy, as Joule heating, in the medium which is measured by the dielectric loss (ε'') defined as

$$\varepsilon'' = \varepsilon' \tan\delta \qquad (2.1)$$

where ε' is the real part of the dielectric constant and $\tan\delta$ is the loss tangent or the energy dissipation factor. In this frequency region the dielectric constant is a complex quantity given by

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \qquad (j = \sqrt{-1}). \qquad (2.2)$$

The relationship between ε', ε'' and δ is illustrated by the diagram.



In a low-frequency electric field there is no lag between the orientation of small polar molecules of a liquid and the variation of the alternating voltage. For such a system the reorientation of dipoles is a molecular process transmitting the electromagnetic energy through the medium. The system corresponds to an ideal dielectric in which the electric energy is transmitted without loss. The corresponding dielectric constant is the static dielectric constant ε_0 of the material.

The Clausius-Mossotti-Debye theories[143] give the total polarization of a polar molecule in an electric field as,

$$P_{\text{total}} = P_E + P_A + P_0 = \frac{4\pi N_0}{3}\left(\alpha_E + \alpha_A + \frac{\mu^2}{3kT}\right) = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\left(\frac{M}{d}\right) \qquad (2.3)$$

where α is the polarizability, N_0 is the Avogadro's number, k the Boltzmann constant, μ the electric dipole moment, T the absolute temperature, M the gram molecular weight, and d the density (gm. per ml.) of the material. The total polarization arises from three simultaneous deformations: (a) electronic polarization, P_E, i.e. electrons are drawn one way and the nuclei the other, (b) atomic polarization, P_A, due to the change in the mean positions of the 'positive-charge-rich' (δ^+) and 'negative-charge-rich' (δ^-) atoms, or the relative angles of polar links, and (c) orientation polarization, P_0, due to orientations of the permanent dipole whose dipole moment is μ. In the orientation process a dipole tends to align its moment against the field such that its potential energy is a minimum.

The Clausius-Mossotti-Debye theories are applicable to gases but are often inadequate when applied to polar liquids due to the invalidity of the Lorentz field used in these theories as a measure of the local field in a dipolar dielectric.

In order to obtain a relation between permittivity and dipole moment which should have a wider range of validity, Onsager[144] considered a polarizable rigid point dipole of moment $\vec{m}$ at the center of a spherical cavity of molecular dimensions in a continuous medium of static permittivity ε_0. The assumption that the cavity in which the molecule lies can be treated as a sphere in a homogeneous medium however limits the validity of the theory to materials in which there are no strong local forces.

The Onsager theory gives the relationship

$$\frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty+2)^2}\,\frac{M}{d} = \frac{4\pi N_0\mu^2}{9kT} \qquad (2.4)$$

where ε_∞ is the very high frequency or optical dielectric constant. At very high frequency when the orientation polarization vanishes Eq. (2.3) becomes

$$\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\,\frac{M}{d} = \frac{4\pi N_0}{3}\,(\alpha_E+\alpha_A) \qquad (2.5)$$

Combination of Eqs. (2.3) and (2.5) gives the Debye equation,

$$\frac{3(\varepsilon_0-\varepsilon_\infty)}{(\varepsilon_0+2)(\varepsilon_\infty+2)}\,\frac{M}{d} = \frac{4\pi N\mu^2}{9kT} \qquad (2.6)$$

Eqs. (2.4) and (2.6) allow a comparison of the values of μ^2 given by the Onsager and Debye equations:

$$\frac{\mu^2(\text{Onsager})}{\mu^2\ (\text{Debye})} = \frac{(2\varepsilon_0+\varepsilon_\infty)(\varepsilon_0+2)}{3\varepsilon_0(\varepsilon_\infty+2)} = i \qquad (2.7)$$

The Onsager equation will be reduced to the Debye equation when ε_0 and ε_∞ are practically identical as for gases at low pressures.

Onsager's original theory does not hold for such associated liquids as water, alcohols and carboxylic acids. Kirkwood[145] pointed out that hindered rotation, due to either intermolecular or intramolecular association, must play a part in the dielectric polarization of polar liquids. Taking the mutual orientations of the molecular dipoles into consideration, Kirkwood[145] and Fröhlich[124] developed theories leading to an additional relationship between ε and μ:

$$\frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty+2)^2}\left(\frac{M}{d}\right) = \frac{4\pi N_0\mu^2 g}{9kT} \qquad (2.8)$$

The factor g which measures the degree of orientation is given by:

$$g = 1 + z(\cos\gamma)_{\text{average}} \qquad (2.9)$$

where z is the average number of molecules showing preferred orientation around one dipole molecule, and $(\cos\gamma)_{\text{average}}$ is the average value of the cosine of the angle between the fixed central dipole and those of adjacent molecules. The divergence of g from unity measures the influence of a dipole on the free rotation of neighbouring molecules. For $g>1$ association predominantly involves the parallel alignment of the near neighbour dipoles, while $g<1$ indicates antiparallel alignment. For nonassociative liquids the g factor departs little from unity; in such case the Fröhlich-Kirkwood equation (2.8) is identical to the Onsager equation.

The molecular polarization is dependent on the frequency of the applied field. At low frequencies the dielectric constant is numerically equal to that obtained when a static field is employed. This value persists as the frequency is increased until the duration of the field becomes comparable with the relaxation period of the molecular species forming the dielectric. At this point the molecules are no longer able to completely follow the reversals of the field. Thus there is an appreciable time lag in the attainment of equilibrium of molecular orientation which leads to a diminution in the orientation polarizability, and ultimately orientation is undetectable. At this point the molecular polarization is given by the atomic and electronic polarizations. At still higher frequencies, however, the atomic nuclei cease to follow the field and the dielectric constant is given solely by the electronic polarization. Figure 2.1 illustrates the frequency dependence of the total polarization.

Electronic polarization is a process requiring about 10^{-15} sec. and corresponds to frequencies in the ultra violet region. Atomic polarization arises from the displacement of the atoms relative to one another in the molecule and requires 10^{-12} to 10^{-14} sec., corresponding to the infrared region. The time required for the orientation polarization process depends on the frictional resistance of the medium to the change in molecular orientation, and for small molecules in liquids of low viscosity, it is about 10^{-11} to 10^{-12} sec., corresponding to the microwave region.

Dielectric relaxation is the exponential decay with time of the polarization in a dielectric when an external field is removed. The relaxation time, τ, is defined as the time in which the polarization is reduced to 1/e times its original value,

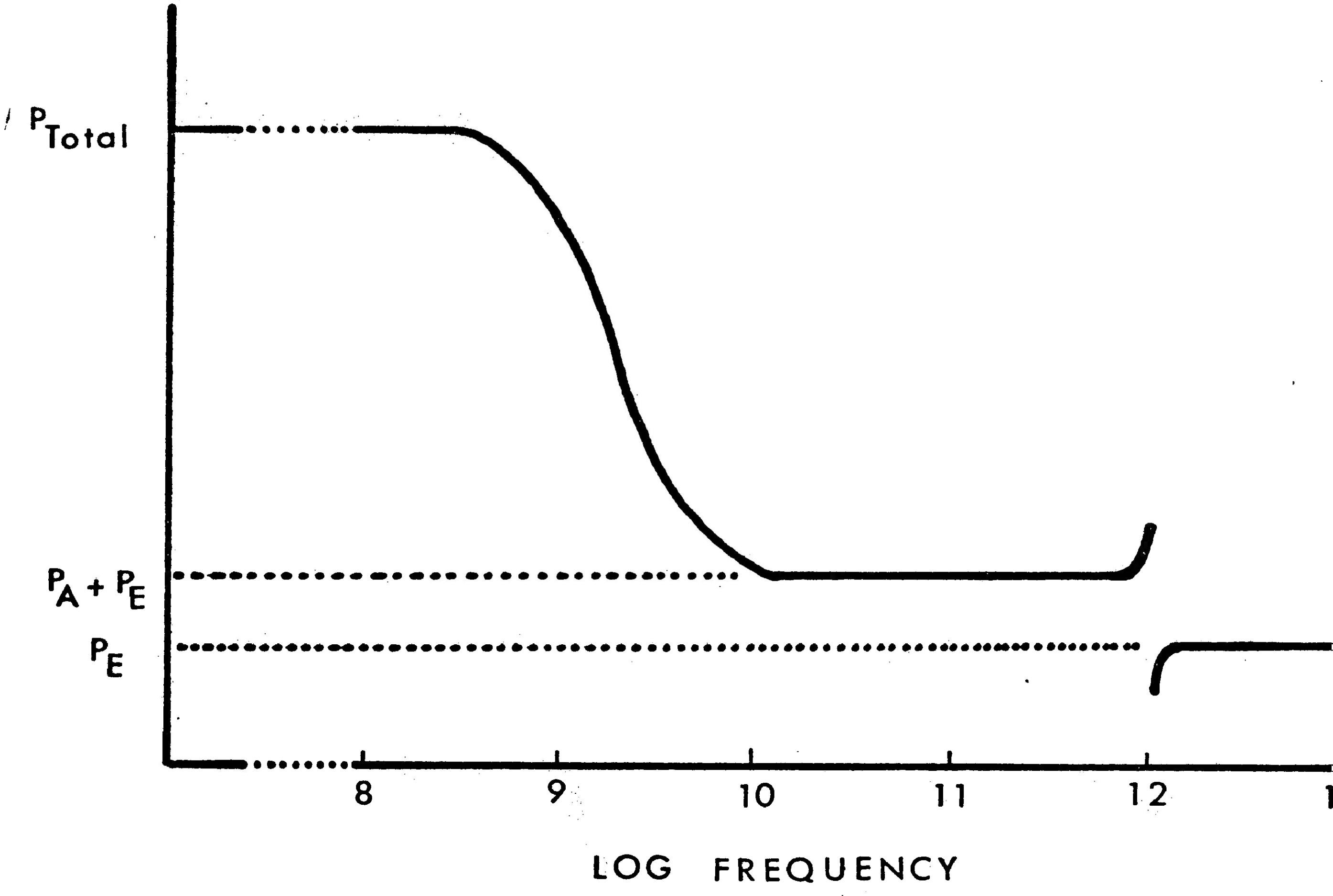


Fig.2.1. Total Polarization versus Log Frequency.

$$P(t) = P_0 \exp(-t/\tau) \qquad (2.10)$$

where, P_0 = specific polarization in a static field,

$P(t)$ = specific polarization at time t in an electromagnetic field.

The frequency dependence of ε' and ε'' in the region of dielectric absorption for a system characterized by a single discrete relaxation time is given by the Debye equation,

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \qquad (2.11)$$

where ω is the angular frequency.

On separation into real and imaginary parts, Equation (2.11) becomes,

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2\tau^2} \qquad (2.12)$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \qquad (2.13)$$

Elimination of $\omega\tau$ from these equations gives

$$\left(\varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2}\right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right)^2 \qquad (2.14)$$

which is the equation of a circle. The locus of ε' and ε'' in an Argand diagram is a semi-circle of radius $(\varepsilon_0-\varepsilon_\infty)/2$ with the center lying on the abscissa, and is known as a Cole-Cole plot.[146]

For many molecules, the dielectric absorption is not characterized by a single discrete relaxation time. Cole and Cole[146] considered the case of a symmetrical distribution about the mean relaxation time τ_o and obtained:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + (j\omega\tau_o)^{1-\alpha}} \tag{2.15}$$

where α, measured in units of $\pi/2$ radians, is the distribution parameter, and may have values between 0 and 1. When $\alpha = 0$ the Debye equation is obtained.

Similarly, Equation (2.15) may be separated into:

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_o\ \varepsilon_\infty)\{(\ 1 + (\omega\tau_o)^{1-\alpha}\sin(\alpha\pi/2)\}}{1 + 2(\omega\tau_o)^{1-\alpha}\sin(\alpha\pi/2) + (\omega\tau_o)^{2(1-\alpha)}} \tag{2.16}$$

$$\varepsilon'' = \frac{(\varepsilon_o-\varepsilon_\infty)(\omega\tau_o)^{1-\alpha}\cos(\alpha\pi/2)}{1 + 2(\omega\tau_o)^{1-\alpha}\sin(\alpha\pi/2) + (\omega\tau_o)^{2(1-\alpha)}} \tag{2.17}$$

In this case, the center of the semi-circle lies below the abscissa.

A large variety of functions have been considered for the representation of non-Debye types of absorption. Fröhlich[124] defined a function for a distribution of relaxation times between two limits,

$$\begin{aligned} f(\tau) &= \frac{1}{A\tau} \quad ; \quad \tau_L \leq \tau \leq \tau_U \\ &= 0 \quad ; \quad \tau < \tau_L\ ,\tau_U < \tau \end{aligned} \tag{2.18}$$

where A is a parameter associated with the distribution of relaxation times. Bergmann[147] has shown that, for a finite range of times, for a material obeying the Fröhlich function, the locus of the complex dielectric constant is very close to a semi-ellipse with the axes $b = (\varepsilon_0 - \varepsilon_\infty)/2$ and $a = \varepsilon''_{max}$

Higasi et. al.[101, 148] have shown that for $A < 4$, the semi-ellipse of Fröhlich function is comparable with the Cole-Cole arc of the same system. For the Cole-Cole arc there is a relation,[146]

$$\tan \frac{\pi}{4}(1-\alpha) = 2\varepsilon''_{max} / (\varepsilon_0 - \varepsilon_\infty) = a/b \qquad (2.19)$$

For the semi-ellipse there is a relation[119] between the ratio of the axes, $\frac{a}{b}$, and the parameter A,

$$a/b = 2\varepsilon''_{max} / (\varepsilon_0 - \varepsilon_\infty) = (2/A)\tan^{-1}\sinh(A/2) \qquad (2.20)$$

Therefore,

$$\alpha = 1 - (4/\pi)\tan^{-1}\Big((2/A)\tan^{-1}\sinh(A/2)\Big)_{(0 \leq \alpha < 1)} \qquad (2.21)$$

It has been found that,

$$\tau_0 = \sqrt{(\tau_u \tau_L)} = 1/\omega_{max} = \tau_L \exp(A/2) = \tau_u \exp(-A/2) \qquad (2.22)$$

The limiting values of τ can be thus expressed in terms of τ_0 and A, the latter being dependent upon α,

$$\tau_L = \tau_0 \exp(-A/2) \qquad (2.23)$$

$$\tau_u = \tau_0 \exp(A/2) \qquad (2.24)$$

τ_L and τ_u are very sensitive to the selection of the value of A. For $\alpha < 1$ and $A < 4$, a good correlation is provided by,

$$A^2 = 37.6\,\alpha \qquad (2.25)$$

The transformation described by Equations (2.23) and (2.24) is permissible only in the range of $1 > \frac{a}{b} > 0.6$, i.e., $\alpha < 0.30$.

Higasi[148] and Smyth et. al.[102] have indicated a more general form of Equation (2.18),

$$\begin{aligned} f(\tau) &= \frac{1}{A\tau^n} \quad ; \quad 0 < n < \infty \\ & \qquad\qquad\quad\; \tau_L \leq \tau \leq \tau_U \\ &= 0 \qquad\; ; \quad \tau < \tau_L, \tau_U < \tau \end{aligned} \tag{2.26}$$

The reduced dielectric constant and losses are given by,

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty \frac{f(\tau)d\tau}{1 + \omega^2\tau^2} \tag{2.27}$$

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty \frac{\omega\tau f(\tau)d\tau}{1 + \omega^2\tau^2} \tag{2.28}$$

For $n = 1$, Equation (2.26) is equivalent to the Fröhlich distribution. The complex-plane locus is a symmetrical curve with maximum distribution for a given value of τ_u/τ_L. For an intermediate value of $n > 1$, it has a maximum left skew, and for an intermediate value of $n < 1$, it has a maximum right skew. As the ratio τ_u/τ_L increases, the distribution for a given n value increases and the skew becomes greater. Thus both the n value and the ratio τ_u/τ_L determine the amount of skew. It has been shown that for various alkyl bromides the reduced complex-plane loci with the data at 4.3 and 2.2 mm wavelengths range from left to right skews.[102]

A distribution similar to a right skewed-arc may also be well represented by the Cole-Davidson distribution function.[71]

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + j\omega\tau)^\beta} \tag{2.29}$$

where β is the asymmetric distribution coefficient.

In the complex plane of the Cole-Davidson distribution function, taken either as ε'' against ε' or, in the reduced version, $\varepsilon''/(\varepsilon_0 - \varepsilon_\infty)$ against $(\varepsilon' - \varepsilon_\infty)/(\varepsilon_0 \quad \varepsilon_\infty)$, the β value is given by the tangent to the locus at high frequencies, where it becomes linear: the angle to the ε' axis is $\beta\pi/2$ and τ is obtained as the reciprocal of the ω value at which the bisector of the limiting angle cuts the locus (Figure 2.2).

Among the various types of distribution functions considered above, the Cole-Cole distribution function appears to be most widely applicable.

For molecules, such as anisole, which contain a rotatable polar group, dipole reorientation about the axes a and b involves rotation of the whole molecule, Fig.2.3. Dipole reorientation about the c-axis may occur by the intramolecular rotation of the polar group. The dielectric absorption of such molecules may often be characterized by two discrete relaxation times corresponding to molecular and intramolecular rotations. Budó[149] considered that for multiple discrete relaxation processes the complex dielectric constant could be represented by the superimposition of overlapping Debye absorptions. For two relaxation times such behaviour is described by the equations found on the following page:

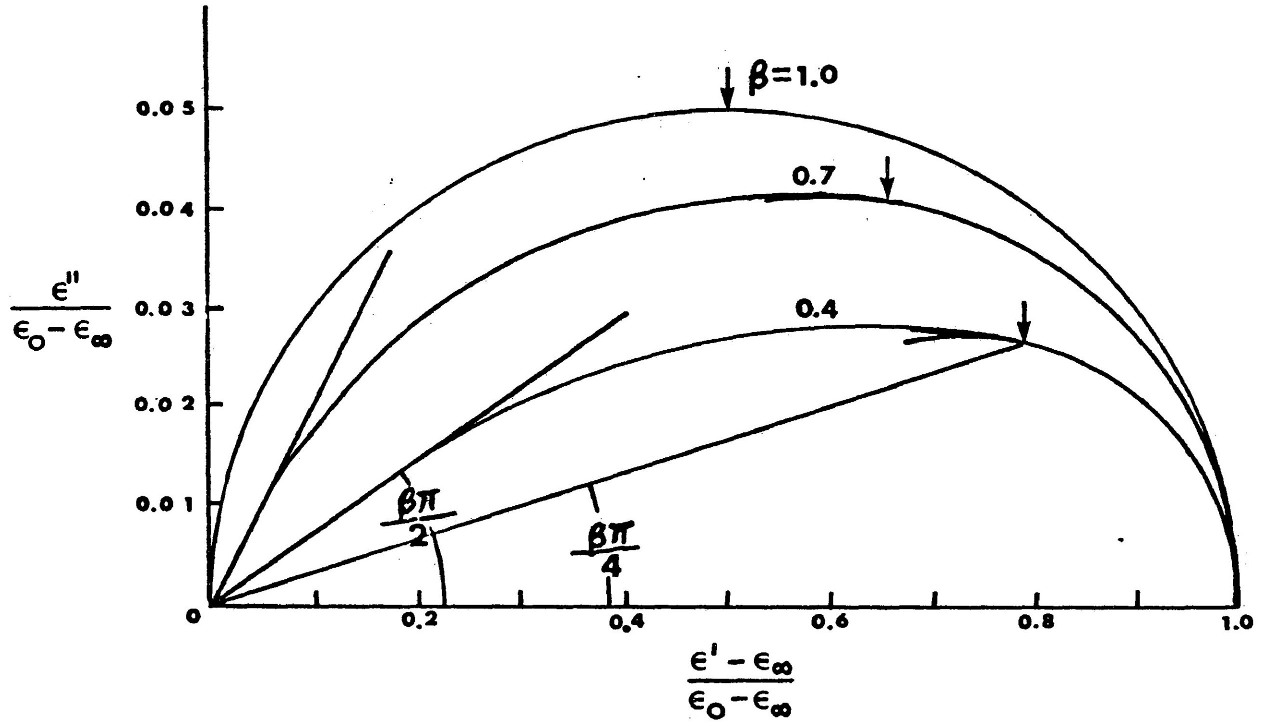


Fig.2.2. The parameters of a skewed-arc representation in the complex plane; the short arrows show where $\omega = 1/\tau$ (after Davidson, ref.71).

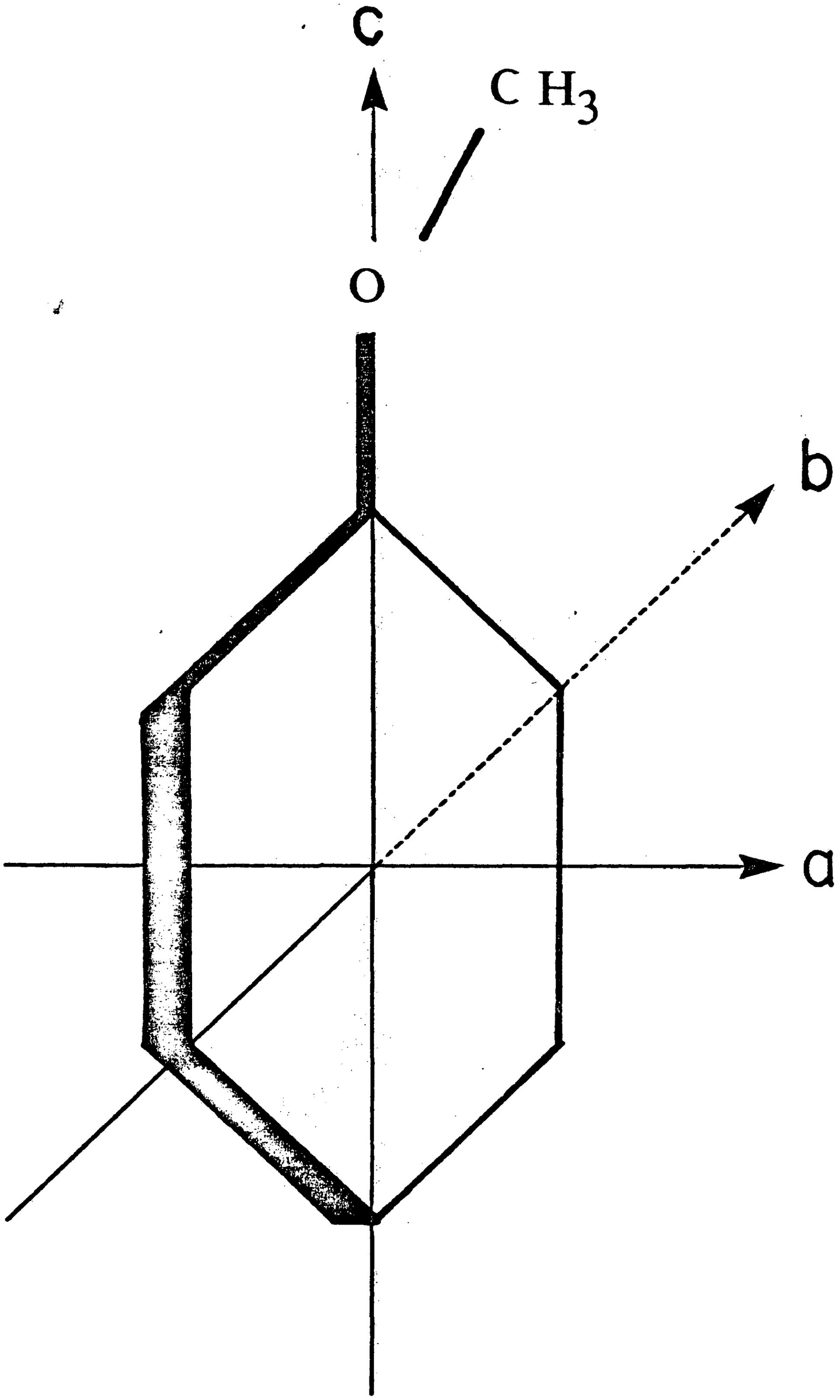


Fig.2.3. Rotations of a rigid polar molecule.

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \left(\frac{C_1}{1 + \omega^2\tau_1^2} + \frac{C_2}{1 + \omega^2\tau_2^2} \right) \qquad (2.30)$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty) \left(\frac{C_1\omega\tau_1}{1 + \omega^2\tau_1^2} + \frac{C_2\omega\tau_2}{1 + \omega^2\tau_2^2} \right) \qquad (2.31)$$

$$C_1 + C_2 = 1 \qquad (2.32)$$

where C_1 and C_2 are the weighting factors of the two contributing absorptions.

It has been shown that the shape of the Cole-Cole plot is influenced by the ratios τ_1/τ_2 and C_1/C_2.[150] For a small C_1/C_2 ratio, the Cole-Cole plot is almost symmetrical. The dielectric absorption data for systems with significant τ_1/τ_2 and C_1/C_2 ratios may separate into two distinct absorption regions.[77] Consequently, the accuracy of analyses for two relaxation times is affected by the magnitude of these ratios. The ideal situation being $C_1 \simeq C_2$ and $\tau_1 >> \tau_2$. Magee and Walker[151] have discussed the errors involved in analyzing Budo type systems in terms of a Cole-Cole symmetrical distribution.

Chapter III. Experimental Methods

3.1.Measurements

(1) Measurements in the frequency region 70 to 145 GHz —— Microwave Interferometer Method

(i) Apparatus

In this region dielectric absorption measurements were made using a free-space interferometric method. At 145 GHz (2 mm) the apparatus was based on that designed by Garg, Kilp and Smyth,[152] which is essentially a microwave equivalent of the Michelson optical interferometer. In this method, a power standing-wave pattern formed by the superimposition of two waves, one from the reference arm of the interferometer and the other reflected from the variable-length dielectric cell is observed as a function of the dielectric-sheet thickness. The probable error in the measured dielectric constant is less than 0.2%. The probable error of the loss measurement is less than ±0.0002 or 2%, whichever is higher.[152]

This method overcomes the difficulties of cell construction and increased metallic losses which occur in the conventional microwave bridge method, e.g., the measured value of attenuation for a rectangular copper waveguide at 140 GHz is 11.1 db/m. Further, it has the advantage that measurements may be made at temperatures in a large range without removing the sample.

In this laboratory two sets of apparatus were available for measuring ε' and ε'' at 4.2 and 2.1 mm, (corresponding to frequencies of $\sim$71 and $\sim$142 GHz respectively).

A schematic diagram of the apparatus for measurement at 2.1 mm is shown in Fig.3.1 That for measurement at 4.2 mm is similar. The Universal Klystron Power Supply A furnishes the operating voltages to the klystron D which generates 4.2 mm waves. A silicon rectifier contained in the power supply set prevents the klystron reflector from becoming positive relative to the cathode. The klystron can be tuned mechanically within range 67.0 to 73.0 GHz. Its output passes through a frequency meter E and an E/H tuner F. The harmonic generator G allows the 2.1 mm waves to pass into a hybrid ring T. At T, the wave splits into two equal parts. One part passes along a waveguide through a variable attenuator K, and is reflected by an adjustable short-circuit R. The other part passes through the transmitting horn N and a plano-convex lens P (made of a lossless dielectric) into free space. The resulting, well-collimated,beam then tranverses the liquid dielectric material in the cell C, and is finally reflected by a reflecting plunger. The reflected waves from both arms re-enter T, where each is once more divided, half passing to the detector M and half towards the generator. The interference between the two reflected beams takes place in the waveguide leading to the detector whose output is amplified by a standing-wave amplifier SWA. The major components of the apparatus are listed in Table 3.1

The dielectric cell for the microwave interferometer is shown in Fig. 3.2. It consists mainly of a 3-in. brass cylinder A (i.d., 1.75 in.) with one end closed by a Teflon window T and

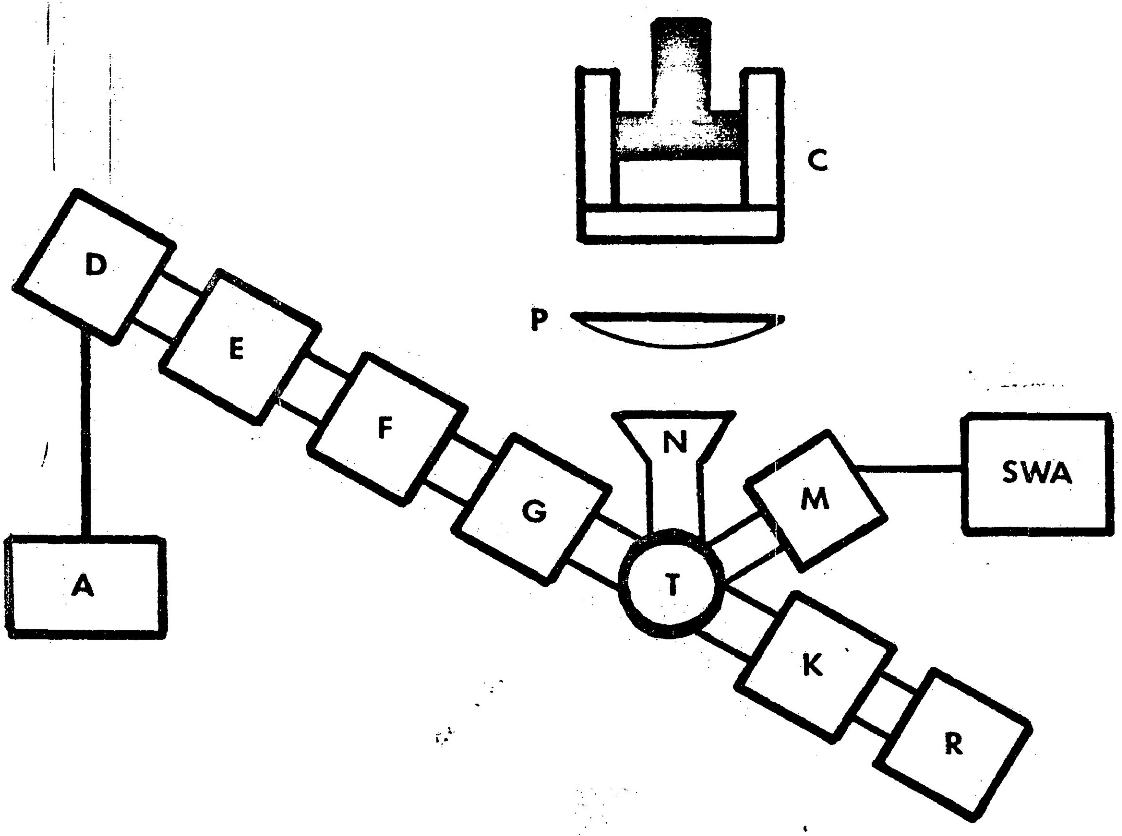


Fig.3.1. Transmission line for microwave analog of the Michelson interferometer.

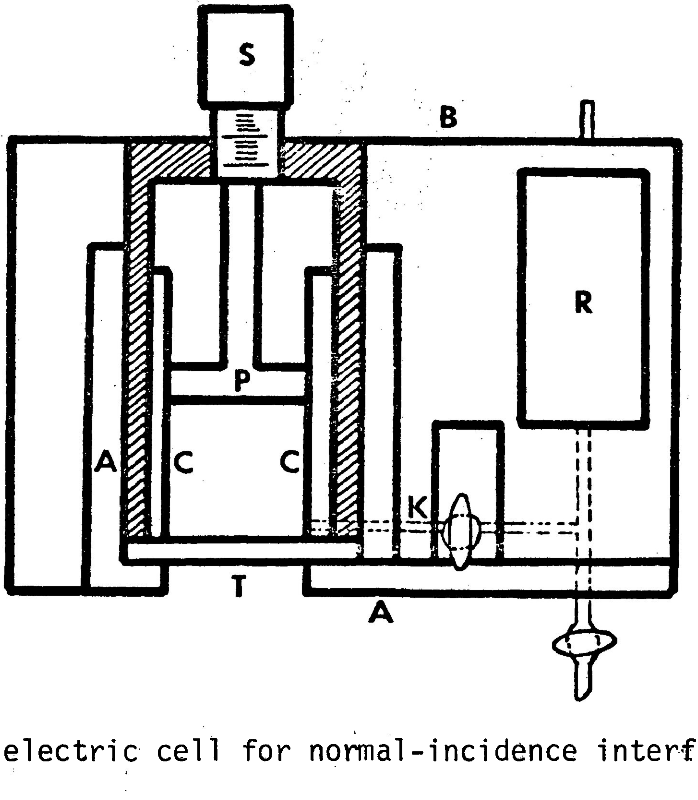


Fig.3.2. Dielectric cell for normal-incidence interferometer.

Table 3.1. Components of Microwave Interferometer.

		2.1 mm Apparatus			4.2 mm Apparatus		
	Component	Supplier	Model	Frequency range(GHz)	Supplier	Model	Frequency range(GHz)
1.	Klystron	Amprerex	DX151	67.0--73.0	(same as 2.1 mm apparatus)		
2.	Universal Klystron Power Supply	Decca	MW59		(-do-)		
3.	Frequency meter	FXR	M410X	50.0--75.0	Philips	PM7065E	65.5--75.0
4.	E/H tuner	FXR	M312B	50.0--75.0	---nil---		
5.	Harmonic generator	FXR	G781B	140.0--220.0	---nil---		
6.	Isolator	---nil---			Philips	PM7040E	
7.	Hybrid ring	TRG	G600	(Center frequency 142GHz)	Philips	PP4050E	60.0--90.0
8.	Transmitting horn	FXR	G638A	140.0--220.0	Philips	PP4080E	60.0--90.0
9.	Dielectric lens	TRG	F850	(Diameter 3 ins.)	(same as 2.1 mm apparatus)		
10.	Variable attenuator	FXR	G163A	140.0--220.0 (0--20dB)	Philips	PM7110E	60.0--90.0 (0--30dB)
11.	Adjustable shorting plunger	FXR	G631A	140.0--220.0	Baytron	3E-95	60.0--90.0
12.	Detector	FXR	G208A	140.0--220.0	Philips	PP4220E	60.0--90.0
13.	Standing-wave amplifier	FXR	B813T		(same as 2.1 mm apparatus)		

the other end terminated by a movable silver-plated reflecting plunger P of 1-inch diameter. A micrometer screw S is used to move the plunger. To eliminate the propagation of higher-order modes which might be present in the cell another cylinder C, of an absorbing material (Teflon impregnated with carbon) of i.d. 1 inch and o.d. 1.75 inches, is tightly inserted into the brass cylinder A.

The thickness χ of the Teflon window is determined by the criterion for zero reflection,

$$\chi = \frac{m\lambda}{2} = \frac{m\lambda_o}{2(\varepsilon')^{\frac{1}{2}}}$$

where m is any integer, λ and λ_o are the wavelengths of the radiation in Teflon and air respectively, and ε', the dielectric constant of Teflon, is 2.10 in this specific range. Thus for a free-space wavelength of 2.1 mm, the window is accurately machined to a thickness of 4.350 mm with a tolerance of about ±0.01 mm. The same cell is used for the 4.2 mm apparatus.

Because of some uncertainty in the thickness of the Teflon window and in the dielectric constant of Teflon at these very high frequencies, a slight adjustment in the frequency of the incident radiation is made so that, in the final set-up of the apparatus, reflections from the window are practically eliminated.

Although water at constant temperature is circulated between the cylinder A and the outer jacket B, the presence of the cylinder C of Teflon impregnated with carbon thermally isolates the liquid inside the cell from the water jacket. The liquid is therefore stored in a thermostated reservoir R and introduced into the cell, using the filling tube K, just before the measurement is taken.

The distance between the cell and the horn is carefully selected to eliminate any diffraction pattern that varies with the plunger setting. The cell is made square to the plane wave by adjusting the levelling screws to give the deepest standing wave minima when using the empty cell. Finally, the detector and amplifier are calibrated against an accurate rotatory vane waveguide attenuator.

(ii) Theory

The total electric field at the detector is given by:

$$E = P_1 E_o + P_2 R\{\exp(jX)\} E_o \tag{3.2}$$

where $j = \sqrt{-1}$, P_1 gives the amplitude and phase change of the wave which reaches the detector without being reflected by the cell. P_2 gives the amplitude and phase change of the wave which reaches the detector having interacted with the cell, but excluding the reflection $R \exp(jX)$ suffered at the cell. E_0 is the electric field at some generator reference plane. Initially the plunger is brought to the Teflon window, which makes $R \exp(jX) = -1$. The variable short-circuit and associated attenuator are adjusted until E is a minimum (ideally zero), which makes $P_1 = P_2$. The electric field at the detector in this condition is then,

$$E = (\mathrm{const})\{\ 1 + R \exp(\ jX\ )\ \} \tag{3.3}$$

An expression for R exp(jX) in terms of the complex index of refraction has been derived previously. It is:

$$R \exp(\ jX\ ) = \frac{\{(1-n^*)/(1+n^*)\}-\{\exp(-2j\beta_0 n^* d)\}}{1-\{(1-n^*)/(1+n^*)\}\exp(-2j\beta_0 n^* d)} \tag{3.4}$$

where $n^* = n(1-jk)$ is the complex index of refraction related to the propagation factor γ according to

$$\gamma = j\,\frac{2\pi}{\lambda}\,n^* = \alpha + j\beta$$

such that $\alpha = k\beta$. $\beta_o = \frac{2\pi}{\lambda_o}$ is the phase constant of the wave in the free space and λ_o is the wavelength in air, d is the length of the liquid, i.e., the distance between the Teflon window and the surface of the reflecting plunger.

The resulting intensity at the detector can be evaluated by multiplying Eq. (3.3) by its conjugate,

$$I \propto \frac{1+\exp(-4\beta_0 kd)-2\exp(-2\beta_0 kd)\cos 2\beta_0 nd}{(1+n)^2+k^2+\{(1-n)^2+k^2\}\exp(-4\beta_0 kd)-2\exp(-2\beta_0 kd)\{(1-n^2-k^2)\cos 2\beta_0 nd + 2k\sin 2\beta_0 nd\}} \tag{3.5}$$

It is apparent that by determining the value of I for various values of d we can calculate n and k from the above equation. In fact only an approximation method is feasible as I is a transcendental function of n and k.

For low-loss liquids, to a very good approximation, the function in Eq. (3.5) can be treated as periodic. For a periodic function it can be seen that the intensity in Eq. (3.5) would be a relative minimum for a value of d such that $\cos 2\beta_0 nd=+1$, and a relative maximum for $\cos 2\ nd=-1$. Therefore,

$$I_{max} \propto \frac{1+\exp(-4\beta_0 kd)+2\exp(-2\beta_0 kd)}{(1+n)^2+k^2+\{(1-n)^2+k^2\}\exp(-4\beta_0 kd)+2(1-n^2-k^2)\exp(-2\beta_0 kd)} \tag{3.6}$$

$$I_{min} \propto \frac{1+\exp(-4\beta_0 kd)-2\exp(-2\beta_0 kd)}{(1+n)^2+k^2+\{(1-n)^2+k^2\}\exp(-4\beta_0 kd)-2(1-n^2-k^2)\exp(-2\beta_0 kd)} \tag{3.7}$$

For $n \gg k$, $k^2 \cong 0$, Eqs. (3.6) and (3.7) are simplified to

$$I_{max} \propto \left\{\frac{1+\exp(-2\beta_0 kd)}{(1+n)+(1-n)\exp(-2\beta_0 kd)}\right\}^2 \tag{3.8}$$

$$I_{min} \propto \left\{\frac{1-\exp(-2\beta_0 kd)}{(1+n)-(1-n)\exp(-2\beta_0 kd)}\right\}^2 \tag{3.9}$$

(iii) Experimental Procedure and Calculation

By moving the reflecting plunger to vary the phase of the reflected radiation relative to the phase of the reference wave, the detected power goes through maxima and minima. For low-loss liquids, the distance between successive minima (or maxima) remains, for all practical purposes, constant and within 0.004% of the true $(1/2)\lambda$.[152] The wavelength of the radiation in the liquid, λ, can thus be determined from the micrometer reading. The accuracy of these measurements can be improved by conventional techniques used in VSWR measurements; the distance between several successive minima is measured and averaged; the location of each minimum is determined more accurately by the use of the double-minimum method. Meanwhile the decibel levels at the maxima and minima are noted, from which the experimental values of the intensity at the detector, I_{expt}, can be calculated. On the other hand, the wavelength of the radiation in the air, λ_o, is measured in a similar manner with the cell empty.

Garg, Kilp and Smyth[152] developed a procedure where $\ln(I_{max}-I_{min})$ for adjacent extrema is plotted against d, to give a straight line of approximate slope $-2\pi k$ which is equivalent to $-\alpha\lambda$. The value of k thus obtained is then used as a first estimate to calculate $\ln(I_{max}-I_{min})$ for different values of d. The value of k is varied in a range about the initial estimate to obtain the best fit with the experimental data.

The dielectric constant ε' and loss ε" are obtained through the relations

$$\varepsilon' = n^2(1-k^2) \qquad (3.11)$$

and

$$\varepsilon'' = 2n^2k \qquad (3.12)$$

Eqs. (3.11) and (3.12) can be approximated respectively as

$$\varepsilon' = n^2 = (\lambda_o/\lambda)^2 \qquad (3.13)$$

and

$$\varepsilon'' = (\varepsilon')^2\alpha\lambda/\pi \qquad (3.14)$$

$$= (\lambda_o^2\alpha)/\pi\lambda \qquad (3.15)$$

These calculations were carried out with an IBM 360/50 computer. The program written in PL/1 language is given in Appendix I.

(2) Measurements in the frequency region 8 to 40 GHz —— Microwave Bridge Method

(i) Apparatus

This technique has been fully described[153, 154] and the errors have been discussed.[155] In this method the output from a signal generator is divided equally into the two arms of a waveguide bridge. One arm contains the dielectric cell and the other contains a calibrated rotary vane attenuator and a phase shifter. The output of the two arms are recombined and their vector sum passed on to a crystal detector connected to a sensitive amplifier and voltmeter. Amplitude and phase balance of the signals in the arms can be achieved so that the detected signal is minimal. The attenuation and phase values for different sample lengths in the specimen cell give the propagation constant and ε' and ε" may be calculated.

The range of frequencies which may be propagated along the waveguides are summarized in Table 3.2. The letter used to designate the band, the actual working frequency, and the possible errors in ε' and ε" are also given.

Table 3.2: Microwave Bridges Employed in this Work.

Letter Characterized Waveband	Waveguide Internal Dimensions (ins.)	Frequency Range (GH_Z)	Working Frequency (GH_Z)	Possible Error in ε'	ε"
Q	0.280X0.140	26.5-40.0	35.11	±0.006	±0.002
K	0.420X0.170	18.0-26.5	23.98	±0.003	±0.002
P	0.622X0.311	12.4-18.0	16.2	±0.005	±0.002
X	0.900X0.400	8.2-12.4	9.313	±0.003	±0.002

A schematic diagram of the bridge apparatus is shown in Fig. 3.3. Monochromatic electromagnetic radiation is generated by a klystron C. The Universal Klystron Power Supply B which incorporates a modulator A also provides a square wave of the reflector voltage at 1 KHz. The resultant amplitude modulation of the microwave signal aids amplification of the output from the crystal detector. The wave is propagated along a rectangular waveguide with the electric field vector oscillating in a direction parallel to the smaller dimension of the waveguide, i.e., the wave is polarized. An isolator D is placed next to the klystron to prevent reflections from entering the klystron and thereby affecting the output frequency. The work-

FIG. 3.3 BLOCK DIAGRAM OF THE BRIDGE APPARATUS

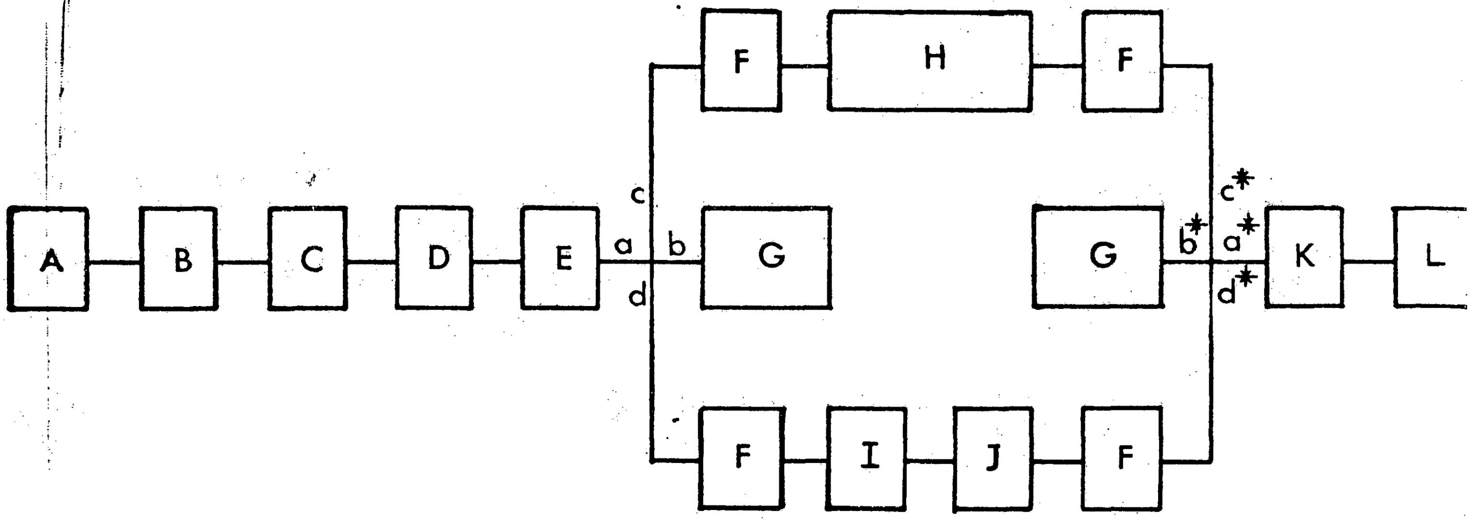
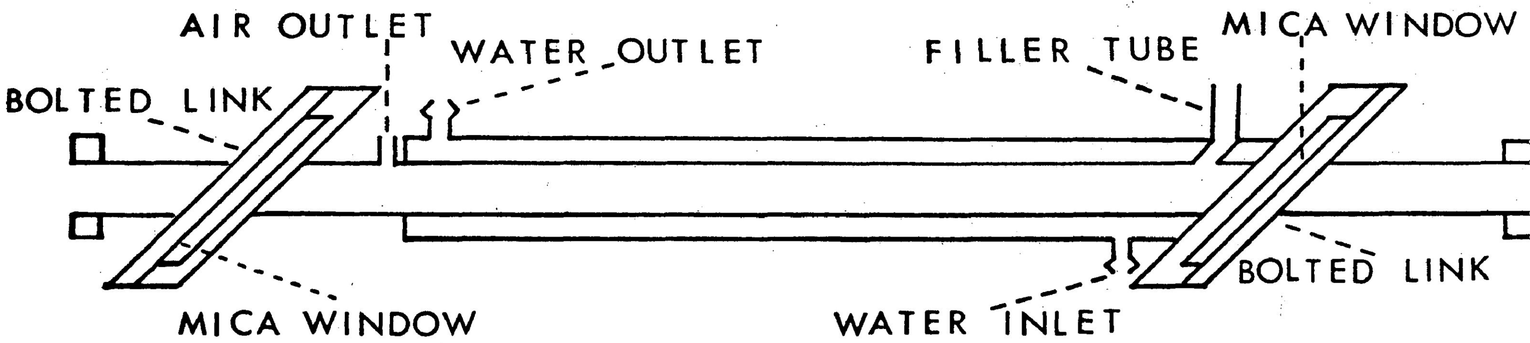


FIG. 3.4 DIAGRAM OF THE CELL



ing frequency for each waveband is checked with the wavemeter E for every run. A magic 'T' splits the output of the signal generator into the two arms of the waveguide bridge. One half passes through the cell H containing the solution and the other half along the arm of the bridge which incorporates the rotary vane attenuator I and phase shifter J. Isolators F, or in some cases attenuators, are placed at the two ends of both arms to prevent reflection of the propagating waves. The waves, which recombine at the second magic 'T', are in antiphase. The field at this point can be reduced to zero by means of the attenuator and phase shifter, i.e. the bridge may be balanced. The signal from the second magic 'T' passes to a crystal detector K and a low noise amplifier and voltmeter L which registers a minimum reading when the bridge is balanced. A matched load G is attached to the arm of each magic 'T' opposite to the arm to the detector in order to absorb the power which passes into this arm when the apparatus is not balanced. At the balance point no power enters G.

The whole circuit is set up on a board inclined at ∿15° to the horizontal. Each bridge is used for a single frequency measurement since the klystrons are only tunable over a small frequency range. In addition, the dimensions of the waveguide are such that only a narrow range of frequency can be accomodated.

The type of cell employed for each bridge is shown in Fig. 3.4. Essentially the cell is a length of waveguide separated from the rest of the apparatus by mica windows. A filler tube is located at the lower end of the cell for Q, K, and P bands, but for X band liquid is added at the top of the cell and some time for drainage is therefore required before a reading is taken. The cell is temperature-controlled by a water jacket which encloses the waveguide. The temperature limits of operation for the technique are dictated by the boiling points of the solvent and the dew point of the air in the cell. The mica windows are inclined $\sim 15^{\circ}$ to the direction of propagation of the wave, i.e. they are horizontal to the bench when the cell is fixed in the circuit. This inclination of the sample surface allows the perpendicular electric field vector to enter gradually into the liquid, hence minimizing reflections. The thickness of the mica windows varies for each band as determined by the criterion of zero reflection.

Water-jacketted burettesare used to add liquid for P and X bands. Q and K bands are filled with 'Agla' micrometer syringes, calibrated in steps of 0.0002 ml, which can also be fitted with a water jacket.

(ii) Theory

Consider a periodic electric field in a medium. The time dependence of the field at any initial point is given by

$$E_1 = E_0 \exp(j\omega t) \qquad (3.16)$$

where $\omega = 2\pi\nu$ is the angular frequency and E_0 is the maximum value of the field intensity, considered for simplicity to occur at $t = 0$.

At a distance x along the direction of propagation of the wave the field intensity has altered to

$$E_2 = E_1 \exp(-\gamma x) \qquad (3.17)$$

where $\gamma = \alpha + j\beta$ is the complex propagation constant of the material. The field strength at the second point is thus given by

$$E_2 = \{ E_o \exp(-\alpha x) \} \exp\{j(\omega t - \beta x)\} \qquad (3.18)$$

The intensity at the second point is reduced by a factor $\exp(-\alpha x)$ and the phase is altered by βx radians. Thus α is the attenuation coefficient and β the phase constant of the material.

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

$$\alpha + j\beta = \frac{2\pi}{\lambda_o}\left(\frac{\lambda_o^2}{4a^2} - (\varepsilon' - j\varepsilon'')\right)^{\frac{1}{2}} \qquad (3.19)$$

where λ_o is the wavelength in cm of the radiation in a vacuum and a is the broader dimension of the cross-section of the waveguide. Separation of Eq. (3.19) into real and imaginary parts gives:

$$\varepsilon' = \frac{\lambda_o^2}{4\pi^2}(\beta^2 - \alpha^2) + \frac{\lambda_o^2}{4a^2} \qquad (3.20)$$

$$\varepsilon'' = \frac{\lambda_o^2}{4\pi^2} (2\alpha\beta) \qquad (3.21)$$

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

(iii) Experimental Procedure and Calculation

The klystron is left to stabilize for an hour before a reading is taken. Enough liquid is added to the cell to cover the window. The attenuation and phase shifter readings required to balance the bridge are then noted. This set of readings serves as the reference starting point with the total volume of liquid and total phase shift regarded as zero. A further volume of liquid is added, sufficient to cause a 360° phase change and again the attenuation and phase shifter readings noted. The volume of liquid required to cause a 360° phase shift varies for different bands. Successive volumes of liquid are added to the cell and balance conditions noted, until the cell is full. By maintaining a constant reading on the phase shifter, attenuation changes introduced by the phase shifter are negligible.

The slope, r, of the graph of attenuation reading against the total volume added is found by the method of least mean squares, assuming that the error lies in the attenuation reading only. The attenuation constant, α, expressed in nepers/cm, is

$$\alpha = \frac{r\ (\mathrm{db/cm^3}) \times \text{Cross-sectional area of waveguide}\ (\mathrm{cm^2})}{8.684} \tag{3.22}$$

Similarly, the slope, s, of the graph of the total phase shift against the total volume added is found. The phase constant, β expressed in radians/cm, is given by

$$\beta = \frac{s\ (\mathrm{deg/cm^3}) \times \text{Cross-sectional area of waveguide}\ (\mathrm{cm^2})}{57.29} + \frac{2\pi}{\lambda_g} \tag{3.23}$$

Here λ_g is the wavelength of the radiation in the waveguide, the term $2\pi/\lambda_g$ being necessary to allow for the phase shift incurred by a wave travelling in air.

Since the cross-sectional area of waveguide and the term $2\pi/\lambda_g$ differ for different wavebands, Eqs. (3.22) and (3.23) can be written in the forms of

$$\alpha = a_1 r \tag{3.24}$$

$$\beta = a_2 s + a_3 \tag{3.25}$$

The values of a_1, a_2 and a_3 are characteristic constants for each waveband over a small temperature range.

With α and β determined, the dielectric constant and the loss factor can then be evaluated from Eqs. (3.20) and (3.21). The whole process of calculation is done by an IBM 360/50 computer. The program written in PL/1 language is given in Appendix I.

(3) Measurements in the frequency region 0.9 to 2.5 GHz —— Grant Cell Method

(i) Apparatus

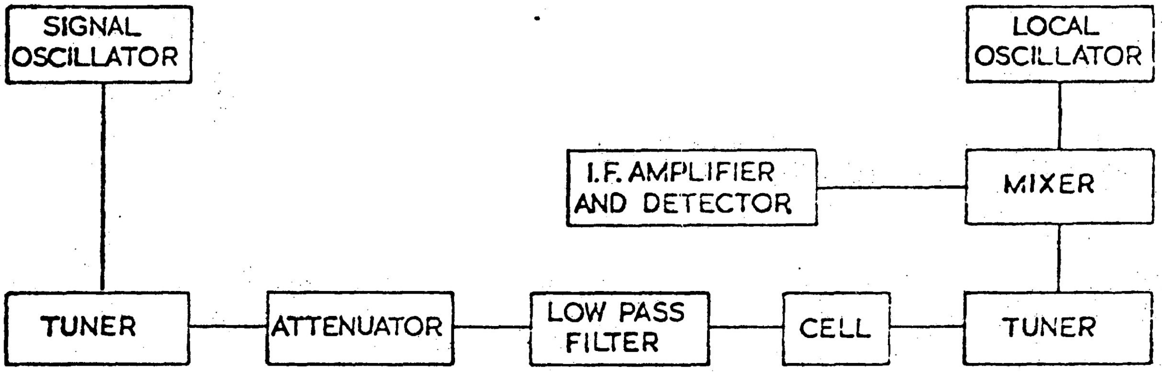
At frequencies less than 9 GHz the bridge technique becomes impractical because of the large amount of solution required for 360^0 phase shifts. An adaption of a coaxial-line technique proposed by Grant and his co-workers[156 - 158] has been found to be suitable for dilute solutions. Apart from using less than 50 ml of solution, depending on the size of the cell, this method has the advantage that measurements may be done at a number of frequencies (between 0.9 to 2.5 GHz) and temperatures without removing the sample. A further advantage of this technique is that the electric field vecotr is sampled within the liquid under investigation and thus, difficulties which arise from reflections from the air-liquid interface are not encountered.

A schematic diagram of the apparatus is shown in Fig. 3.5(a). Radiation from a signal generator enters the cell containing the specimen solution, and is reflected from a silver short circuiting plate at the opposite end. The electric vector of the resulting standing wave pattern is sampled by a probe which projects from the inner conductor of the coaxial cell. The output is mixed with the signal from a local oscillator tuned to a frequency 30 MHz away from the input signal. The resulting beat frequency is fed into an intermediate frequency amplifier which has a calibrated db scale that allows the power level to be determined at the probe position within the liquid.

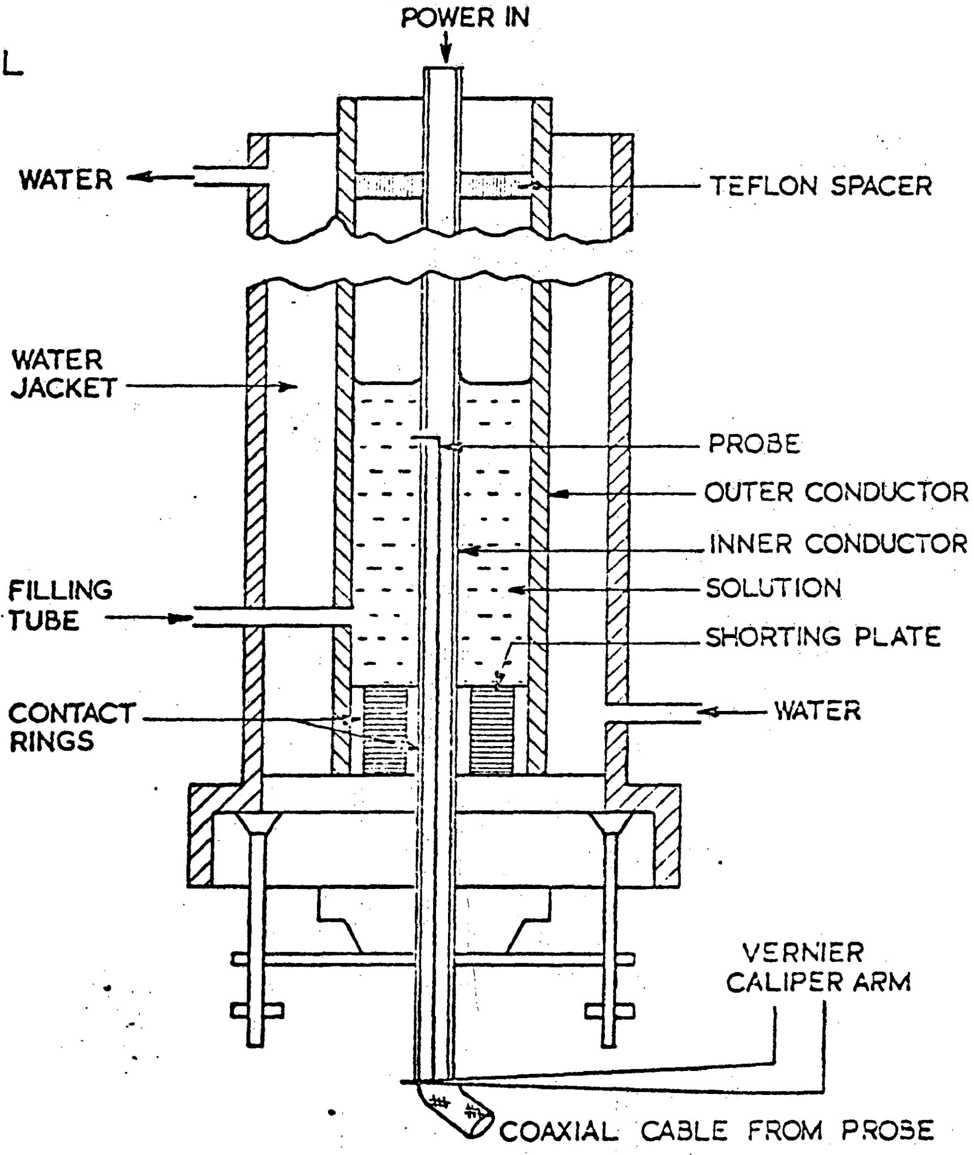
The frequency of the input radiation is checked using a Rohde and Schwarz U.H.F. Resonance Frequency meter type WAL.BH 4321/2 and to prevent pulling of this oscillator a pad attenuator was employed. Harmonics generated by the source are eliminated by low pass filters, covering the appropriate measuring frequency range, inserted in the line between the oscillator and the cell. Tuners are used in the line between the cell and the mixer, to match the impedances of the circuit components. All connectors between

FIG.3.5 THE COAXIAL LINE APPARATUS

(a.) SCHEMATIC DIAGRAM



(b.) CELL



components are of the locking type (General Radio Type QBL) to reduce reflections in the line and avoid any stray electromagnetic fields. The major components of the circuit are listed in Table 3.3.

Table 3.3. Grant Cell Components

Component	Frequency Range (GHz)	Supplier	Model
Oscillators	2.5 - 0.5	Rohde and Schwarz	SLRD
	2.0 - 0.9	General Radio	1218B
Tuners	2.0 - 0.9	General Radio	874LTL
		Microlab	S305N
Low-pass filters	<0.5, <1.0	General Radio	874L
	<2.0, <4.0	General Radio	874L
Cell		Lakehead University	
Mixer	2.5 - 0.5	General Radio	MRAL
I.F. Amplifier and Meter	30	General Radio	1236

The cell itself is essentially a length of coaxial line terminated by a short circuit, (Fig. 3.5(b)). The coaxial line consists of an outer conductor (i.d. 14.3 mm) and an inner conductor (o.d. 4.1 mm). To ensure good electrical contact all three components were made out of silver and to further increase the contact, serrated silver collars were inserted between both conductors and the short circuit. The center conductor passes through a telescopic tube, ensuring axial movement along the cell, which is supported by two machined teflon plugs and is connected to the center contact of the input locking connector.

The probe emerges through a small opening in the tubular center conductor, sealed in it by a plug of polyethylene which prevents any solution entering the tube. Its position within the cell is determined by a vernier calliper (or a micrometer measuring device), accurate to within 0.02 mm. The specimen solution is introduced to the space between the outer and inner conductors by a small tube at the base of the cell. A water jacket enables thermostating by the usual means.

(ii) Theory

As discussed earlier, the change in the field strength of a wave on travelling a distance x is given by Eq. (3.18) which can be rewritten as

$$E_2 = \{E_o \exp(-\alpha x)\}\{\cos(\omega t-\beta x)+j\sin(\omega t-\beta x)\} \tag{3.26}$$

A standing wave is created by the short circuit reflecting the incident radiation back towards the source, the field strength of which is given by

$$E = E_o \exp(j\omega t)\{\exp(\gamma x)-\exp(-\gamma x)\} \tag{3.27}$$

since the two combining waves are travelling in opposite directions (+x and -x). From this equaiton it can be shown[156] that the field strength at a distance x cm from the short circuit is

$$E = E_o\{2(\cosh 2\alpha x - \cos 2\beta x)\}^{\frac{1}{2}} \tag{3.28}$$

By differentiating this and solving for the positions of the maxima and minima of the standing wave, the values of x at which they occur are given by:

$$2\beta x_n = n\pi + (-1)^n \sin^{-1}\{-(\alpha/\beta)\sinh 2\alpha x_n\} \qquad (3.29)$$

where n is an integer, odd for the maxima and even for the minima.[158]

Low loss liquids have been defined as possessing an attenuation constant which is very much less than its phase constant, i.e., $\alpha << \beta$, therefore,

$$\beta = n\pi/2x_n \qquad (3.30)$$

which is actually equivalent to $2\pi/\lambda$ as usually defined since

$$\begin{aligned} \lambda &= \text{wavelength of the radiation in the liquid} \\ &= 2(x'_n - x'_{n-1}) \qquad (3.31) \\ &= 2x_2 \qquad (3.32) \end{aligned}$$

where x_2 is the position of the first minimum from the short circuit, and (x')'s may be the relative positions given by the vernier reading.

The standing wave ratio, defined as

$$r = \frac{\text{Amplitude of minimum}}{\text{Amplitude of maximum}}$$

may be obtained from Eq. (3.28)

$$r = \frac{E_{min}}{E_{max}} = \frac{(\cosh 2\alpha x_2 - \cos 2\beta x_2)^{\frac{1}{2}}}{(\cosh 2\alpha x_1 - \cos 2\beta x_1)^{\frac{1}{2}}} \qquad (3.33)$$

For medium and low loss liquids when $\alpha^2 << \beta^2$ and $\cosh\alpha x_1 \simeq 1$, Eq. (3.33) can be simplified[156] to give

$$r \simeq \frac{\sinh\alpha x_2}{\cosh\alpha x_1} \simeq \sinh\alpha x_2 \qquad (3.34)$$

For coaxially propagated waves α and β are related to ε' and ε'' by

$$\varepsilon' = (\beta^2-\alpha^2)\frac{\lambda_o^2}{4\pi^2} \qquad (3.35)$$

and

$$\varepsilon'' = (\alpha\beta)\frac{\lambda_o^2}{2\pi^2} \qquad (3.36)$$

The correction for cut-off wavelength in calculating ε' is not applicable in this case (c.f. Eqs. (2.8) and (2.9)).

Grant and his co-workers deduced much of the above theory on the assumption that the circuit was perfectly reflecting and that the probe had no perturbing effect on the field. They found that errors in α resulted if these two conditions were not fulfilled. Cooke[159] in this laboratory tested the efficiency of the short circuit and the suitability of the probe using acetone and found that the cell was satisfactory up to a frequency of 2.5 GHz.

(iii) Experimental Procedure and Calculations

The standing wave ratio, r, was determined by the half-minimum method.[160, 161] The positions of the minima in the liquid were measured by taking the vernier (or micrometer) reading 3 db either side of the minimum; the minimum position being midway between the two points. The wavelength in the medium, λ, was determined by Eq. (3.31). At both vernier readings on either side of a minimum, the output was twice the minimum value. Consequently, the distance, Y, which separates the two points, could be used to obtain the standing wave ratio from

$$r = \frac{\sin(\pi Y/\lambda)}{\{2 - \cos^2(\pi Y/\lambda)\}^{\frac{1}{2}}} \qquad (3.37)$$

The position of the short circuit was given by

$$s = x_n' - (n\lambda/2) \qquad (3.38)$$

from which the exact positions of the minima from the short circuit could then be found. Eq. (3.34) therefore yielded α as

$$\alpha = \frac{1}{x_n} \sinh^{-1} r \qquad (n = \text{even integer}) \qquad (3.39)$$

α was determined for successive minima and averaged.

Evaluation of ε' and ε'' from Eqs. (3.35) and (3.36) was done by using an IBM 360/50 computer with the PL/1 program given in Appendix I.

(4) Static dielectric constant

Static dielectric constants were measured at 2 MHz using a Wiss-Tech-Werkstatten dipolmeter Type DM01. Cyclohexane and p-xylene were used as calibrating liquids, and the calibration was repeated for every set of measurements. The ε_o values were reproducible to ±0.002.

(5) Refractive index

Refractive indices were measured using an Abbe refractometer Type 58273, manufactured by Carl Zeiss, at the frequency of the sodium D line.

3.2 Treatment of Data

(1) Solvent corrections

In the frequency range of both the bridge and interferometer methods, some nonpolar solvents show small but detectable dielectric absorptions. The ε' and ε'' values for the solutions were corrected according to:

ε' correction factor, $(\varepsilon'_{corr}) = \varepsilon_o(\text{solvent}) - \varepsilon'(\text{solvent})$

and ε'' correction factor, $(\varepsilon''_{corr}) = \varepsilon''(\text{solvent})$

and the true ε' and ε'' values for solution were obtained from

$$\varepsilon'_{true} = \varepsilon'_{measured} + \varepsilon'_{corr} \qquad (3.40)$$

$$\varepsilon''_{true} = \varepsilon''_{measured} - \varepsilon''_{corr} \qquad (3.41)$$

(2) Analysis for τ_0, α and ε_∞

The ε' and ε'' values at each frequency and the ε_0 value were fed into an IBM 360 computer programmed to solve the Cole-Cole equations for τ_0, α and ε_∞. The program, and the one used for τ_1, τ_2, C_1 analyses, was originally compiled in Autocode for an Elliot 803 computer by M.D. Magee[155] and R.B. Dagnall of Aston University. At Lakehead these programs were rewritten by P.F. Mountain[162] in this Laboratory in PL/1 language for an IBM 360 computer using the same subroutine format with minor changes required for the more sophisticated computer. Later, they were translated by D. Watson of the Lakehead Computer Center from PL/1 language into APL language so that the analyses could be manipulated through a more convenient typewritter-form terminal. The programs in both languages are shown in Appendix I.

Initial estimates of τ_0, α and ε_∞ are inserted into the appropriate equations and values of ε' and ε'' are calculated and compared with the observed values by use of a function A, where

$$A = \Sigma\ (\varepsilon''_{obs} - \varepsilon''_{calc})^2 + \Sigma\ \{(\varepsilon'_{obs} - \varepsilon'_{calc})/n\}^2 \qquad (3.42)$$

the second term containing a scaling factor n chosen to reduce the errors in ε' to about the same magnitude as those in ε''. Generally n = 4 has been chosen for data at all frequencies used. The computer takes each variable parameter in turn and augments it by given step-sizes so that A is reduced. The variables have upper and lower limits within which the computer works. The step sizes are reduced until two complete cycles fail to improve A, then the final values of the variables and the dielectric constant and loss at each frequency are recorded together with the final function value of A. The size of A indicates how well the final analysis fit the experimental points. For reliable results no less than four points (excluding ε_0) are required.

(3) Analysis for τ_1, τ_2 and C_1

The computer analysis for τ_1, τ_2 and C_1 requires the same input data as in (2) with the exclusion of the solvent dielectric constant and the inclusion of ε_∞, together with the expected limits of the relaxation times. The analysis is repeated with different ε_∞ values.

(4) Analysis in terms of two limiting values

The experimental ε' and ε'' values are analysed by the computer method for τ_0, α and ε_∞. An iteration is then carried out, by the computer, to obtain the best A value for α from Eq. 2.21; the first approximation of A is provided by Eq. 2.25 The computer program, written in APL language, is given in Appendix I.

(5) Dipole moment

The Onsager equation (Eq. 2.4) may be rewritten to give the Dipole moment of a polar solute as

$$\mu = 0.22119 \left\{ \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0 \ (\varepsilon_\infty + 2)} V \right\}^{\frac{1}{2}} \text{ Debye} \qquad (3.43)$$

where V is the volume of solution in ml. per unit mole of solute. V may be approximately expressed as

$$V = \frac{f_1M_1 + f_2M_2}{f_2(f_1d_1 + f_2d_2)}$$

where M is the gram molecular weight, d the density (gm/ml) and f the mole fraction. The subscripts 1 and 2 refer to the solvent and solute respectively.

(6) Miscellaneous

The experimental and calculated ε' and ε'' values are listed in Appendix (II). Relevant analyses are shown in the discussion sections of Chapters 4 and 5.

3.3 Materials

Cyclohexane, p-dioxane and p-xylene were refluxed over sodium (24 hours for p-dioxane) and distilled through a two foot column packed with glass rings. They were stored in well closed amber bottles over sodium wire. The purity of p-dioxane was checked periodically by dielectric constant measurements.

All the solutes were obtained from commercial sources as listed, Table 3.4. Liquids were dried over suitable drying agents and distilled under vacuum. Solids were recrystallized from suitable solvents and dried over phosphorus pentoxide under vacuum.

Table 3.4. Sources of Solutes

	Chemical	Source
(1)	Amines	
	n-Butyl	K & K Labs.
	n-Hexyl	-do-
	n-Nonyl	-do-
	2-Nonyl	-do-
	5-Nonyl	-do-
	n-Decyl	K & K Labs. and Aldrich Chemical Co.
	n-Undecyl	Aldrich Chemical Co.
	N-Methyl-n-octyl	K & K Labs.
	N,N-Dimethyl-n-octyl	-do-
	N,N-Diethyl-n-octyl	-do-
(2)	α,ω-Diaminoalkanes	
	1,4-Diaminobutane	K & K Labs.
	1,6-Diaminohexane	-do-
	1,9-Diaminononane	-do-
(3)	Bromoalkanes	
	n-Bromooctane	Eastman Organic Chemicals.
	n-Bromodecane	Baker Chemical Co.
	n-Bromododecane	-do-
	n-Bromohexadecane	-do-
	n-Bromooctadecane	-do-
	2-Bromooctane	K & K Labs.
	4-Bromooctane	-do-
	1,10-Dibromodecane	Baker Chemical Co.

Chapter IV. Dielectric Relaxation of Aliphatic Bromides in Cyclohexane

4.1 Introduction

The dielectric absorptions of some pure liquid alkyl halides have been represented by Cole-Cole semi-circular arc plots. The relaxation parameters together with the limiting relaxation time values τ_U (upper limit) and τ_L (lower limit) calculated from τ_o and α values are listed in Table 4.1.[101]
A few investigations have been reported for alkyl bromides in dilute solutions,[114, 116] which also show a Cole-Cole distribution of relaxation times (Table 4.2). The study of intramolecular motions in polar molecules is probably best examined in dilute solution in non-polar solvents where the complicating viscosity, internal field and dipole interaction factors are minimized or are reasonably constant.

Price[113] reported measurements on several α, ω-dibromoalkanes at 1 — 8 GHz (Table 4.3), and found that the high-frequency intercept (ε_∞) of the Cole-Cole plot was significantly greater than the square of the refractive index (n_D^2). Garg and Smyth[163] measured 1,4- and 1,6-dibromoalkanes as the pure liquids at 2- and 4- mm wavelength, and found ε_∞ to be only slightly greater than n_D^2. They indicated that the distribution function proposed by Higasi et. al.[101] and Vaughan et. al.[102] fails for α, ω-dibromoalkanes.

Recently, Chandra and Prakash[108] reported measurements in the frequency range 2 — 37 GHz on the α, ω-dibromo derivatives

Table 4.1. Relaxation Parameters for the n-Alkyl Bromides, $C_nH_{2n+1}Br$, at 25°C. (from ref.101)*

n	α	τ_0(ps)	τ_L (ps)	τ_U (ps)
2	0.055	3.8	1.8 (1.8)	8.0 (8.0)
3	0.087	5.8	2.2 (2.2)	15.2 (15.3)
4	0.098	8.7	3.1 (3.1)	24.6 (24.6)
5	0.143	12.1	3.3 (3.3)	44.5 (44.6)
6	0.172	15.7	3.6 (3.6)	67.8 (68.3)
7	0.204	19.2	3.7 (3.7)	99.8 (99.9)
8	0.226	21.8	3.7 (3.7)	128 (128)
9	0.243	28.5	4.3 (4.4)	187 (184)
10	0.251	33.7	4.9 (5.0)	231 (229)
12	0.259	48.9	6.9 (6.9)	348 (347)
14	0.270	53.8	7.0 (7.1)	413 (408)
16	0.287	69.6	8.1 (8.3)	597 (586)

---

* τ_L and τ_U values in brackets are calculated with Program # 8 in Appendix I .

Table 4.2. Relaxation Parameters for two Alkyl Bromides in Dilute Solutions. (from ref.114)

SOLUTE	SOLVENT	t $^{\circ}$C	η(SOLVENT) (mps)	λ_m (cm)	τ_0^* (ps)	α (π/2 rad.)
Ethyl bromide	n-heptane	20	4.16	0.3	1.59	0.1
	benzene	20	6.47	0.6	3.18	0.2
	cyclohexane	20	9.7	0.4	2.12	0.2
	n-hexadecane	20	36	0.4	2.12	0.2
n-Octyl bromide	n-heptane	20	4.16	2.07	10.98	0.24
		25**	(f_2**=0.032)		11.2	0.16
			=0.053)		12.7	0.28
			=0.076)		12.7	0.19
			=0.112)		12.7	0.19
	cyclohexane	20	9.7	3.14	16.66	0.29
	n-hexadecane	20	36	3.64	19.31	0.30

* Calculated from $\tau_0 = \lambda_m / 2\pi C$, $C = 3 \times 10^{10}$ cm/sec.

** Data from Johari et.al. (ref. 116) ; f_2 refers to mole fraction of solute.

Table 4.3. Dielectric Properties of Three α,ω-Dibromoalkanes (from ref.113).

SUBSTANCE	t °C	η (cps)	τ_0^*(ps)	ϵ_∞	n_D^2
1,4-Dibromobutane	0		38	3.38	
	18.5	2.88	30	3.54	2.31
	34.5	2.13	22	3.07	2.28
1,6-Dibromohexane	0		48	2.77	
	19.0	4.13	34	3.03	2.27
	41.8	2.57	27	3.13	2.24
1,8-Dibromooctane	20.0	6.01	45	2.90	2.24
	31.5	4.25	37	2.84	2.23
	44.0	2.23	32	2.78	2.21

* Analyzed by means of Fuoss-Kirkwood equation (R.M.Fuoss and J.G.Kirkwood, J. Am. Chem. Soc., 63 , 385 (1941))

of propane, butane, pentane and hexane as the pure liquids at 30 — 60^{o}C and in benzene solution at 35^{o}C. They represented their data by a skewed-arc function and presented analyses in terms of (i) the Cole-Davidson distribution function and (ii) the Budó distribution function (Table 4.4). They considered the former to be the result of intramolecular co-operative relaxations in which reorientation of one segment triggers many other segmental reorientations and consequently the rotating group does not relax independently. The Budo distribution function was attributed to two non-interacting Debye-type absorptions, one for the terminal -CH_2Br group rotation and the other for the rotation of the whole molecule.

4.2 Results

The experimental dielectric constant and loss values for cyclohexane solutions ($f_2 \sim 0.07$) of 1-bromooctane, 2-bromooctane, 4-bromooctane, 1-bromodecane, 1-bromododecane, 1-bromohexadecane, 1-bromooctadecane and 1, 10-dibromodecane are presented as Cole-Cole plots in Fig. 4.1. In all cases it is possible to draw depressed center semicircular arcs through most of the experimental points. The data, for all systems, were analyzed in terms of a mean relaxation time (τ_o), a Cole-Cole distribution parameter (α) and a high frequency dielectric constant (ε_∞). The agreement between the experimental ε' and ε'' values and those calculated from the computer analyses is quite good over the whole range of frequencies. The experimental and calculated values of

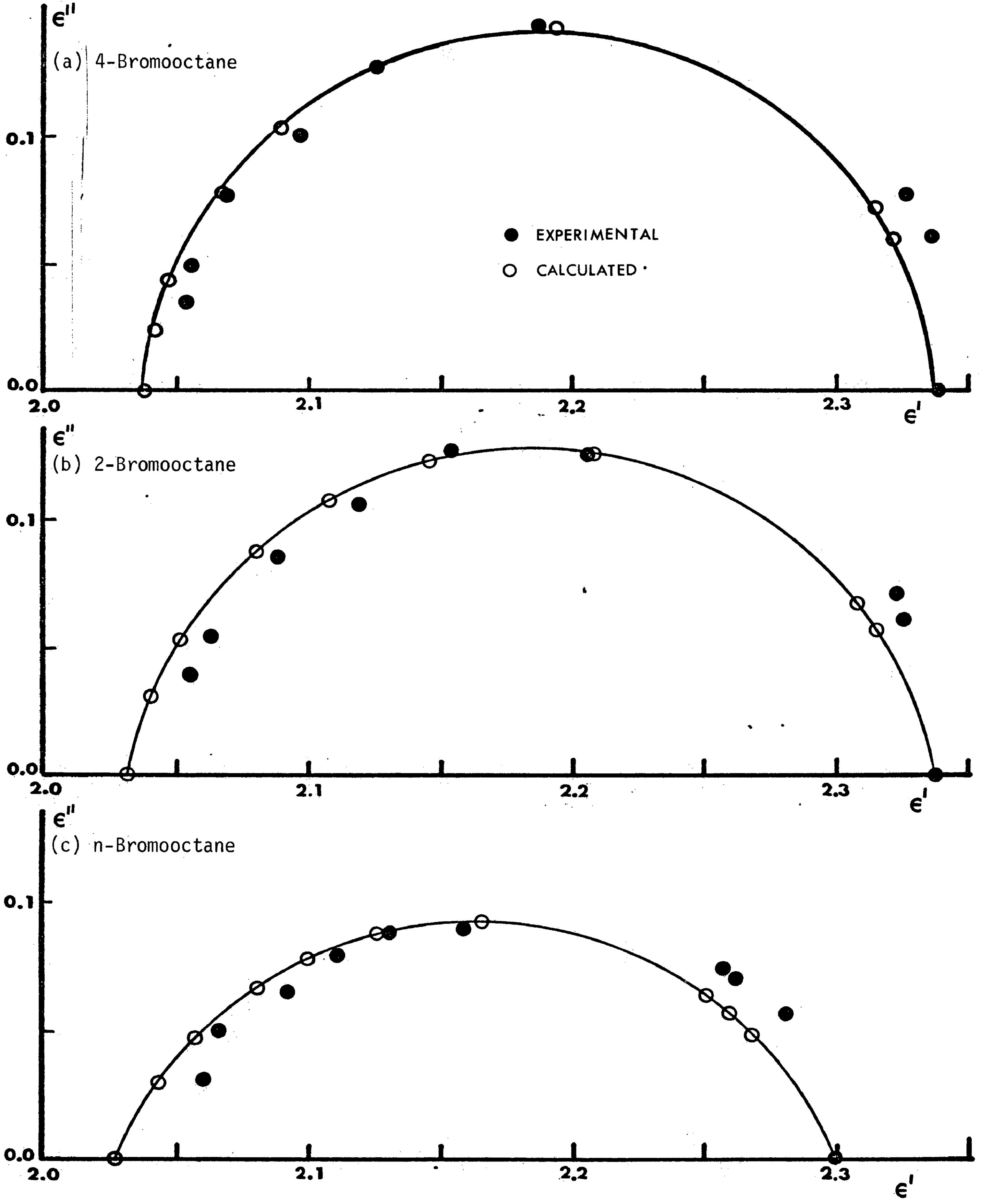
Table 4.4. Dielectric Relaxation Parameters of Four α,ω-Dibromoalkanes as Pure Liquids and in Benzene Solutions at 35°C. (from ref. 108).

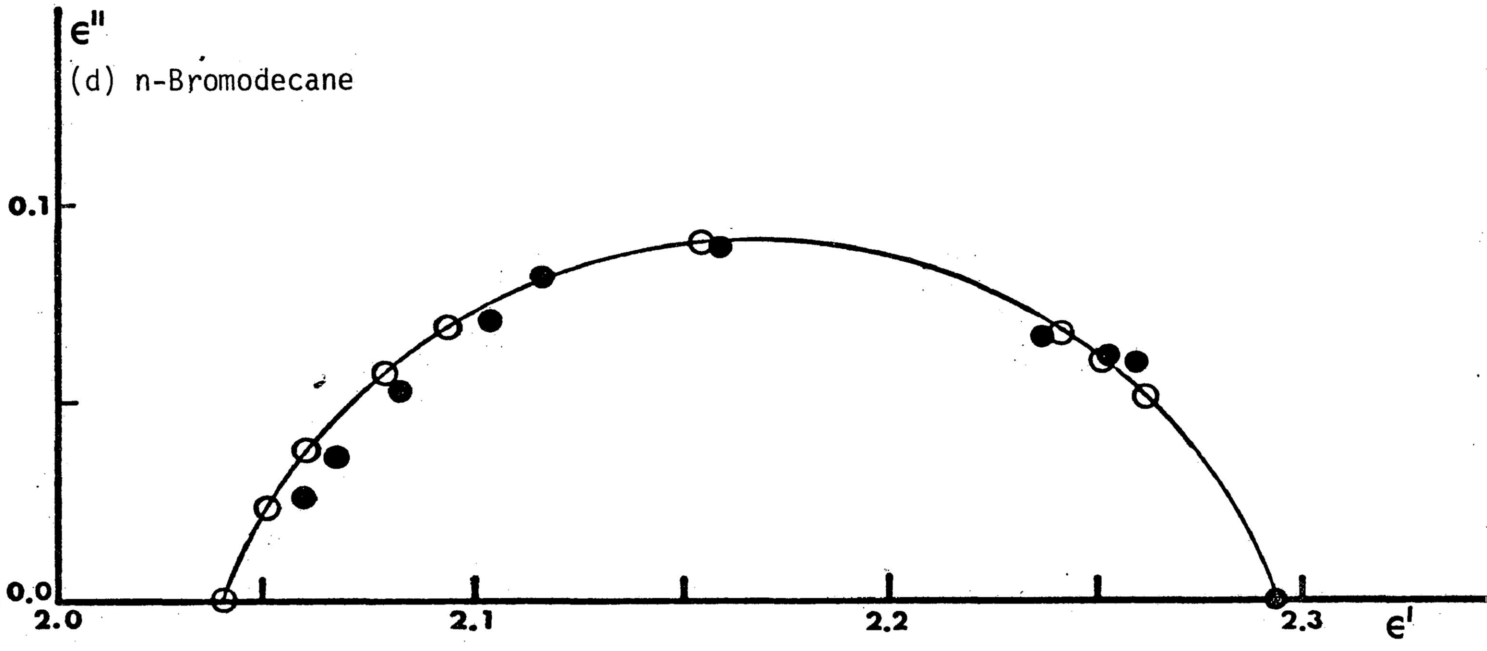
SUBSTANCE	STATE**	$\eta_{t^\circ C}$ (cps)	COLE-DAVIDSON DISTRIBUTION β	COLE-DAVIDSON DISTRIBUTION τ_c(ps)	BUDŌ DISTRIBUTION τ_1(ps)	BUDŌ DISTRIBUTION τ_2(ps)	BUDŌ DISTRIBUTION C_1
1,3-Dibromopropane	L	1.6_{30}	0.57	20.7	12.9	2.5*	0.72
	B		0.73	7.3	6.4	2.8	
1,4-Dibromobutane	L	2.2_{30}	0.55	33.0	22.2	2.5*	0.78
	B		0.67	12.3	9.1	3.1	
1,5-Dibromopentane	L	2.6_{30}	0.54	37.5	23.0	2.5*	0.82
	B		0.63	15.0	11.2	2.8	
1,6-Dibromohexane	L	3.0_{30}	0.53	47.4	26.4	2.5*	0.84
	B		0.59	20.7	14.4	3.2	

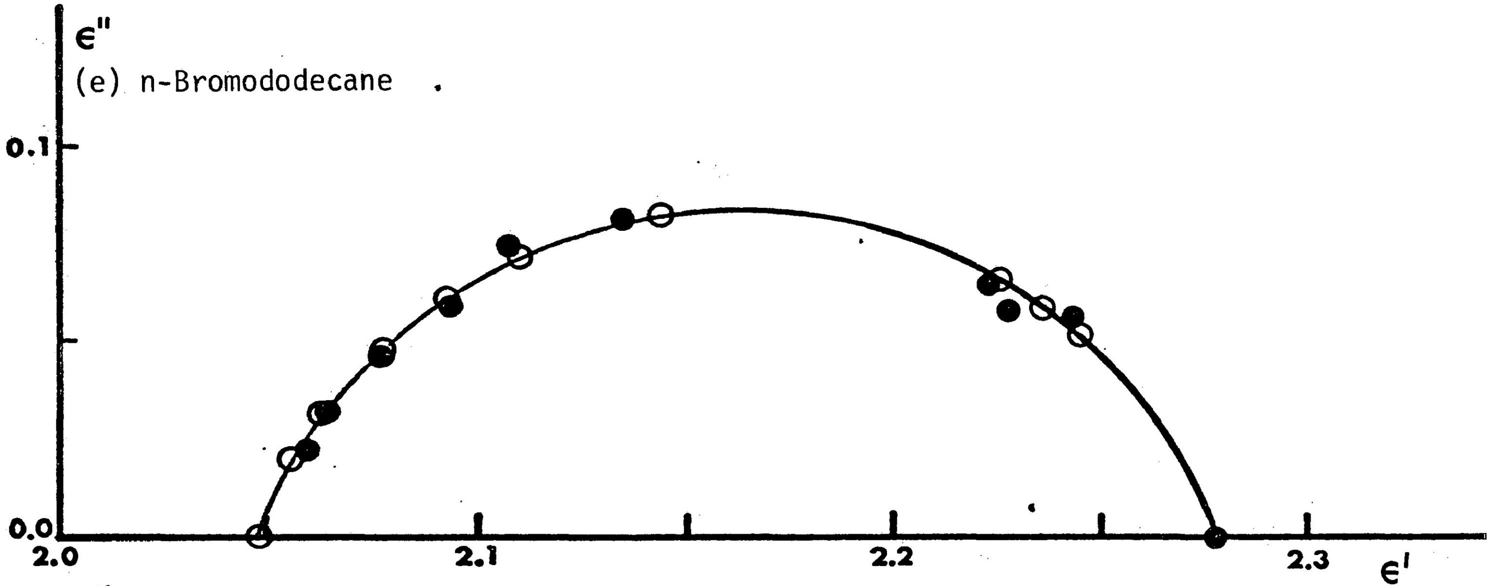
** L and B refer to pure liquid and benzene solution respectively.

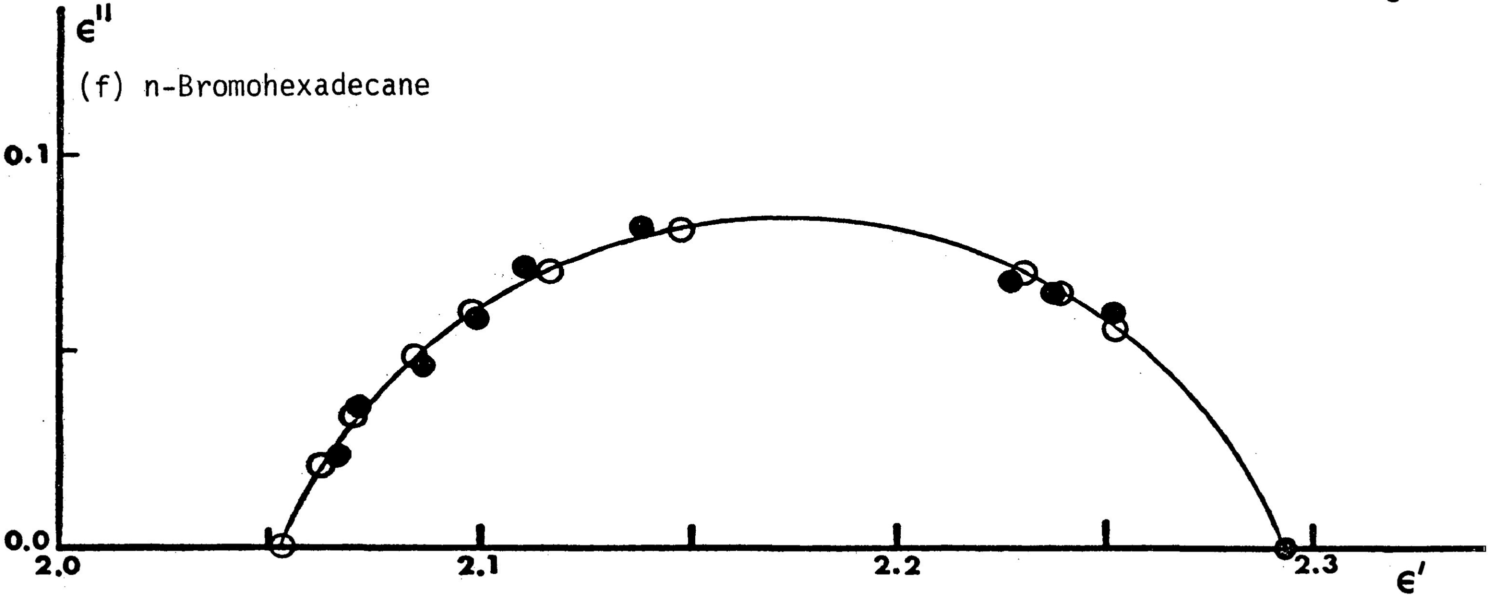
* Average value.

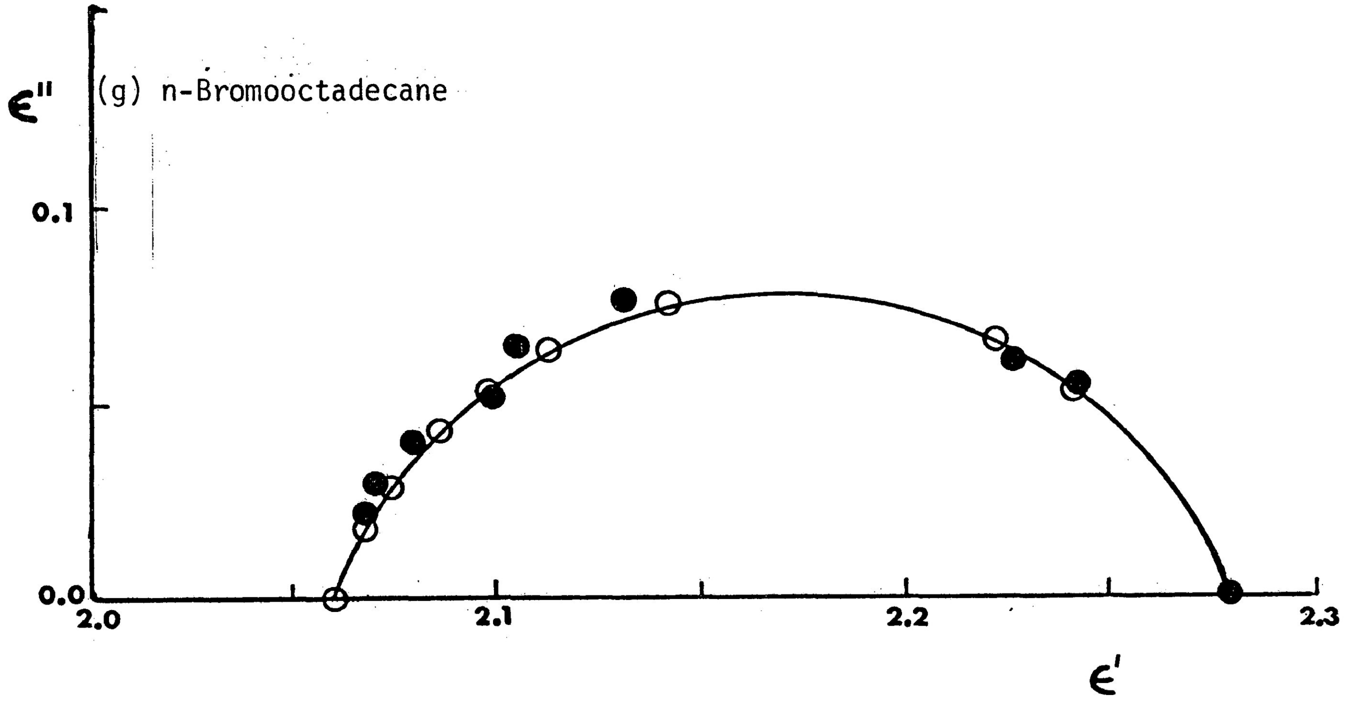
FIGURE 4.1


ε''
(a) 4-Bromooctane
0.1
0.0
2.0
2.1
2.2
2.3
ε'
● EXPERIMENTAL
○ CALCULATED
ε''
(b) 2-Bromooctane
0.1
0.0
2.0
2.1
2.2
2.3
ε'
ε''
(c) n-Bromooctane
0.1
0.0
2.0
2.1
2.2
2.3
ε'

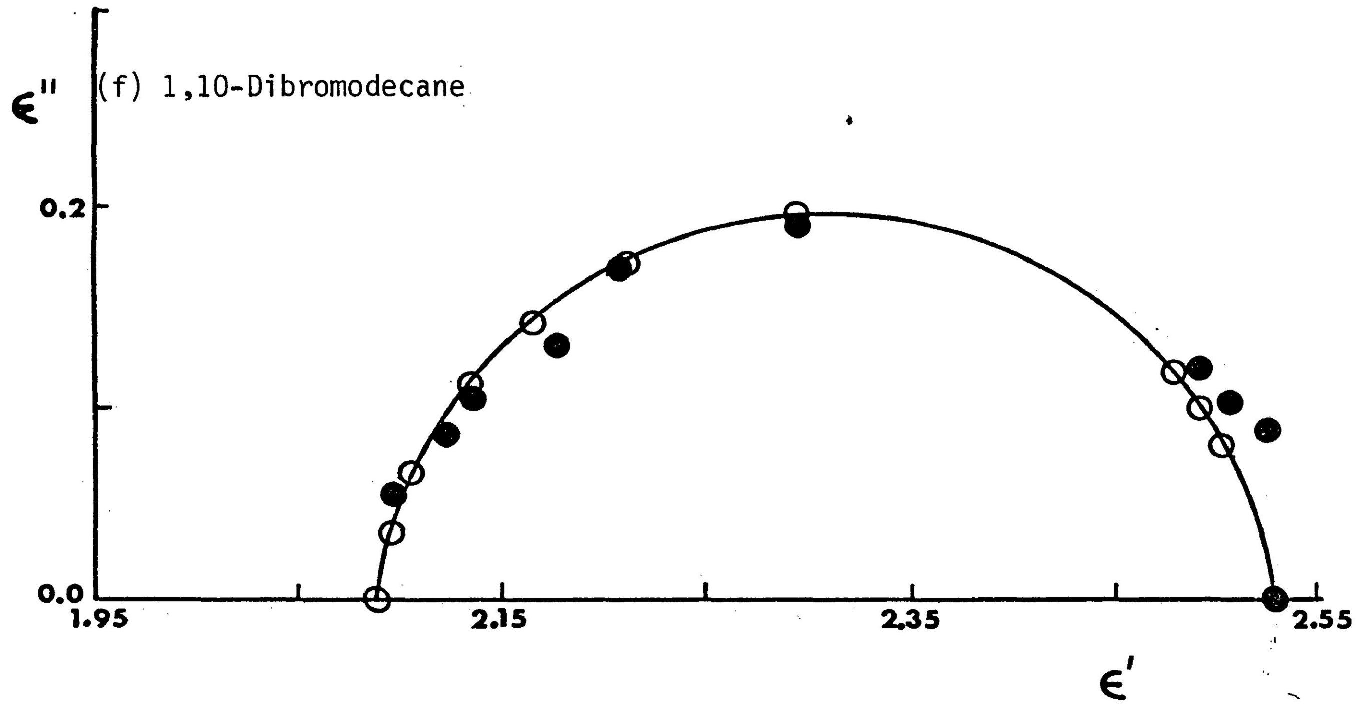

ε''
(d) n-Bromodecane
0.1
0.0
2.0
2.1
2.2
2.3
ε'


ε''
(e) n-Bromododecane
0.1
0.0
2.0
2.1
2.2
2.3
ε'


ε''
(f) n-Bromohexadecane
0.1
0.0
2.0
2.1
2.2
2.3
ε'



(g) n-Bromooctadecane
ε''
0.1
0.0
2.0
2.1
2.2
2.3
ε'



(f) 1,10-Dibromodecane
ε''
0.2
0.0
1.95
2.15
2.35
2.55
ε'

ε' and ε'' are listed in Appendix II. As mentioned, previous workers have represented the dielectric dispersions of bromoalkanes[104] as pure liquids and α, ω-dibromoalkanes[108] in benzene solution with a Cole-Davidson skewed-arc function. However, in the present work, the ε_∞ values are close to n_D^2 and there is no indication of skewed-arc behavior. The values of τ_o, α, ε_∞, n_D^2 and the dipole moments, μ, calculated from Eq. (3.43) are listed in Table 4.5. The μ values obtained by conventional methods[2, 164] are included for comparison.

4.3 Discussion

Crossley[165] has measured a number of aliphatic ketones in cyclohexane solution at up to nine frequencies between 1.5 and 145 GHz at 25°C. The results, Table 4.6, indicate that rotation of the polar end group is the dominant mechanism of dipole reorientation except when the dipole is located away from the chain end in the longer molecules. The τ_o values for the bromoalkanes in Table 4.5 are considerably longer than those for analogous ketones, and are also longer than the τ_L values which have been attributed to $-CH_2Br$ group rotation in pure liquid bromoalkanes (Table 4.1). However, for the longer bromoalkanes τ_o shows only a slight increase with increased molecular size which suggests that while rotation of the terminal $-CH_2Br$ group is not the dominant mechanism of dipole reorientation, the contribution from intramolecular rotation, especially for the larger bromoalkanes, is not negligible.

Table 4.5. The Dielectric Relaxation Parameters, ε_∞ , n_D^2 , and Dipole Moments for Bromoalkanes and 1,10-Dibromodecane at Mole Fraction f_2 in Cyclohexane Solution at 25°C.

SUBSTANCE	f_2	τ_0 (ps)	α	ε_∞	n_D^2	μ(expt) (D)	μ(lit) t°C(*) (D)
1-Bromooctane	0.07075	16.2	0.24	2.0270	2.0335	1.96	1.96 25(H)
2-Bromooctane	0.06969	13.8	0.11	2.0323	2.0335	2.08	† 2.07 20(C)
4-Bromooctane	0.06999	16.3	0.04	2.0382	2.0321	2.06	
1-Bromodecane	0.07034	20.0	0.21	2.0395	2.0355	1.92	1.90 25(L)
1-Bromododecane	0.06976	23.1	0.21	2.0461	2.0386	1.86	1.89 25(L)
1-Bromohexadecane	0.06979	25.5	0.24	2.0513	2.0458	1.95	1.87 25(L)
1-Bromooctadecane	0.07007	26.6	0.22	2.0573	2.0475	1.87	†† 1.94 20(B)
1,10-Dibromodecane	0.06998	18.7	0.08	2.0930	2.0512	2.68	2.54 45(L) 2.55 25(B) 2.69** (F)

(Unless otherwise stated the μ(lit) values are cited from ref. 164.)

* L, B, C, H, and F refer to pure liquids, solutions in benzene, carbon tetrachloride, n-heptane and hypothetical state of free rotation respectively.

** Datum cited from ref. 2.

† Datum for the iodo analog.

†† Datum for the chloro analog.

Table 4.6. Relaxation Times (ps), Distribution Parameters, High Frequency Dielectric Constants and Dipole Moments (in D units) for Ketones at Mole Fraction f_2 in Cyclohexane Solution at 25°C. (from ref. 165).

KETONE	f_2	τ_0	α	ε_∞	μ
2-Hexanone	0.02409	4.0	0.04	2.032	2.62
2-Nonanone	0.02618	5.9	0.14	2.023	2.73
3-Nonanone	0.02662	6.5	0.08	2.033	2.60
4-Nonanone	0.02995	8.1	0.03	2.041	2.52
5-Nonanone	0.03147	7.2	0.06	2.029	2.63
2-Decanone	0.02749	6.7	0.08	2.041	2.55
4-Decanone	0.02348	8.3	0.00	2.040	2.49
2-Pentadecanone	0.02765	6.8	0.15	2.029	2.51
4-Pentadecanone	0.02679	11.0	0.17	2.029	2.57
8-Pentadecanone	0.02914	17.1	0.13	2.031	2.57
2-Nonadecanone	0.02550	8.3	0.18	2.032	2.61
10-Nonadecanone	0.02664	22.0	0.15	2.031	2.58

Table 4.7 lists the measured values for energy barriers to internal rotation of several representative substances.[167 - 169] The values reported for ethane are uncertain. The near constancy of the barrier in such series as CH_3CX_3 and CH_3COX, where X may be H, F, Cl, Br or I, indicates that electrostatic or steric effects of the conventional kind such as those due to van der Waals forces do not seem to affect the barrier height appreciably. There is, however, a systematic change of barrier height with the symmetry properties of the bond under consideration. Molecules with an sp^2 hybridized carbon (planar) attached to a methyl group have lower barriers than those with an sp^3(tetrahedral) carbon.[170] Consequently, in constrast to the ketones, the potential barrier to rotation of the polar end group in bromoalkanes is similar (possibly slightly greater) to that for rotation about the C-C bonds of the hydrocarbon chain. Thus intramolecular rotation of the $-CH_2Br$ group and a variety of molecular segments and rotation of the whole molecule may all contribute to the absorption of the bromoalkanes. The dielectric absorption of the pure liquids has been considered in similar terms.[101] However, the relaxation times of the pure liquid bromoalkanes are longer and lengthen much more markedly with increased molecular size than those for the dilute solutions. This is probably due to internal field and viscosity effects. Curves for macroscopic viscosity and τ_o, for the liquids, plotted against the number of carbon atoms are very similar.[99]

Table 4.7. Measured Values for Barriers to Internal Rotation.(Kcal/mole).

SUBSTANCE	Barrier	Worker(s)	Reference(s)
Ethane	2.88	Lide(1958)	169
		Laurie(1959)	169
		Karplus et.al.(1963)	169
	2.85	Bak et.al.(1960)	169
	2.3	Hecht et.al.(1960)	169
	1.77 &		
	2.63	Cignitti(1964)	169
	3.33	Pitzer(1964)	169
	2.4	Wyatt et.al.(1966)	169
	0.7 --		
	2.1	Goodisman(1966)	169
	2.75		167
Propane	3.3	Harris et.al.(1959)	169
	>2.7	Lide(1960)	168, 169
Fluoroethane	3.30	Herschbach(1956)	167, 168
1,1-Difluoroethane	3.18	Herschbach(1956)	167, 168
1,1,1-Trifluoroethane	3.48	Minden et.al.(1951)	168
Chloroethane	3.68	Schwendeman(1962)	168
Iodoethane	3.22	Kasuya(1960)	168
Cyanoethane	3.05	Laurie(1959)	168
Bromoethane	3.57	Lide(1959)	167, 169
	3.56	Laurie(1959)	169
	3.68	Flanagan et.al.(1963)	168
trans 1-Bromopropane	2.36	Radeliffe et.al.(1966)	169
gauche 1-Bromopropane	2.65	Radeliffe et.al.(1966)	169
Propene	1.99	Hirota(1966)	168
1-Buten-3-one	1.25	Foster et.al.(1965)	169
1-Butyn-3-one	1.07	Stiefvater et.al.(1963)	169
Acetyl fluoride	1.04	Pierce et.al.(1959)	168
Acetyl chloride	1.29	Sinnott(1961)	168
Acetyl bromide	1.30	Krisher(1960)	168
Acetyl iodide	1.30	Moloney et.al.(1966)	168
Methyl acetate	1.17		167
Acetaldehyde	1.16	Kilb et.al.(1957)	168
		Herschbach(1959)	168
Acetone	0.78	Swalen et.al.(1959)	169
		Nelson et.al.(1965)	168, 169
Acetic acid	0.48	Tabor(1957)	167, 168

According to the treatment of Debye,[143] Eq. (1.2),

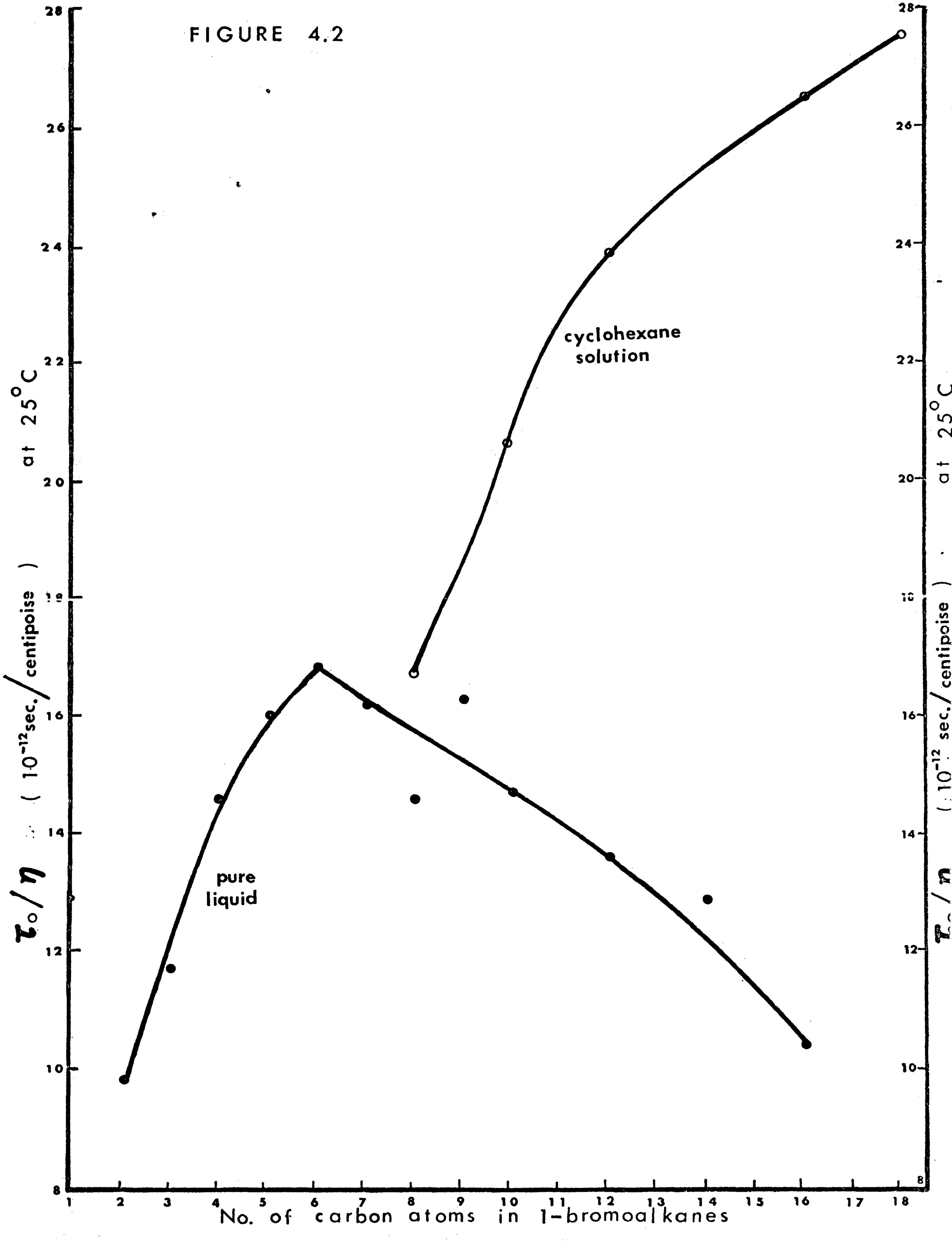
$$\tau_o = \frac{4\pi\eta a^3}{kT}$$

the molecule is pictured as a sphere of radius, a, rotating in a medium of viscosity, η. This equation may be rearranged and written in the form

$$V_D = \frac{4}{3}\pi a^3 N = \frac{RT\tau_o}{3\eta} \qquad (4.1)$$

where V_D is the hypothetical volume of the N molecules in a mole. Smyth et.al.[99] have already shown the dependence of V_D, for the n-alkyl bromides at 25°C, upon chain length. Plots of τ_o/η versus number of carbon atoms for pure liquids (C_2 — C_{16}) and cyclohexane solutions (C_8 — C_{18}) of 1-bromoalkanes are given in Figure 4.2. The values of τ_o/η (proportional to V_D) for pure liquids, which rise to a maximum for the six carbon chain, show that the increasing internal orienting power of the molecular chains causes the increase in relaxation time with increasing chain length to fall farther and farther behind the increase in viscosity. Moreover, Raman spectroscopy has indicated that stretched-chain forms are non-existent for chains with greater than 16 carbon atoms.[171] The end-over-end rotation of a long molecule occurs less frequently with increasing carbon number. The τ_o/η values for dilute solutions show a non-linear increase with increasing

FIGURE 4.2



τ_o/η (10^{-12} sec./centipoise) at 25°C
28
26
24
22
20
18
16
14
12
10
8
cyclohexane solution
pure liquid
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
No. of carbon atoms in 1-bromoalkanes

chain length.

The α - values for the 1-bromoalkanes do not show any significant increase with increased chain length, and the relaxation times for the C_{16} and C_{18} bromides are essentially the same. These results suggest that intramolecular reorientation is dominated by the smaller segments, the maximum unit of which has been shown to be ten to twelve carbon atoms from the dipole.[99] In addition, increased coiling probably occurs with increased chain length and the molecular relaxation time may not lengthen significantly with molecular size for the longer molecules.

It is interesting to note that the location of the dipole has little effect on the relaxation times for bromooctanes, which is also the case for the nonanones. However, the α - values for 2- and 4-bromooctane are significantly smaller than those for the 1-bromoalkanes, and decrease as the location of the dipole is moved from the chain end. This is not unreasonable since the number of different length molecular segments having a terminal $-CH_2Br$ group is greatest when the polar group is located at the chain end.

The mean relaxation times for liquid α, ω-dibromoalkanes[108] (Table 4.3) are much longer than those for analogous bromoalkanes.[101] (Table 4.1) In contrast, the mean relaxation times for 1,10-dibromodecane and 1-bromodecane in cyclohexane at 25°C are essentially the same. However the α - value for the former is considerably smaller than that for the latter. For an α, ω-dibromoalkane, there is more than one axis of rotation between the dipole. Consequently the calculation of the mean moment in terms of the group or bond moments of the substituents is complex. Eyring[172] and Smyth[2] were able to calculate the mean moments for such molecules by assuming that internal rotation is completely unrestricted and all positions attainable by rotation about each axis are equally probable. Smyth and Walls[173] found that in the polymethylene dibromides and dicyanides, the first members of the series measured in benzene solutions at 25 — 50°C have moments far below the values calculated for free rotation owing to repulsions between the terminal polar groups which favor a trans configuration in the chain. However, nonamethylene and decamethylene dibromide and decamethylene dicyanide have moments very close to the free-rotation values. The present measured dipole moment of 2.68 D for 1,10-dibromodecane in cyclohexane at 25°C is almost identical to Smyth's calculated value of 2.69 D. Smyth suggested that there are so many possible configurations for these long-chain molecules, because of the almost completely random orientation of the two dipoles relative to each other, that the mean moment is indistinguishable from that for free rotation. The terminal $-CH_2Br$ groups and a variety of chain segments in the 1,10-dibromodecane molecule may compete in simultaneous rotation at both ends of the molecule such that the probabilities of shorter segmental reorientations outnumber those of longer ones.

The absorption data, at ten frequencies, for

1,10-dibromodecane in cyclohexane provide a good estimate for ε_∞, which is close to n_D^2. Chandra and Prakash[108] used a Cole-Davidson distribution function to describe the absorption of several short chain α, ω-dibromoalkanes in benzene. The high frequency portion in the present Cole-Cole plot (Fig. 4.1) is adequately represented by a depressed center semicircular arc. The intramolecular co-operative reorientation mechanism proposed by Chandra and Prakash is not unreasonable in view of the repulsion between the two terminal dipoles; but it is far from conclusive because they only employed four frequencies, all below 37 GHz.

Analyses for two discrete relaxation times for the monobromoalkanes do not yield sensible results.

Higasi et. al.[101] analysed the dielectric data for pure liquid n-alkyl bromides in terms of two limiting values of relaxation times (Table 4.1). Similar analyses have been carried out for the n-ethyl and n-octyl bromide data given in Table 4.2, and also for the relaxation data in Table 4.5. The results are listed in Tables 4.8 and 4.9. These analyses are influenced by the α - values, and thus ε_∞, and are based on several assumptions which may not be valid for the n-alkylbromides. However, the results in Table 4.1 are consistent with the interpretations for τ_o given above. The analyses given in Tables 4.8 and 4.9 are not as sensible as those obtained by Higasi et. al. but they do show similar trends. The τ_U values for all the 1-bromoalkanes lengthen with increased molecular size, and may be ascribed to molecular end-over-end rotations.

Table 4.8. Limiting Relaxation Times (ps) for Two Alkyl Bromides in Solutions at 20°C. (Analyses based on data from ref. 114).

SOLUTE	SOLVENT	τ_L	τ_U
Bromoethane	n-heptane	0.56	4.55
	benzene	0.62	16.2
	cyclohexane	0.42	10.8
	n-hexadecane	0.42	10.8
1-Bromooctane	n-heptane	1.71	70.5
	cyclohexane	1.95	142
	n-hexadecane	2.13	175

Table 4.9. Limiting Relaxation Times (ps) for Several Alkyl Bromides in Cyclohexane at 25°C.

SOLUTE	τ_L	τ_U
1-Bromooctane	2.5	103.9
2-Bromooctane	4.5	41.9
4-Bromooctane	8.6	30.7
1-Bromodecane	3.7	107.5
1-Bromododecane	4.3	124.2
1-Bromohexadecane	4.0	163.6
1-Bromooctadecane	4.7	151.0

The drop for 1-bromooctadecane may be due to coiling of the long chain. An extended chain of more than 16 carbon atoms has been shown to be rare.[171] For 1-bromooctane τ_U increases with increased solvent viscosity. (Table 4.8) The discrepancy between the two τ_U values for this compound in cyclohexane (Table 4.8 and 4.9) may be partly due to the 5°C temperature difference. The relatively small increase in τ_L with increasing molecular chain length, (Table 4.9) and with increasing solvent viscosity in the case of 1-bromooctane (Table 4.8) indicates that rotation of the $-CH_2Br$ group is the probable mechanism. The increase in size of the smallest orientating unit may be a factor responsible for the increase in the τ_L values from 1-bromo to 4-bromooctane. Conversely, the significant decrease in the τ_U values (if real) in the same series is remarkable. The difference in the total volume swept out by molecular end over end reorientation of these three molecules may partially account for the variation of the τ_U values. When the bromo group is removed from the chain end it is not inconceivable that rotations about the axes perpendicular to the hydrocarbon chain are negligible. Thus the long relaxation time which contributes to the absorption of 1-bromooctane may be absent for 2- and 4-bromooctane.

Summary

The dielectric absorption data for bromoalkanes in cyclohexane solution are adequately described by symmetrical Cole-Cole plots and show no evidence of skewed-arc behavior. It is probable that the intramolecular rotation of a variety of segments all contribute to the absorption.

Chapter V. Dielectric Relaxation of Aliphatic Amines in Dilute Solution.

5.1 Introduction

The dielectric absorptions of aliphatic amines as pure liquids[141] and in n-heptane solution[116] have been characterized by two relaxation processes. The longer process has been attributed to the orientation of the molecule as a whole. Assignment of the shorter, probably intramolecular process, is complicated by the possibility of inversion of the nitrogen atom as a relaxation mechanism. Johari et. al.[116] found that the τ_1 value of $\sim$16 ps for the molecular relaxation of n-octylamine in n-heptane at 25°C is of the same order as that for n-octylaldehyde. This indicates that self-association of alkyl amines is not an important factor in dilute solution. In contrast, Tucker and Walker[174] suggested that a relaxation process due to hydrogen-bond formation in liquid pyrrolidine (τ_o = 13 ps at 20°C)[175] and for pyrrolidine and piperidine in both cylclohexane and p-dioxane solution ($\tau_o \simeq 2.5 - 6.7$ ps at 25°C)[174] gave rise to significantly longer mean relaxation times than those of other compounds of a similar shape and size such as tetrahydrofuran, furan and thiophene (τ_o = 2.9, 1.7, 2.7 ps respectively as pure liquid at 20°C;[175] τ_o = 1.82, 1.37, 2.05 ps respectively in cyclohexane at 20°C[176]).

Aromatic amines have been extensively studied.[138, 150, 177 - 179] The intramolecular relaxation process has been attributed to both inversion of the nitrogen atom and the rotation of the amino or alkylamino group. In particular, the extremely short relaxation time found for the large triphenylamine molecule[150, 180] and the abnormally short high frequency relaxation times for aniline and N,N-dimethylaniline have been taken as evidence for dipole orientation by molecular inversion.[177, 180] Kadaba and Eloranta[178] examined three chlorine substituted anilines as the pure liquids and also at several concentrations in carbon tetrachloride solution at 24 – 60°C and 1 – 10 cm wavelengths. The relaxation times, $\tau_2 \sim 0.3 - 0.6$ ps, which were attributed to the inversion of the nitrogen atom, deviate considerable from those obtained by Tucker and Walker[139] from ε' vs $\varepsilon''\omega$ plots ($\tau_2 \sim 2 - 3$ ps) for cyclohexane and p-xylene solutions measured at frequencies up to 70 GHz at 25°C. The discrepancy could probably arise from the difference in the frequency ranges and the methods of analyses employed. Furthermore, the contribution from group relaxation, $C_2 \sim 0.1$, is so small that τ_2 values are very unreliable.

Fong et. al.[181] ascribed the shorter relaxation times of 2.2 – 2.8 ps for 2,6-dimethylaniline at 20°C in benzene to rotation of the amino group. These τ_2 values are longer than those estimated from earlier data by Grubb and Smyth[138] and much larger than those obtained for pure liquid[177] aniline ($\tau_2 = 0.9$ ps at 20°C) and N,N-dimethylaniline ($\tau_2 = 1.5$ ps at 20°C). Garg and Smyth[177] suggested that the above-mentioned results for aniline and N,N-dimethylaniline would not be expected from a comparison of the volume swept out by rotation of the NH_2

and $N(CH_3)_2$ groups. Consequently, inversion of the nonpolar configuration of the nitrogen bonds could probably account for the high frequency relaxation process. They argued that the relaxation times are short because the displacement required for reversing the dipole direction by inversion is small. Eloranta and Kadaba[179] compared the dispersion and thermodynamic parameters for aniline, o-chloroaniline, m-chloroaniline, p-chloroaniline and benzidine. They discussed the dependence of the relaxation time and the potential barrier to the inversion upon the angle to be inverted, and the variation of the angle between the NH_2 group and the phenyl ring with the location of the substituted Cl atom. Williams[182] has also given a theoretical discussion on the inversion process of aniline and related compounds.

Tables 5.1 and 5.2 list a number of reported relaxation parameters for aliphatic amines.[43, 116, 141] It can be seen that the τ_L (or τ_2) values for aliphatic primary amines show little dependence on concentration, temperature and hence viscosity. These τ_L (or τ_2) values at 25°C are in general longer than that for aniline.[177] Davies[183] suggested that the delocalization energy in aromatic amines will favour a more planar configuration for the nitrogen valencies than in aliphatic amines, and thus the energy barrier to inversion, which in ammonia and trimethylamine[184] are 5.9 and 8.19 Kcal $mole^{-1}$ respectively, will be appreciably smaller. Evans[185] has reported a barrier of at least 4.5 Kcal/mole for inversion in aniline from

Table 5.1. Dielectric Relaxation Parameters for Several Aliphatic Amines. (from refs. 43 and 141).

AMINE	t°C	COLE-COLE DISTRIBUTION		FROHLICH DISTRIBUTION	
		α	τ_o(ps)	τ_L(ps)	τ_U(ps)
Ethyl amine	0	0.07	4.72	1.5	13.5
	-10	0.11	5.75	2.0	19.9
(f.p. -80.6°)	-20	0.13	7.39	2.5	24.9
	-30	0.16	9.16	2.5	37.2
	-40	0.17	17.04	3.0	60.3
n-Propylamine	0	0.0	4.0	1.5	12.2
	-10	0.05	4.95	2.0	12.1
(f.p. -83°C)	-20	0.05	6.94	2.0	13.4
	-30	0.12	8.97	3.0	24.5
	-40	0.13	12.78	3.0	27.1
	-50	0.15	15.31	4.0	59.5
	-60	0.18	24.77	4.0	119.8
	-70	0.09	35.71	4.0	439.8
n-Butylamine	0	0.0	5.74	2.0	9.9
	-10	0.02	6.12	2.0	16.3
(f.p. -50.5°C)	-20	0.08	8.66	3.0	27.1
	-30	0.13	10.84	3.0	27.1
	-40	0.17	15.23	3.0	60.3
	-49	0.21	17.25	2.5	203
n-Amylamine	0	0.08	5.01	2.0	16.3
	-10	0.11	6.12	2.0	24.4
(f.p. -55°C)	-20	0.13	7.12	2.0	32.8
	-30	0.18	10.23	2.0	60.0
	-40	0.22	13.17	2.0	66.2
	-50	0.29	17.55		
Diethylamine	0	0.07	8.16		
	-10	0.07	12.32		
(f.p. -50°C)	-20	0.12	17.40		
	-30	0.14	23.96		
	-40	0.19	30.68		
	-49	0.21	48.10		
Di-n-propylamine	0	0.13	12.44		
	-10	0.17	17.70		
	-20	0.18	21.10		
	-30	0.23	30.95		
	-40	0.13	45.15		
	-50	0.13	56.97		
Di-n-butylamine	0	0.0	17.09		
	-10	0.01	21.51		
	-20	0.06	25.88		
	-30	0.05	32.53		
	-40	0.12	39.08		
	-50	0.16	54.02		
	-60	0.20	30.71		

Table 5.2. Dielectric Relaxation Parameters for n-Octylamine in n-Heptane at Mole Fraction f_2 at 25°C. (from ref. 116).

f_2	COLE-COLE DISTRIBUTION*		BUDO DISTRIBUTION		
	α	τ_0(ps)	τ_1(ps)	τ_2(ps)	C_2
0.072	0.28	1.6	15.4	1.9	0.83
0.124	0.24	2.1	15.4	1.9	0.83
0.164	0.20	1.3	16.4	1.3	0.83
0.198	0.0	2.0	15.4	1.8	0.75

* Calculated from data in ref. 116 with Program # 4 in Appendix I.

infrared studies. From the data listed in Table 5.1, Kadaba and co-workers[141] were able to conclude that freedom of rotation of the $-NH_2$ group around the C-N axis exists in alkyl primary amines with 2 – 5 carbon atoms.

The work presented here is a systematic study of the dielectric relaxation behaviour of aliphatic amines in solution. The size of the alkyl group and the location and size of the polar group are varied. In addition, the dielectric absorptions of several α, ω-diaminoalkanes are examined in various solvents.

5.2 Results.

The experimental dielectric constant and loss values for each amine when plotted in the complex plane give no clear indication of distinct separations into more than one dispersion region. It is possible to draw relatively smooth depressed center, semicircular arcs through the experimental points. The data for each system were analyzed for a mean relaxation time (τ_0), a Cole-Cole distribution parameter (α) and a very high frequency dielectric constant (ε_∞) by a computer fit to the Cole-Cole equation.[146] The results together with the static dielectric constants (ε_0), and the dipole moments (μ) calculated from Eq. 3.43, are presented in Table 5.3 (a), (b) and (c). Analyses for two discrete relaxation times have been unsuccessful except in the cases of N-methyl-n-octylamine, N,N-dimethyl-n-octylamine and N,N-diethyl-n-octylamine, Table 5.4. The exper-

Table 5.3(a). Relaxation Times (ps), Distribution Parameters, Static Dielectric Constants, High Frequency Dielectric Constants and Dipole Moments (in D units) for Aliphatic Primary Amines at Mole Fraction f_2 in Solutions at 25°C.

SYSTEM	f_2	τ_0	α	ε_0	ε_∞	μ(expt)
n-Butylamine/ cyclohexane	0.0960	1.6	0.0	2.1753	2.016	1.26
	0.1445	1.6	0.11	2.2914	2.016	1.33
	0.1908	2.0	0.12	2.3940	2.038	1.30
n-Butylamine/ p-dioxane	0.1478	4.2	0.06	2.6319	2.235	1.34
n-Hexylamine/ cyclohexane	0.1005	2.2	0.05	2.1912	2.023	1.28
	0.1521	2.5	0.03	2.2791	2.047	1.22
	0.2012	2.1	0.07	2.3682	2.016	1.31
n-Hexylamine/ p-dioxane	0.1549	5.2	0.06	2.5513	2.234	1.21
n-Nonylamine/ cyclohexane	0.1005	2.5	0.27	2.2373	2.028	1.45
	0.1504	3.3	0.21	2.3554	2.067	1.40
	0.2007	3.6	0.18	2.4698	2.092	1.39
n-Nonylamine/ p-dioxane	0.1481	5.0	0.16	2.5134	2.210	1.28
2-Nonylamine/ cyclohexane	0.0998	3.5	0.20	2.1976	2.016	1.36
	0.1483	4.0	0.22	2.2826	2.016	1.37
	0.1987	4.7	0.13	2.3715	2.052	1.18
2-Nonylamine/ p-dioxane	0.1467	9.9	0.09	2.5495	2.226	1.29
5-Nonylamine/ cyclohexane	0.0990	3.4	0.14	2.1700	2.019	1.25
	0.1506	3.6	0.16	2.2459	2.025	1.24
	0.1985	3.8	0.04	2.3140	2.051	1.18
5-Nonylamine/ p-dioxane	0.1488	6.3	0.10	2.4745	2.213	1.16
n-Decylamine/ cyclohexane	0.0935	3.0	0.02	2.2224	2.039	1.22
	0.1494	2.9	0.12	2.2683	2.057	1.22
	0.2017	3.2	0.12	2.3495	2.077	1.68
n-Decylamine/ p-dioxane	0.1526	7.9	0.24	2.6954	2.232	1.52
n-Undecylamine/ cyclohexane	0.1007	3.2	0.10	2.1873	2.057	1.16
	0.2007	3.7	0.07	2.3400	2.101	1.14

Table 5.3(b). Relaxation Times (ps), Distribution Parameters, Static Dielectric Constants, High Frequency Dielectric Constants and Dipole Moments (in D units) for Secondary and Tertiary n-Octylamines at Mole Fraction f_2 in Solutions at 25°C.

SYSTEM	f_2	τ_0	α	ε_0	ε_∞	μ(expt)
N-Methyl-n-octylamine/ cyclohexane	0.0932	8.9	0.0	2.1391	2.041	1.16
N-Methyl-n-octylamine/ p-dioxane	0.1492	12.9	0.0	2.3867	2.213	0.95
N,N-Dimethyl-n-octylamine/ cyclohexane	0.0998	16.0	0.0	2.0663	2.019	0.71
	0.1502	13.4	0.17	2.0888	2.022	0.70
	0.2011	13.6	0.07	2.1104	2.027	0.78
N,N-Diethyl-n-octylamine/ cyclohexane	0.1941	26.7	0.0	2.1358	2.041	0.79

Table 5.3(c). Relaxation Times (ps), Distribution Parameters, Static Dielectric Constants, High Frequency Dielectric Constants and Dipole Moments (in D units) for α,ω-Diaminoalkanes at Mole Fraction f_2 in Solutions at 25°C.

SOLVENT	f_2	τ_0	α	ε_0	ε_∞	μ(expt)
		1,4-Diaminobutane				
Cyclohexane	0.02024	1.8	0.31	2.0806	2.018	1.79
p-Xylene	0.01976	2.7	0.01	2.3381	2.281	1.54
p-Dioxane	0.02000	4.9	0.17	2.3381	2.230	1.96
		1,6-Diaminohexane				
Cyclohexane	0.02090	2.5	0.14	2.0915	2.031	1.98
p-Xylene	0.02030	3.6	0.01	2.3277	2.280	1.39
p-Dioxane	0.01999	5.7	0.06	2.3256	2.231	1.74
		1,9-Diaminononane				
Cyclohexane	0.01891	3.2	0.30	2.0558	2.020	1.88
p-Xylene	0.01895	3.4	0.06	2.3149	2.273	1.47
p-Dioxane	0.01890	6.3	0.15	2.4482	2.256	2.65

Table 5.4. Dielectric Relaxation Parameters in terms of Budo Distribution for Some Secondary and Tertiary n-Octylamines at Mole Fraction f_2 in Solutions at 25°C.

SYSTEM	f_2	ε_∞	τ_1 (ps)	τ_2 (ps)	C_1
N-Methyl-n-octylamine/ cyclohexane	0.0932	2.035	26.3	7.2	0.24
N,N-Dimethyl-n-octylamine/ cyclohexane	0.0998	2.016	34.1	5.8	0.48
	0.1502	2.020	33.8	5.7	0.48
	0.2011	2.028	21.2	5.2	0.64
N,N-Diethyl-n-octylamine/ cyclohexane	0.1941	2.036	40.5	6.9	0.70

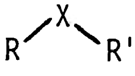
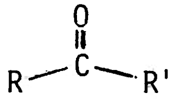
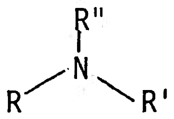
imental and calculated values of ε' and ε'' are listed in Appendix II.

Because of the short relaxation times shown by the majority of the amines examined here, the high frequency side of the arc plots are not well defined. The data given in Table 5.3 provide the best fit to the experimental results but the ε_∞ and α values may be in error. Certainly the latter are to be regarded with caution and the author has refrained from basing conclusions on their magnitude. The mean relaxation time is not so seriously affected by the lack of high frequency data and reasonable variations of ε_∞ and α indicate that the τ_0 values are accurate to at least ±20%. Errors of this magnitude do not affect the following interpretations of the data.

5.3. Discussion

The mean relaxation times of the seven primary amines in cyclohexane (Table 5.3(a)) are considerably shorter than those obtained for the analogous n-alkyl bromides (Tables 4.1 and 4.2), and are of the same magnitude as the relaxation times attributed to the intramolecular relaxation of small polar groups in aromatic molecules such as 2,6-di-t-butyl-p-cresol[181] ($\tau_2 \simeq 3.34$ ps at 20^oC) and 2,6-dimethylaniline[181] ($\tau_2 \simeq 2.81$ ps at 20^oC). No significant increase in τ_0 with increased size of the alkyl group, or with the location of the amino group in the nonylamine is apparent. These results suggest that dipole orientation in primary n-alkyl amines occurs predominantly by a fast intramolecular process, and rotational orientation of the whole molecule makes little or no detectable contribution to the absorption. In contrast, the mean relaxation times for N-methyl-, N,N-dimethyl-, and N,N-diethyl-n-octylamine are considerably longer than those for the primary amines and lengthen with increased number and size of the N-alkyl groups. A survey of relaxation times reported for pure liquid amines[43, 141, 186] reveals a similar pattern, i.e., τ_o values for primary amines are almost independent of the alkyl group whereas the values for many secondary and tertiary amines lengthen with increased size of the N-alkyl groups. The lengthening of τ_o for the n-octylamines, Table 5.3(b), is greater than would be anticipated if an intramolecular process dominated their absorption. The relaxation time for N,N-diethyl-n-octylamine ($R\text{-}N(C_2H_5)_2$) is considerably longer than that for pure liquid diethylamine[43] ($H\text{-}N(C_2H_5)_2$), ∿8 ps at 0°C. Thus, reorientational rotation of the whole molecule probably makes a significant contribution to the absorption of secondary and tertiary amines and apparently increases with the size of the N-alkyl groups.

The nature of the intramolecular mechanism which dominates the absorption of the primary amines, and undoubtedly makes an appreciable contribution for N-methyl-n-octylamine, was not discussed above. Dielectric absorption data for primary, secondary and tertiary aromatic amines may be analyzed in terms of two relaxation times.[150, 177, 178] Rotation of the amino group about the aromatic C-N bond or inversion of the nitrogen atom have been considered as possibilities for the faster process as indicated in the previous section. Tucker and Walker[140] examined N-methyl, N,N-dimethyl-, and N,N-diethylaniline, and found τ_2 values for their cyclohexane solutions at 25°C as 1.2, 1.5 and 15 ps respectively. It is noteworthy that the τ_2 values for N-methyl- and N,N-dimethylaniline are very similar and comparable to the τ_2 values of 0.9 and 1.5 ps for aniline and N,N-dimethylaniline respectively as pure liquids measured by Garg and Smyth.[177] If a nitrogen inversion mechanism were responsible for the rapid relaxation of primary aliphatic amines then, by analogy with aromatic amines, the relaxation times for the secondary and tertiary octylamines should be similar to those for the primary amines. The relaxation behaviour of the octylamines may be explained by an increased contribution from molecular rotation for secondary and tertiary amines due to steric restriction of intramolecular rotation about C-N bonds. As with the aromatic amines it is not possible to rule out either the inversion or rotation process and both may be involved to some extent. However, the potential barrier to inversion in aliphatic amines is significantly greater than that for rotation whereas the reverse is true for aromatic amines.

The structure  in which R and R' represent alkyl groups is common to both aliphatic ketones, X being a C=O group, and ethers, X being an oxygen atom. When R is small the mean relaxation times are almost independent of the size of R' and dipole reorientation occurs mainly by intramolecular rotation. Dipole reorientation by whole molecular rotation only makes a detectable contribution to the absorption when both R and R' are relatively large.[165] The relaxation times for the 2-alkanones (Table 4.6) are somewhat longer than those for the primary amines due to the difference in size of the polar end groups, $-COCH_3$ and $-NH_2$ respectively. Relaxation times for other alkanones (Table 4.6) and secondary and tertiary amines, which are appreciably longer than those for the 2-alkanones and primary amines respectively, indicates a decrease in the contribution from the intramolecular process and a corresponding increase in the contribution from whole molecule rotation. This effect is brought about with far smaller R' groups for amines, $R-NR'_2$, than for ketones, RCOR'. The reason is readily apparent from an examination of molecular models. In ketones,  $R-\overset{\overset{O}{\|}}{C}-R'$, the carbonyl group is co-planar with the R-C and R'-C bonds. Steric hindrance to rotation about these bonds only occurs with relatively large R and R' groups. The amines,  , are pyramidal and the RNR' angle ($(CH_3)_2NH$: 112.2°; $(CH_3)_3N$: 108.7°)[168] is smaller than the RCR' angle ($(CH_3)_2CO$: 117.2°).[168] This gives rise to some steric restriction to rotation about the

R-N bond for secondary amines with a small N-alkyl group and the effect is considerable for tertiary amines. It is probable that intramolecular rotation in N,N-diethyl-n-octylamine only makes a very small contribution to the dielectric absorption. The results shown in Table 5.4 are not necessarily unique. They represent the most probable sets of relaxation parameters in terms of Budo distribution for the n-octylamines. The ε_∞ values chosen for the analyses are not always identical to those obtained from the Cole-Cole analyses, but have been limited to a reasonable range around ε_∞(Cole-Cole).[151] It can be seen that C_1 increase significantly with the number and size of the N-alkyl group. Potential barriers to internal rotation in methylamine, dimethylamine and trimethylamine of 1.976, 3.200 and 4.400 Kcal/mole respectively have been reported.[168] These results support the above interpretation for the relaxation behaviour of the n-octylamines.

No significant increase in τ_0 with increased concentration is evident for any of the amines in cyclohexane. In contrast, intermolecular association is an important factor in the dielectric absorption of aliphatic alcohols and their relaxation times and dipole moments are extremely sensitive to the alcohol concentration.[91] In general the dipole moments in Table 5.3 compare favourably with values obtained for these amines by conventional methods,[2] and any variations with concentration are probably a reflection of the errors in the ε_∞ values.

Although self-association of aliphatic amines is not detectable in cyclohexane, solute-solvent interactions in p-dioxane solution are indicated by the τ_o values which are approximately double those for cyclohexane solutions. Because of the errors in the ε_∞ values, any quantitative analysis, with physical significance, based upon the difference in dipole moments in the two solvents is not justifiable. The difference in free energy of activation ($\Delta\Delta G_o^\ddagger$) for molecular reorientation in the two solvents may be calculated using[187]

$$\frac{\tau_{o\,\text{p-dioxane}}}{\tau_{o\,\text{cyc.}}} = \exp(\Delta\Delta G_o^\ddagger /RT) \qquad (5.1)$$

in which $\tau_{o\,\text{cyc.}}$ is the relaxation time in cyclohexane or an inert solvent and $\tau_{o\,\text{p-dioxane}}$ the observed value in p-dioxane where intermolecular forces are involved. The values of $\Delta\Delta G_o^\ddagger$ and $\tau_{o\,\text{p-dioxane}}/\tau_{o\,\text{cyc.}}$ for the amines are given in Table 5.5. These $\Delta\Delta G_o^\ddagger$ values are similar to those obtained for a number of chloroethanes[188, 189] and may be attributed to weak interactions between the amino group and the oxygen lone pair electrons of p-dioxane. The viscosity of p-dioxane, 1.2 cps at 25°C, is larger than that of cyclohexane, 0.9 cps at 25°C, but this effect alone cannot account for the relaxation behaviour and, indeed, for small nearly spherical molecules such as n-butylamine, the relaxation times might be almost independent of the macroscopic viscosity. The relaxation times for the primary amines are very short in both solvents and consequently the values in Table 5.5

Table 5.5. Differences in Free Energy of Activation ($\Delta\Delta G_o^{\ddagger}$), in cal/mole, based on the Mean Relaxation Times (τ_o) of the Aliphatic Amines in p-Dioxane and Cyclohexane at 25°C.

	$\frac{\tau_{o\,p\text{-dioxane}}}{\tau_{o\,cyc}}$	$\Delta\Delta G_o^{\ddagger}$
n-Butylamine	2.37	506
n-Hexylamine	2.28	486
n-Nonylamine	1.75	323
2-Nonylamine	2.47	529
5-Nonylamine	1.76	332
n-Decylamine	2.60	564
N-Methyl-n-octylamine	1.45	220

must be regarded with caution. The value for n-nonylamine appears to be anomalously low. Steric factors are probably responsible for the weak solvent-solute interaction for 5-nonylamine and N-methyl-n-octylamine.

For the aliphatic amines in p-dioxane solute-solvent interaction should slow down the $-NH_2$ group rotation process. It was anticipated that this effect might decrease the contribution from group rotation and the contribution from whole molecule or long segments would become more important and possibly give rise to two dispersion regions. However, a clear separation is not obvious. Analyses have been performed for τ_1, τ_2 and C_1 for these systems. The results, Table 5.6, are inconsistent.

It may be possible that the potential barrier for the internal rotation about the C-N bond would be increased by solute-solvent interaction in the p-dioxane-amine systems, and analyses for two limiting relaxation times in terms of a Fröhlich distribution may be reasonable. The results, Table 5.6, show that τ_L values give a better representation for the group relaxation time than the τ_2 values obtained from the Budō analyses. However, the Fröhlich analysis is greatly dependent upon the Cole-Cole distribution parameter, α. Both ε_∞ and α values are inaccurate for the systems studied, and the results in Table 5.6 are to be regarded with caution.

The τ_0 values for the α, ω-diaminoalkanes and the

Table 5.6. Dielectric Relaxation Parameters in terms of Budó Distribution and Fröhlich Distribution for Some Aliphatic Primary Amines at Mole Fraction f_2 in p-Dioxane at 25°C.

			BUDÓ DISTRIBUTION			FRÖHLICH DISTRIBUTION	
Amine	f_2	ε_∞	τ_1(ps)	τ_2(ps)	C_1	τ_L(ps)	τ_U(ps)
n-Butylamine	0.1478	2.2348	7.3	2.0	0.58	1.9	9.2
n-Hexylamine	0.1549	2.2341	27.0	4.5	0.15	2.4	11.4
n-Nonylamine	0.1481	2.2000	7.8	0.9	0.70	1.2	20.3
2-Nonylamine	0.1467	2.2256	17.1	5.3	0.53	3.7	26.6
5-Nonylamine	0.1488	2.2128	9.4	2.3	0.67	2.2	18.0
n-Decylamine	0.1526	2.2324	21.0	2.8	0.52	1.2	50.7

analogous normal primary amines are very similar in cyclohexane and p-dioxane, Table 5.3. But the Cole-Cole distribution parameters, α, for the former are larger than those for the latter except 1,6-diaminohexane and 1,9-diaminononane in p-dioxane. In contrast, 1,10-dibromodecane has a considerably smaller α - value than n-bromodecane (Table 4.5), both in cyclohexane at 25^{o}C. The α - values cannot be regarded with any certainty because the τ_o values are so short that it is difficult to estimate high-frequency intercepts of the Cole-Cole plots with any accuracy. The τ_o values of the α, ω-diaminoalkanes in p-dioxane, like those for the n-alkylamines, are approximately double those for cyclohexane solutions. The α, ω-diaminoalkanes show near Debye-type absorption (i.e. $\alpha \simeq 0.0$) in p-xylene with τ_o values in between those in cyclohexane and in p-dioxane. In all solvents, the τ_o values show only a very slight lengthening with increased molecular size. For α, ω-diaminoalkanes, it is probable that the intramolecular relaxation of both amino groups dominates the absorption. The results do not indicate that group rotation is slowed down to such an extent that molecular reorientation becomes important in the p-dioxane solutions.

Recently, Ellison and Meyer[190] have studied the dimerization of N-methylaniline in cyclohexane and benzene. It is possible that α, ω-diaminoalkanes may exist in intermolecular hydrogen bonded forms while the terminal group rotation still prevails, or, for the shorter molecules, in intramolecular H-bonded units. However, the evidence in the present study is insufficient to discuss this aspect any further.

Summary

The dielectric data have been analyzed for mean relaxation times and Cole-Cole distribution parameters. Primary n-alkyl amines in cyclohexane are characterized by short relaxation times which are almost independent of the size of the alkyl group and the location of the $-NH_2$ group. Considerably longer values are obtained for the secondary and tertiary amines. A fast intramolecular relaxation process probably dominates the absorption of primary n-alkyl amines but its contribution decreases significantly with increased number and size of N-alkyl groups. Steric restriction of intramolecular rotation about C-N bonds of the secondary and tertiary n-octylamines has been considered. Analyses for relaxation parameters in terms of Budo distribution may be significant for the secondary and tertiary n-octylamines. The relaxation times for the α,ω-diaminoalkanes and the analogous normal primary amines are very similar. The increase in relaxation times for these amines in p-dioxane is probably due to solute-solvent interactions; however, the $-NH_2$ group rotation remains the predominant process.

PUBLICATIONS

The following papers have been accepted for publication:

(1) "Dielectric Relaxation of Aliphatic Amines in Cyclohexane Solution", to be published in Journal of Chemical Physics. (accepted in December 1971).

(2) "Dielectric Relaxation of Aliphatic Bromides in Cyclohexane Solution", to be published in Canadian Journal of Chemistry. (accepted in March 1972).

APPENDIX I

COMPUTER PROGRAMS USED FOR ANALYSES

PROGRAM #1

for

MICROWAVE INTERFEROMETER MEASUREMENTS

```
INTER:PROC OPTIONS(MAIN) REORDER;
      /***************************************************/
      /*   MICROWAVE INTERFEROMETER PROGRAM              */
      /*   BASED ON PRINCETON UNIV. FORTRAN IV PROGRAM   */
      /*   WRITTEN INTO PL/1 BY C. K. MCLELLAN           */
      /***************************************************/
 DCL (DBMAX(20),DBMIN(20),X(20),REXP(20),RCAL(20),DELTALAST,FREQ,
     DELTANOW,WLAIR,WLDIEL,POSNMIN(20)) FLOAT DEC (16);
 DCL (TITLE, CARD) CHAR (80), (STEPS,POINTS) BIN FIXED(15,0);
 DCL CHANGE FLOAT DECIMAL(16), SP BIN FLOAT, NAME CHAR(2);
 DCL PHRASE CHAR(35);
 PHRASE='THE FOLLOWING DATA REPRESENT EVERY ';
      /***************************************************/
      /*   DBMAX AND DBMIN ARE THE DB LEVELS AT THE      */
      /*   MAXIMA AND MINIMA, RESPECTIVELY               */
      /*   WLAIR IS THE AIR WAVELENGTH                   */
      /*   POSNMIN IS THE POSITION OF THE MINIMUM        */
      /*   SP IS THE SPACING OF THE MINIMA THAT ARE      */
      /*   ON THE DATA CARDS. FOR EXAMPLE,               */
      /*            SP=1 FOR EVERY MINIMUM               */
      /*            SP=2 FOR EVERY SECOND MINIMUM        */
      /*           SP=10 FOR EVERY TENTH MINIMUM         */
      /*   FREQ IS FREQUENCY IN GIGAHERTZ.  IF FREQ=0    */
      /*   IS INPUT, FREQ IS CALCULATED FROM WLAIR.      */
      /***************************************************/
   ON ENDFILE (SYSIN) BEGIN;
      NODATA=0;
      GO TO CALC;
   END;
     NODATA=1;
     PI=3.1415926E+00:
     CLIGHT=2.9979E+01;
   ON CONVERSION GO TO CALC;
 DATA:GET EDIT(CARD) (A(80));
       IF CARD=' ' THEN GO TO DATA:
DATA2:GET STRING(CARD) EDIT(TITLE) (A(80));
    PUT PAGE EDIT(TITLE) (X(10),A):
    PUT SKIP EDIT('MICROWAVE INTERFEROMETER MEASUREMENT') (X(10),A);
    PUT SKIP(2) EDIT('INPUT DATA') (X(30),A);
    PUT SKIP(0) EDIT((10)'_') (X(30),A):
BLANK1:GET EDIT(CARD) (A(80));
      IF CARD=' ' THEN GO TO BLANK1:
      GET STRING(CARD) LIST(WLAIR,SP,FREQ);
      IF SP=1 THEN DO;
        PUT SKIP(2) EDIT(PHRASE,'SUCCESSIVE MINIMUM.') (X(10),A,A);
        GOTO HEADINGS:  END;
      ELSE IF SP=2 THEN NAME='ND';
      ELSE IF SP=3 THEN NAME='RD';
      ELSE NAME='TH';
    PUT SKIP(2) EDIT(PHRASE,SP,NAME,' SUCCESSIVE MINIMUM.')
      (X(10),A,F(2),A(2),A);
HEADINGS:PUT SKIP EDIT('MINIMUM','POSITION','DB(MAX)','DB(MIN)')
  (X(10),A,X(10),A,X(10),A,X(10),A):
    PUT SKIP EDIT('NUMBER','(CM.)','(DB)','(DB)')
      (X(10),A,X(12),A,X(13),A,X(13),A):
    PUT SKIP(0) EDIT((7)'_',(8)'_',(7)'_',(7)'_')
      (X(10),A,X(10),A,X(10),A,X(10),A);
```

```
INTER:PROC OPTIONS(MAIN) REORDER;

               DO  I=1 BY 1;
      BLANK2:  GET EDIT (CARD) (A(80));
               IF CARD=' ' THEN GO TO BLANK2;
               GET STRING (CARD) LIST (DBMAX(I),DBMIN(I),POSNMIN(I));
               POINTS=I;
               PUT SKIP EDIT(POINTS,POSNMIN(I),DBMAX(I),DBMIN(I))
               (X(12),F(2),X(11),F(10,5),X(11),F(5,2),X(12),F(5,2));
               END;
       CALC:WLDIEL=0;
           IF FREQ=0 THEN FREQ=CLIGHT/WLAIR;
               DO  I=2 TO  POINTS;
               WLDIEL=WLDIEL+(POSNMIN(I)-POSNMIN(I-1));
               END;
           WLDIEL=WLDIEL*2.0E0/(SP*(POINTS-1));
          PUT SKIP(2) EDIT('NO. OF DATA POINTS = ',POINTS) (X(10),A,F(2)
          PUT SKIP EDIT('WAVELENGTH IN AIR =          ',WLAIR,' CM.')
            (X(10),A,F(10,5),A);
          PUT SKIP EDIT('WAVELENGTH IN DIELECTRIC = ',WLDIEL,' CM.')
            (X(10),A,F(10,5),A);
            FACTOR=4.342945;
              DO  I=1  TO  POINTS;
                  X(I)=0.25E0*(2.0E0*SP*(I-1)+1.0E0);
                  PMAX=EXP(-DBMAX(I)/FACTOR);
                  PMIN=EXP(-DBMIN(I)/FACTOR);
                  REXP(I)=LOG(PMAX-PMIN);
              END;
            A1=REXP(5)-REXP(POINTS-1);
            A2=REXP(6)-REXP(POINTS);
            AM=(A1+A2)/2.0E0;
            ET=WLAIR/WLDIEL;
            ADLD=AM/(2.0E0*(X(POINTS)-X(6)));
            ALPHAEST=ADLD/WLDIEL;
             E2=(WLAIR**2*ALPHAEST)/(PI*WLDIEL);
          PUT SKIP(2) EDIT('STRAIGHT LINE APPROXIMATION RESULTS:')
            (X(10),A);
          PUT SKIP EDIT('ALPHA(EST) = ',ALPHAEST) (X(20),A,F(10,7));
          PUT SKIP EDIT('DIEL. LOSS = ',E2) (X(20),A,F(10,7));
            A=ET+1;  ASQ=A**2;
            B=ET-1;  BSQ=B**2;
            ADLD=ADLD*0.25E0;
              DO  I=1  TO 400;
                 ADLD=1.005*ADLD;
                 DELTANOW=0;
                    DO  M=1  TO  POINTS;
                     PMAX=EXP(-DBMAX(M)/FACTOR);
                     PMIN=EXP(-DBMIN(M)/FACTOR);
                     ARG=-(2.0E0*ADLD*X(M));
                     EXSQ=(EXP(ARG))**2;
                     C=A+B*EXSQ;
                     D=ASQ-BSQ*EXSQ;
                     DSQ=D**2;
                     COR=8.0E0*ET*C/DSQ;
                     RCAL(M)=ARG+LOG(COR);
                     DELTANOW=DELTANOW+ABS(RCAL(M)-REXP(M));
                    END;
                 STEPS=I;
                 IF  I<2  THEN  GO  TO  LOOP1;
```

```
                CHANGE=DELTALAST-DELTANOW;
                IF CHANGE<=0 THEN GO TO RESULTS;
  LOOP1:        DELTALAST=DELTANOW;
              END;
      PUT SKIP(2) EDIT('ITERATION DISCONTNUED -- TOO MANY LOOPS.')
         (X(10),A);
      PUT SKIP(0) EDIT((40)'_') (X(10),A);
  RESULTS:EPS1=ET**2;
         EPS2=EPS1*ADLD/PI;
         TAND=EPS2/EPS1;
      PUT SKIP(2) EDIT('NO. OF ITERATION STEPS = ',STEPS) (X(10),
         A,F(3));
      PUT SKIP(2) EDIT('DELTA(MINIMUM) = ',DELTANOW)
         (X(10),A,F(10,7));
      PUT SKIP(2) EDIT('MINIMUM','LN (IMAX-IMIN)') (X(10),A,X(18),A);
      PUT SKIP EDIT ('NUMBER','EXPERIMENTAL','CALCULATED') (X(10),A,
         X(10),A,X(10),A);
      PUT SKIP(0) EDIT((6)'_',(12)'_',(10)'_') (X(10),A,X(10),A,
         X(10),A);
              DO I=1 TO POINTS;
                 PUT SKIP EDIT(I,REXP(I),RCAL(I)) (X(12),F(2),X(13),
                  F(10,7),X(11),F(10,7));
              END;
         W=2*PI*FREQ*1.0E+09;
      PUT SKIP(2) EDIT('FINAL RESULTS') (X(20),A);
      PUT SKIP(0) EDIT((13)'_') (X(20),A);
      PUT SKIP EDIT('FREQUENCY = ',FREQ,' GIGAHERTZ.')
         (X(20),A,F(9,4),A);
      PUT SKIP EDIT('=    ',FREQ/CLIGHT,'  WAVENUMBERS.')
         (X(30),A,F(6,3),A);
      PUT SKIP EDIT('OMEGA = ',W*1.0E-09, ' GIGARADIANS/SEC.')
         (X(24),A,F(9,4),A);
      PUT SKIP EDIT('(BASE 10)  LOG(OMEGA) =    ',LOG10(W))
         (X(8),A,F(7,4));
      PUT SKIP(2) EDIT('ALPHA = ',ADLD/WLDIEL,' NEPERS/CM.')
         (X(20),A,X(19),F(10,7),A);
      PUT SKIP(2) EDIT('EPSYLON 1 = ',EPS1) (X(20),A,X(15),F(8,5));
      PUT SKIP EDIT('EPSYLON 2 = ',EPS2) (X(20),A,X(15),F(8,5));
      PUT SKIP EDIT('LOSS TANGENT = ',TAND) (X(20),A,X(12),F(10,7));
      PUT SKIP EDIT('(EPSYLON 2) X (OMEGA) = ',EPS2*W)
         (X(20),A,X(4),E(11,5));
      PUT SKIP EDIT('(EPSYLON 2) / (OMEGA) = ',EPS2/W)
         (X(20),A,X(4),E(11,5));
   IF NODATA=1 THEN GO TO DATA2;
FINISHED:END INTER;
```

PROGRAM #2

for

MICROWAVE BRIDGE MEASUREMENTS

```
MOUNTAIN:PROCEDURE CPTIONS(MAIN);
DECLARE  (    C(0:20),D(0:20),E(0:20),X(0:20),Y(0:20),Z(0:20),
M(0:2),V(0:20),W(0:20),F,G,K ) BINARY FLCAT(30);
      PUT PAGE;
      LABEL1:
      PUT SKIP(4);
     CALL READ_TITLE;
              GET LIST (J);
      PUT SKIP;
      PUT EDIT ('DIELECTRIC CONSTANT AND LCSS.P.F.MOUNTAIN.CHEM.',
              'INPUT DATA','__________','VOL','ATTN','P.S.')
          (X(6),A(47),SKIP(2),A(10),COLUMN(0),A(10),SKIP,X(5),A(3),
              X(5),A(4),X(6),A(4));
      DO I=1 TO J BY 1;
      GET LIST (X(I),Y(I),Z(I));
      PUT EDIT (X(I)+.00005,Y(I)+.005,Z(I)+.05)
           (SKIP,F(9,4),F(8,2),F(9,1));
      C(I)=X(I);
      D(I)=Y(I);
      E(I)=Z(I);
V(I)=Y(I)*Y(I);
W(I)=Z(I)*Z(I);
      Y(I)=X(I)*Y(I);
      Z(I)=X(I)*Z(I);
      X(I)=X(I)*X(I);
      LABEL9: END;
      K=FLOAT(J);
      L=J-1;
 DO I=1 TO L BY 1;
      C(I+I)=C(I)+C(I+1);
      D(I+1)=D(I)+D(I+1);
E(I+1)=E(I)+E(I+1);
X(I+1)=X(I)+X(I+1);
Y(I+1)=Y(I+1)+Y(I);
Z(I+1)=Z(I)+Z(I+1);
V(I+1)=V(I)+V(I+1);
W(I+1)=W(I)+W(I+1);
LABEL10: END;
C(0)=C(J)/K;
D(0)=D(J)/K;
  E(0)=E(J)/K;
 C(0)=C(0)*C(J);
D(1)=D(0)*C(J);
E(1)=E(0)*C(J);
F=D(0)*D(J);
G=E(0)*E(J);
      D(0)=Y(J)-D(1);
E(0)=Z(J)-E(1);
C(0)=X(J)-C(0);
M(1)=D(0)/C(0);
M(2)=E(0)/C(0);
V(0)=V(J)-F;
      W(0)=W(J)-G;
V(0)=V(0)/C(0);
W(0)=W(0)/C(0);
M(0)=M(1)*M(1);
V(0)=V(0)-M(0);
```

```
M(0)=M(2)*M(2);
W(0)=W(0)-M(0);
K=K-1;
V(0)=V(0)/K;
W(0)=W(0)/K;
V(0)=SQRT(V(0));
W(0)=SQRT(W(0));
      V(0)=2.6*V(0);
      W(0)=2.6*W(0);
IF M(2)>1500 THEN GOTO LABEL2;
IF M(2)>500 THEN GOTO LABEL3;
IF M(2)>150 THEN GOTO LABEL4;
IF M(2)>50 THEN GOTO LABEL5;
IF M(2)>20 THEN GOTO LABEL6;
IF M(2)<20 THEN GOTO LABEL7;
LABEL2: C(0)=0.0055332;
D(0)=0.00083872;
E(0)=10.6077;
F=0.0046431;
G=0.4770;
K=43.98;
GOTO LABEL8;
      LABEL3: C(0)=0.029116;
D(0)=0.00441901;
E(0)=5.911;
F=0.018468;
G=0.37242;
K=22.061;
GOTO LABEL8;
LABEL4: C(0)=0.05304;
D(0)=0.00804;
E(0)=4.0752;
F=0.039568;
G=0.3443;
K=15.08;
GOTO LABEL8;
LABEL5: C(0)=0.14374;
D(0)=0.021784;
E(0)=2.7537;
F=0.086726;
G=0.34318;
K=10.18;
GOTO LABEL8;
LABEL6: C(0)=0.2675;
D(0)=0.040548;
E(0)=1.3834;
F=0.26263;
G=0.49579;
K=5.850;
GOTO LABEL8;
LABEL7: C(0)=0.63407;
D(0)=0.096096;
E(0)=1.0768;
F=0.50725;
G=0.41221;
K=3.3;
LABEL8: X(0)=M(1)*C(0);
```

```
  Y(0)=M(2)*D(0);
  PUT EDIT ('FREQ     E**     DE**       E*       DE*')
                (SKIP(3),A(39));
  Y(0)=Y(0)+E(0);
  Z(0)=X(0)*Y(0);
  Z(0)=2*Z(0);
  Z(0)=Z(0)*F;
  X(1)=V(0)*C(0);
  Y(1)=W(0)*D(0);
  M(1)=Y(0)*X(1);
  M(2)=X(0)*Y(1);
        M(1)=M(1)+M(2);
  M(1)=F*M(1);
  M(1)=2*M(1);
       PUT EDIT(K+.005,Z(0)+.000005,M(1)+.000005)
          (SKIP,F(5,2),F(9,5),F(9,5));
                                    Y(0)=Y(0)*Y(0);
  X(0)=X(0)*X(0);
  Y(0)=Y(0)-X(0);
  Y(0)=Y(0)*F;
  Y(0)=Y(0)+G;
  M(1)=Y(0)*Y(1);
  M(2)=X(0)*X(1);
  M(1)=M(1)+M(2);
  M(1)=F*M(1);
  M(1)=2*M(1);
        PUT EDIT (Y(0)+.00005,M(1)+.000005)(F(8,4),F(9,
  GOTO LABEL1;
READ_TITLE:PROCEDURE;
        DECLARE  CHAR CHARACTER(1);
  AGAIN:GET EDIT(CHAR) (A(1));
        IF CHAR ¬= '=' THEN GOTO AGAIN;
  TRY_AGAIN:  GET EDIT (CHAR)(A(1));
              IF CHAR ¬=';' THEN PUT EDIT (CHAR) (A(1))
              ELSE RETURN;
              GOTO TRY_AGAIN;
        END;
  END;
```

PROGRAM #3

for

GRANT CELL MEASUREMENTS

```
BRCH: PROC CPTIONS(MAIN);


        BRCH: PROC GPTIONS(MAIN);
                   DCL X(10),
                      Y(10),
                      TITLE CHAR(80) VARYING;
                   DCL LO DEC FLCAT(6);
                   ON ENDFILE (SYSIN) GOTO END;
          SS: GET LIST(TITLE,NN);
              DO IBQ=1 TO NN;
              PUT PAGE ECIT(TITLE, 'GRANT CELL LCW LOSS')(COLUMN(10),A,
              X(3),A);
              GET DATA(N);
              GET LIST(FREQ);
              PUT SKIP(2) EDIT('N = ',N, 'FREQ = ',FREQ) (COLUMN(10),A,
              F(4), X(7), A,F(9,4));
                   SI=0;
                   AV=0;
              DO I=1 TO N;
              GET LIST(X(I),Y(I));
              IF I=1 THEN GCTO END1;
                   SI=X(I)-X(I-1)+SI;
         END1: END;
                   P=3.14159;
                   LO=29.979/FREQ;
                   SA=2*SI/(N-1);
              IF Y(1)=0 THEN DO;
                   K=2; CA=X(1); END;
              ELSE DO;
                   K=1;
                   CA=0;
              DO I=K TO N;
                   C=X(I)-I*(SA/2);
                   CA=CA+C;
              END; CA=CA/(N-K+1);
              END;
              PUT SKIP EDIT('SHORT POSITION =', CA) (CCLUMN(10),A,F(7,3));
              DO I=K TO N;
              ZZ=(P*Y(I))/SA;
                   R=(SIN(ZZ))/SQRT(2-COS(ZZ)**2);
              A=ARCSINH(R)/(X(I)-CA);
              PUT SKIP EDIT('A',I,'=', A) (CCLUMN(10),A,F(1),A,F(10,6));
                   AV=AV+A;
              END;
                   AA=AV/(N-K+1);
                   E1=(LO/SA)**2-((LO*AA)/(2*P))**2;
                   E2=(LO**2*AA)/(P*SA);
                   W=2*P*FREQ;
                   W1=E2*W;
                   W2=E2/W;
              PUT SKIP(3) EDIT('X','Y') (CCLUMN(16),A,COLUMN(25),A);
             DO I=1 TO N;
             PUT SKIP(2) EDIT(X(I), Y(I)) (CCLUMN(10),2 F(9,4));
             END;
             PUT SKIP(2) EDIT('LO = ', LO, 'LM = ', SA, 'ALPHA (AVERAGE) = ',
                  AA, 'E1 = ', E1, 'E2 = ', E2, 'E2*W = ', W1, 'E2/W = ',
                  W2) (COLUMN(10),A,F(10,4), SKIP, COLUMN(10),A,F(10,4),
                  (5) (SKIP, COLUMN(10),A,F(10,6)));
             END;
```

```
     GOTO SS;
   ARCSINH: PROC(X);
      RETURN(LOG(X+SQRT(X*X+1)));
     END;
END: END BRCH;
```

PROGRAM #4

for

ANALYSES FOR τ_0, α and ε_∞

(PL/1)

```
MOUNTAIN: PROCEDURE OPTIONS (MAIN);


          MOUNTAIN: PROCEDURE OPTIONS (MAIN);
        ON SIZE SNAP SYSTEM;
         DECLARE (I(0:3),N(0:4),J,K) STATIC FIXED BINARY (31) ;
         DECLARE (A(0:4),D(0:3),E(0:2),L(0:3),U(0:3),X(0:4),Y(0:3),
        W(0:6),S(0:6),F(0:6),G(0:6),M(0:6),T(0:6),P,R,B,C,Z,H)
 STATIC FLOAT BINARY(30) ;
        SUBR:PROCEDURE(NN) RECURSIVE;
         DCL NN FIXED BINARY;
 DCL LABEL(30) LABEL;
        GOTO LABEL (NN);
        ON SUBSCRIPTRANGE SNAP SYSTEM;
               DCL CARD CHAR(80);
               LABEL(27):
 GET EDIT(CARD) (A(80));
 PUT PAGE EDIT(CARD) (A(80));
         GET LIST (J);
         DO K=1 TO J BY 1;
 GET LIST(G(K),F(K),W(K));
         END;
         GET LIST (X(1),X(2),X(3),B,C);
        L(1)=X(1)/20;
        U(1)=X(1)*10;
        L(2)=0;
        U(2)=0.9;
        L(3)=C;
        U(3)=B;
  PUT SKIP;
        PUT EDIT('TAO,EINF ANAL. P.MCUNTAIN','INPUT DATA',
        '-----------','N','EPS|','EPS"','FREQUENCY')
         (X(6),A(26),SKIP(2),A(10),SKIP  (0),A(10),SKIP,X(1),A(1),
         X(5),A(4),X(6),A(5),X(4),A(9));
         DO K=1 TO J BY 1;
         PUT EDIT (K,G(K)+.00005,F(K)+.00005,W(K)+.0000005)
       (SKIP,F(2),F(9,4),F(9,4), E(16,6));
         END;
       PUT EDIT (B+.00005,C+.00005)(SKIP,X(2),F(7,4),SKIP,X(2),F(7,4
       PUT SKIP(4);
      PUT EDIT ('FIRST GUESS','___________','TAO','ALPHA','EINF')
          (A(11),COLUMN(0),A(11),SKIP(2),X(5),A(3),X(10),A(5),
            X(12),A(4));
       PUT SKIP(4);
       PUT EDIT(X(1)+.00005E-10,X(2)+.00005E-10,X(3)+.005)
       (E(10,3),F(16,3),F(11,4));
       PUT SKIP(4);
      D(1)=0.2*X(1);
        D(2)=0.2*X(2);
        D(3)=B-C;
        D(3)=0.2*D(3);
        GOTO LABEL(26);
        LABEL(2):A(0)=0;
        DO K=1 TO J BY 1;
        S(0)=W(K);
        S(0)=S(0)*X(1);
        S(0)=LOG(S(0));
       S(1)=1-X(2);
       S(0)=S(1)*S(0);
       S(1)=EXP(S(0));
```

```
        S(2)=S(1)*S(1);
        S(3)=1-X(2);
        S(3)=S(3)/2;
        S(4)=COS(S(3) *3.1415927);
        S(5)=SIN(S(3) *3.1415927);
        S(6)=S(4)*S(1);
        S(4)=1+S(6);
        S(6)=S(4)+S(6);
        S(6)=S(6)+S(2);
        S(2)=S(1)*S(5);
        S(4)=S(4)/S(6);
        S(2)=S(2)/S(6);
        S(1)=B-X(3);
        S(4)=S(4)*S(1);
        S(2)=S(2)*S(1);
        S(4)=X(3)+S(4);
        M(K)=S(4);
        T(K)=S(2);
        S(0)=F(K)-S(2);
        S(0)=S(0)*S(0);
        A(0)=A(0)+S(0);
         S(0)=G(K)-S(4);
  S(0)=S(0)/4;
         S(0)=S(0)*S(0);
         A(0)=A(0)+S(0);
        S(0)=A(0)*X(2);
        A(0)=A(0)+S(0);
        END;
          RETURN;
          LABEL(26):N(0)=3;
          IF ¬(N(0)>0) THEN GOTO LABEL(17);
         DO I(0)=1 TO N(0) BY 1;
         IF U(I(0))<L(I(0)) THEN GOTO LABEL(17);
         Y(I(0))=X(I(0));
          END;
         PUT EDIT('I','X(I)','D(I)','A','STEPS')
        (SKIP(2),X(2),A(1),X(8),A(4),
                X(13),A(4),X(16),A(1),X(6),A(5));
         PUT SKIP(2);
          CALL SUBR (2);
          I(2)=0;
          A(1)=A(0);
          PUT EDIT (' ')(A(36));
  PUT EDIT(A(1)+.5E-8) (F(13,8));
         LABEL(18):I(1)=-2*N(0);
          I(3)=0;
          N(2)=1;
          N(4)=0;
  LABEL(4): DO N(1) =1 TO N(0);
          N(3)=0;
         DO I(0)=N(1) TO N(1)+(N(2)-1) BY 1;
       IF I(0)=3 THEN GOTO IAA;
      IAA:
         X(I(0))=Y(I(0))+D(I(0));
         IF X(I(0))>U(I(0)) THEN GOTO LABEL(6);
         IF ¬(X(I(0))<L(I(0))) THEN GOTO LABEL(7);
          LABEL(6):IF N(4)=1 THEN GOTO LABEL(10);
```

```
108         D(I(0))=-D(I(0));
109          LABEL(7):END;
110          LABEL(13):E(1)=0;
111         DO I(0)=N(1) TO N(1)+(N(2)-1) BY 1;
112    IF I(0)=3 THEN GOTO IAB;
114         X(I(0))=Y(I(0))+D(I(0));
115     IAB:
116         IF¬(X(I(0))>U(I(0))) THEN GOTO LABEL(8);
117         X(I(0))=U(I(0));
118         LABEL(8): IF¬(X(I(0))<L(I(0))) THEN GOTO LABEL(9
120         X(I(0))=L(I(0));
121        LABEL(9): E(0)=X(I(0))-Y(I(0));
122          E(0)=ABS(E(0));
123          E(1)=E(1)+E(0);
124          END;
125     I(0)=N(1)+N(2)-1;
126          CALL SUBR (2);
127          I(2)=1+I(2);
128    IF (ABS((A(0)-A(1))/A(1))-1E-9)<0
129       THEN GOTO LABEL(19);
130          IF ¬(A(0)<A(1)) THEN GOTO LABEL(10);
132         IF ¬(N(3)>0) THEN GOTO LABEL(11);
134          N(3)=1+N(3);
135          A(3)=A(1)-A(0);
136          A(3)=A(3)/E(1);
137          A(4)=A(2)-A(1);
138          A(4)=A(4)/E(2);
139          A(3)=A(3)-A(4);
140          A(3)=A(3)/A(4);
141          A(3)=A(3)*A(3);
142          A(3)=A(3)+.17;
143          A(3)=.3/A(3);
144         A(3)=A(3)+.25;
145          GOTO LABEL(12);
146          LABEL(11):N(3)=2;
147          A(3)=1;
148         LABEL(12): DO I(0)=N(1) TO N(1)+(N(2)-1) BY 1;
149         D(I(0))=A(3)*D(I(0));
150         Y(I(0))=X(I(0));
151          END;
152      I(0)=N(1)+N(2)-1 ;
153          A(2)=A(1);
154          A(1)=A(0);
155          LABEL(15): E(2)=E(1);
156          GOTO LABEL(13);
157          LABEL(10): IF ¬(N(4)=1) THEN GOTO LABEL(21);
159     IF N(4)=2 THEN GOTO LABEL(19);   N(4)=2;
162          E(0)=2;
163          CALL SUBR (5);
164          GOTO LABEL(18);
165          LABEL(21): IF N(3)>0 THEN GOTO LABEL(14);
167          N(3)=1;
168         D(I(0))=-D(I(0));
169          A(2)=A(0);
170          GOTO LABEL(15);
171          LABEL(14): IF N(3)=1 THEN GOTO LABEL(19);
173         I(3)=1+I(3);
```

```
       I(1)=0;
        LABEL(20): E(0)=4;
        CALL SUBR(5);
        IF I(3)=N(0) THEN GCTO LABEL(3);
END;
        GOTC LABEL(4);
        LABEL(3): N(2)=N(0);
        N(4)=1;
        GOTC LABEL(4);
        LABEL(19): I(1)=1+I(1);
        I(3)=0;
       IF ¬(I(1)>2*N(0)) THEN GOTO LABEL(20);
       LABEL(16): PUT EDIT('MINIMUM REACHED')(SKIP,A(15));
       PUT SKIP(2);
        N(3)=I(2)+1;
        N(1)=1;
        N(2)=N(0);
        CALL SUBR (22);
       LABEL(17): GCTO FINISH;
       LABEL(5): DO I(0)=N(1) TO N(1)+(N(2)-1) BY 1;
       D(I(C))=D(I(0))/E(C);
   IF I(0)=3 THEN GOTO IAC;
       X(I(C))=Y(I(0));
   IAC:
        END;
        I(C)=N(3)-1;
       LABEL (23):RETURN;
       LABEL(22): DO I(0)=N(1) TO N(1)+(N(2)-1) BY 1;
       PUT EDIT(I(0),X(I(0)))(SKIP,F(5),E(12,3));
        IF D(0)<.00001 THEN GOTO LABEL(24);
        IF D(C)>10000  THEN GOTO LABEL(24);
       PUT EDIT (D(I(0)))(F(10),A(6));
        GOTO LABEL(25);
       LABEL(24): PUT EDIT(D(I(0)))(E(18,5));
        LABEL(25): END;
       PUT EDIT (ROUND(A(1),8))(F(23,8));
       I(0)=N(3)-1;
       PUT EDIT (I(0),'E','E"')
       (F(9),SKIP(2),X(5),A(2),X(8),A(3),SKIP);
        DO K=1 TO J BY 1;
       PUT EDIT (ROUND(T(K),4),ROUNC(M(K),5),ROUND(W(K),9))
      (SKIP,F(9,4),F(9,4),E(18,5));
        END;
      RETURN;
        END;
NUMB:
        CALL SUBR(27);
       FINISH:
GO TO NUMB;
 QUIT:
        END;
```

PROGRAM # 5

for

ANALYSES FOR τ_1, τ_2 and C_1

(PL/1)

(SUBRG,SIZE):

```
 (SUBRG,SIZE):
         MOUNTAIN: PROCEDURE CPTIONS (MAIN);
ON ENDFILE(SYSIN) GO TO QUIT;
       ON SIZE SNAP SYSTEM;
         DCL SUBR ENTRY(FIXED BINARY);
 DCL (I0,I1,I2,I3,N0,N1,N2,N3,N4,J,K) STATIC FIXED BINARY(31,0
;
 DCL (A0,A1,A2,A3,A4,D(0:3),E0,E1,E2,L(0:3),U(0:3),X(0:4),
Y(0:3),W(0:16),F(0:16),G(0:16),M(0:16),T(0:16),S,P,R,B,C,Z,H)
STATIC
    FLOAT BINARY(30);
CCL ERR(16) FLOAT BIN(30) STATIC;
       SUBR:PROCEDURE(NN) RECURSIVE;
        DCL NN FIXED BINARY;
              DECLARE LABEL (30) LABEL;
       GOTO LABEL (NN);
       ON SUBSCRIPTRANGE SNAP SYSTEM;
              DCL CARD CHAR(80);
              LABEL(27):
GET LIST(CARD);
PUT PAGE EDIT(CARD) (A);
PUT SKIP(2);
        GET LIST (J);
        DO K=1 TO J BY 1;
 GET LIST(G(K),F(K),W(K),ERR(K));
        END;
        GET LIST (X(1),X(2),X(3),B,C);
        B=B-C;
        GET LIST (L(1));
        L(2)=L(1);
        GET LIST (U(1));
       U(2)=U(1);
       PUT EDIT('TA1,TA2 AHAL. P.MOUNTAIN','INPUT DATA',
'___________','N','EPS''','EPS"','FREQUENCY')
(X(6),A(26),SKIP(2),A,SKIP(0),A,SKIP,X(1),A,
        X(5),A(4),X(6),A(5),X(4),A(9));
        DO K=1 TO J BY 1;
PUT EDIT(K,G(K),F(K),W(K))
      (SKIP,F(2),F(9,4),F(9,4), E(16,6));
        END;
PUT EDIT(B,C) (SKIP,X(2),F(7,4),SKIP,X(2),F(7,4));
      PUT SKIP(4);
PUT EDIT('FIRST GUESS','___________','TA1','TA2','C1')
(A(11),SKIP(C),A,SKIP(2),X(5),A,X(10),A,
               X(12),A(2));
      PUT SKIP (4);
PUT EDIT(X(1),X(2),X(3))
      (E(10,3),E(16,3),F(11,2));
      PUT SKIP (4);
        D(1)=C.2*X(1);
        D(2)=C.2*X(2);
       D(3)=C.2*X(3);
        L(3)=C;
        U(3)=1;
       GOTO LABEL(26);
LABEL(2):
 A0=0;
```

```
        (SUBRG,SIZE):

 45                 X(4)=1-X(3);
 46                 DO K=1 TO J;
 47                S=W(K)*W(K)*X(1)*X(1)+1;
 48                    H=X(3)/S;
 49                    S=W(K)*X(1)*X(3)/S;
 50                    P=W(K)**2*X(2)**2+1;
 51                    Z=X(4)/P;
 52                    S=((W(K)*X(2)*X(4))/P+S)*B;
 53                    H=(H+Z)*B+C;
 54                    M(K)=S;
 55                    T(K)=H;
 56                    S=(F(K)-S)**2;
 57                H=((G(K)-H)/ERR(K))**2;
 58                    A0=A0+S+H;
 59                    END;
 60                       RETURN;
 61                LABEL(26):
                   N0=3;
 62                 DO I0=1 TO 3;
 63                IF U(I0)<L(I0) THEN GO TO LABEL(17);
 65                    Y(I0)=X(I0);
 66                    END;
 67                 PUT EDIT('I','X(I)','D(I)','A','STEPS')
                       (SKIP(2),X(2),A,X(8),A,X(13),A,X(16),A,X(6),A);
 68                PUT SKIP(2);
 69                        CALL SUBR (2);
 70                 I2=0;
 71                 A1=A0;
 72                PUT EDIT(A1) (X(36),F(13,8));
 73                LABEL(18):
                     I1=-2*N0;
 74                 I3=0;
 75                 N2=1;
 76                 N4=0;
 77                LABEL(4):
                     DO N1=1 TO N0;
 78                    N3=0;
 79                    DO I0=N1 TO N1+N2-1;
 80                      IF I0=3 THEN GO TO IAA;
 82                       X(I0)=Y(I0)+D(I0);     /* AUGMENT X */
 83                      IAA :
 84                IF X(I0)>U(I0) THEN GO TO LABEL(6);
 85                IF X(I0)>=L(I0) THEN GO TO LABEL(7);
 87                LABEL(6):
 88                IF N4=1 THEN GO TO LABEL(10);
 89                       D(I0)=-D(I0);
 90                        LABEL(7):END;
 91                LABEL(13): E1=0;
 92                    DO I0=N1 TO N1+N2-1;
 93                      IF I0=3 THEN GO TO IAB ;
 95                       X(I0)=Y(I0)+D(I0);
 96                      IAB :
 97                IF X(I0)<=U(I0) THEN GO TO LABEL(8);
 98                       X(I0)=U(I0);
 99                LABEL(8): IF X(I0)>=L(I0) THEN GO TO LABEL(9);
101                       X(I0)=L(I0);
102                LABEL(9): E0=ABS(X(I0)-Y(I0));
```

```
(SUBRG,SIZE):

                 E1=E1+E0;
                END;
         I0=N1+N2-1;
                 CALL SUBR (2);
         I2=1+I2;
           IF (ABS((A0-A1)/A1)-1E-9)<0 THEN GO TO LABEL(19);
         IF A0>=A1 THEN GO TO LABEL(10);
         IF N3<=0 THEN GO TO LABEL(11);
             N3=N3+1;
             A3=(A1-A0)/E1;
             A4=(A2-A1)/E2;
             A3=.3/(((A3-A4)/A4)**2+.17)+.25;
                 GOTO LABEL(12);
         LABEL(11): N3=2;
             A3=1;
         LABEL(12): DO I0=N1 TO N1+N2-1 BY 1;
                D(I0)=A3*D(I0);
                Y(I0)=X(I0);
                END;
         I0=N1+N2-1;
             A2=A1;
             A1=A0;
         LABEL(15): E2=E1;
                 GOTO LABEL(13);
         LABEL(10): IF N4¬=1 THEN GO TO LABEL(21);
         IF N4=2 THEN GO TO LABEL(19);
         N4=2;
             E0=2;
                 CALL SUBR (5);
                 GOTO LABEL(18);
         LABEL(21): IF N3>0 THEN GO TO LABEL(14);
             N3=1;
             D(I0)=-D(I0);
             A2=A0;
                 GOTO LABEL(15);
         LABEL(14): IF N3=1 THEN GO TO LABEL(19);
             I3=I3+1;
             I1=0;
         LABEL(20): E0=4;
                 CALL SUBR(5);
         IF I3=N0 THEN GO TO LABEL(3);
                 END;
                 GOTO LABEL(4);
         LABEL(3): N2=N0;
          N4=1;
                 GOTO LABEL(4);
         LABEL(19): I1=I1+1;
          I3=0;
         IF I1<=2*N0 THEN GO TO LABEL(20);
                LABEL(16): PUT EDIT('MINIMUM REACHED')(SKIP,A(15
                PUT SKIP(2);
          N3=I2+1;
          N1=1;
          N2=N0;
                 CALL SUBR (22);
                LABEL(17): GOTO FINISH;
         LABEL(5):
```

```
(SUBRG,SIZE):

         DO IO=N1 TO N1+N2-1;
             D(IO)=D(IO)/E0;
               IF IO=3 THEN GO TO IAC ;
             X(IO)=Y(IO);
              IAC :
                 END;
          IO=N3-1;
                LABEL (23):RETURN;
         LABEL(22): DO IO=N1 TO N1+N2-1;
             PUT EDIT(IO,X(IO))(SKIP,F(5),E(10,3));
                 IF D(0)<.00001 THEN GOTO LABEL(24);
                 IF D(0)>10000  THEN GOTO LABEL(24);
             PUT EDIT(D(IO),' ') (F(10),A(6));
                 GOTO LABEL(25);
         LABEL(24): PUT EDIT(D(IO)) (E(18,5));
                 LABEL(25): END;
          PUT EDIT (ROUND(A1,8)) (F(23,8));
          IO=N3-1;
          PUT EDIT (IO,'E''','E"')
         (F(9),SKIP(2),X(5),A,X(8),A);
          DO K=1 TO J;
         PUT EDIT(T(K),M(K),W(K))
          (SKIP,F(9,4),F(9,4),E(18,5));
             END;
                 RETURN;
                 END;
         NUMB:
                 CALL SUBR(27);
                FINISH:
         GO TO NUMB;
         QUIT:
                 END;
```

PROGRAM #6

for

ANALYSES FOR τ_o, α and ε_∞

(APL)

```
      ∇CONA[⎕]∇
    ∇ CONA;A0;A1;A2;A3;A4;DA;DAA;DEN;DI;E0;E1;E2;I0;I1;I2;
      I3;M;N0;N1;N2;N3;N4;P;PD;PDD;T;U;Y
[1]   Y←3⍴0
[2]   SUBRA 27
[3]   40 PLOT(0,F,(⍴F)⍴0) AND(0,((⍴F)⍴0),T) VS X[3],G,M
    ∇
      ∇SUBRA[⎕]∇
    ∇ SUBRA NN
[1]   →(NN= 2 5 22 27)/L2,L5,L22,L27
[2]  L27:'Y OR N?'
[3]   →('Y'ε,⍞)/L28
[4]   X←⎕,0⍴⎕←'TRIAL ESTIMATES.   ATT: TO NEW PAGE BEFORE R
      ETURN'
[5]   →L29
[6]  L28:SOLN←⎕,0⍴⎕←'SOLN'
[7]   G←⎕,0⍴⎕←'ε'''
[8]   F←⎕,0⍴⎕←'ε'''''
[9]   W←⎕,0⍴⎕←'FREQUENCIES'
[10]  B←⎕,0⍴⎕←'ε0SOLN'
[11]  C←⎕,0⍴⎕←'ε0SOLV'
[12]  X←⎕,0⍴⎕←'TRIAL ESTIMATES.  ATT: TO NEW PAGE BEFORE RE
      TURN'
[13] L29:SOLN
[14]  '                   INPUT_DATA       '
[15]  '     ε''MEAS     ε''''MEAS   FREQUENCY'
[16]  ⍉(3,⍴G)⍴G,F,W
[17]  '     NO. OF DATA POINTS = ';⍴G
[18]  ERR←4,0⍴⎕←'     ERROR RATIO = 4'
[19]  '     ε0SOLN = ';B
[20]  '     ε0SOLV =  ';C
[21]  '            TRIAL_ESTIMATES'
[22]  '      TAO        ALPHA        EINF '
[23]  ⍉ 3 1 ⍴X[1],X[2],X[3]
[24]  L←(X[1]÷20),0,C,0⍴U←(X[1]×10),
      0.9,B,0⍴D←0.2×(2↑X),B-C
[25]  →L26
[26] L2:M←X[3]+(DI←B-X[3])×PDD÷DEN←(PDD←1+PD)+(PD←P×
      2○○DAA←(DA)÷2)+(P←(W×X[1])*DA←1-X[2])*2
[27]  →0,0⍴A0←+/(⌽(1+X[2])*⍳⍴G)×((F-T←DI×P×(1○○DAA)÷DEN)*
      2)+((G-M)÷ERR)*2
[28] L26:N0←3×I0←1
[29]  →(∧/U<L,0⍴Y←X)/0
[30]  SUBRA 2
[31]  'INITIAL VALUE OF FACTOR TO BE MINIMIZED= ';A1←A0+I2←
      0
[32] L18:I1←-2×N0+I3←N4←0×N2←1
[33] L4:N1←1
[34] REP3:N3←0×I0←N1
[35] REP4:→(I0>3)/L7
[36]  X[I0]←Y[I0]+D[I0]
[37] IAA:→(X[I0]>U[I0])/L6
[38]  →(X[I0]≥L[I0])/L7
[39] L6:→(N4=1)/L10
[40]  D[I0]←-D[I0]
[41] L7:→((I0←I0+1)≤N1+N2-1)/REP4
[42] L13:E1←0×I0←N1
[43] REP5:→(I0>3)/L30
[44]  X[I0]←Y[I0]+D[I0]
[45] IAB:→(X[I0]≤U[I0])/L8
[46]  X[I0]←U[I0]
[47] L8:→(X[I0]≥L[I0])/L9
[48]  X[I0]←L[I0]
[49] L9:E0←|X[I0]-Y[I0]
```

```
[50]  E1←E1+E0
[51] L30:→((I0←I0+1)≤N1+N2-1)/REP5
[52]  I0←N1+N2-1
[53]  SUBRA 2
[54]  I2←1+I2
[55]  →(1E¯9>|(A0-A1)÷A1)/L19
[56]  →(A0≥A1)/L10
[57]  →(N3≤0)/L11
[58]  N3←N3+1
[59]  A3←(A1-A0)÷E1
[60]  A4←(A2-A1)÷E2
[61]  A3←(0.3÷(((A3-A4)÷A4)*2)+0.17)+
      0.25
[62]  →L12
[63] L11:N3←2,0ρA3←1
[64] L12:I0←N1
[65] REP6:D[I0]←A3×D[I0]
[66]  Y[I0]←X[I0]
[67]  →((I0←I0+1)≤N1+N2-1)/REP6
[68]  I0←N1+N2-1
[69]  A2←A1
[70]  A1←A0
[71] L15:E2←E1
[72]  →L13
[73] L10:→(N4≠1)/L21
[74]  →(N4=2)/L19
[75]  N4←2,0ρE0←2
[76]  SUBRA 5
[77]  →L18
[78] L21:→(N3>0)/L14
[79]  N3←1
[80]  D[I0]←-D[I0]
[81]  A2←A0
[82]  →L15
[83] L14:→(N3=1)/L19
[84]  I3←I3+1+I1←0
[85] L20:E0←4
[86]  SUBRA 5
[87]  →(I3=N0)/L3
[88]  →((N1←N1+1)≤N0)/REP3
[89]  →L4
[90] L3:N2←N0,0ρN4←1
[91]  →L4
[92] L19:I1←I1+1+I3←0
[93]  →(I1≤2×N0)/L20
[94]  'FINAL VALUE OF FACTOR TO BE MINIMIZED=    ';A1
[95]  N3←I2+N1+1,0ρN2←N0
[96]  SUBRA 22
[97]  →0
[98] L5:I0←N1
[99] REP7:→(I0>3)/IAC
[100] D[I0]←D[I0]÷E0
[101] X[I0]←Y[I0]
[102]IAC:→((I0←I0+1)≤N1+N2-1)/REP7
[103] I0←N3-1
[104]L23:→0
[105]L22:'         X            D'
[106] ⍉ 2 3 ρX,D
[107] '                    F̲I̲N̲A̲L̲ V̲A̲L̲U̲E̲S̲ '
[108] '     ∊''CALC     ∊''''CALC     FREQUENCY'
[109] ⍉(3,ρG)ρM,T,W
    ∇
```

PROGRAM #7

for

ANALYSES FOR τ_1, τ_2 and C_1

(APL)

```
     ∇CONB[⎕]∇
   ∇ CONB;A0;A1;A2;A3;A4;D;E0;E1;E2;I0;I1;I2;I3;M;N0;N1;N2
     ;N3;N4;T;Y;WT1;WT2;R1;R2;PP
[1]    Y←4⍴0
[2]    SUBRB 27
[3]    PP←C
[4]    50 PLOT(0,F,(⍴F)⍴0) AND(0,((⍴F)⍴0),M) VS C,G,T
   ∇
     ∇SUBRB[⎕]∇
   ∇ SUBRB NN
[1]    →(NN= 2 27 22 5)/L2,L27,L22,L5
[2]   L27:'Y OR N ?'
[3]    →('Y'∊,⍞)/L28
[4]    B←B-C←⎕,0⍴⍞←'∊INF'
[5]    X←⎕,0⍴⍞←'ENTER TRIAL ESTIMATES. ATT: TO NEW PAGE BEFO
       RE RETURN'
[6]    →L29
[7]   L28:SOLN←⎕,0⍴⍞←'SOLN'
[8]    G←⎕,0⍴⍞←' ∊'''
[9]    F←⎕,0⍴⍞←' ∊'''''
[10]   W←⎕,0⍴⍞←' FREQUENCY'
[11]   B←⎕,0⍴⍞←'∊0SOLN'
[12]   B←B-C←⎕,0⍴⍞←'∊INF'
[13]   L←⎕,0⍴⍞←'LOWER LIMITS'
[14]   U←⎕,0⍴⍞←'UPPER LIMITS'
[15]   X←⎕,0⍴⍞←'TRIAL ESTIMATES. ATT: TO NEW PAGE BEFORE RET
       URN'
[16]  L31:SOLN
[17]   '                 INPUT_DATA                 '
[18]   '      ∊''MEAS      ∊''''MEAS    FREQUENCY'
[19]   ⍉(3,⍴G)⍴G,F,W
[20]   '      NO. OF DATA POINTS = ';⍴G
[21]   ERR←4,0⍴⍞←'      ERROR RATIO = 4 '
[22]   '      ∊0SOLN = ';B+C
[23]   '      ∊INF = ';C
[24]   '                 TRIAL_ESTIMATES
            TAI           TA2            C1       '
[25]   ⍉ 3 1 ⍴X[1],X[2],X[3]
[26]   L←L,0
[27]   U←U,1
[28]  L29:D←0.2×X←X,0
[29]   →L26
[30]  L2:M←B×(WT1×R1←X[3]÷1+(WT1←X[1]×W)*2)+WT2×R2←(X[
       4]←1-X[3])÷1+(WT2←X[2]×W)*2
[31]   →0,A0←+/((F-M)*2)+((G-T←C+B×R1+R2)÷ERR)*2
[32]  L26:N0←3×I0←1
[33]  REP1:→(U[I0]<L[I0])/0
[34]   Y[I0]←X[I0]
[35]   →((I0←I0+1)≤3)/REP1
[36]   SUBRB 2
[37]   A1←A0+I2←0
[38]   'INITIAL VALUE OF FACTOR TO BE MINIMIZED= ';A1
[39]  L18:I1←-2×N0+I3←N4←0×N2←1
[40]  L4:N1←1
[41]  REP2:I0←N1+N3←0
[42]  REP3:→(I0<1)/L7
[43]   X[I0]←Y[I0]+D[I0]
[44]  IAA:→(X[I0]>U[I0])/L6
[45]   →(X[I0]≥L[I0])/L7
[46]  L6:→(N4=1)/L10
[47]   D[I0]←-D[I0]
[48]  L7:→((I0←I0+1)≤N1+N2-1)/REP3
[49]  L13:I0←N1+E1←0
[50]  REP4:→(I0<1)/L30
[51]   X[I0]←Y[I0]+D[I0]
```

```
[52] IAB:→(X[I0]≤U[I0])/L8
[53]  X[I0]←U[I0]
[54] L8:→(X[I0]≥L[I0])/L9
[55]  X[I0]←L[I0]
[56] L9:E0←|X[I0]-Y[I0]
[57]  E1←E1+E0
[58] L30:→((I0←I0+1)≤N1+N2-1)/REP4
[59]  I0←N1+N2-1
[60]  SUBRB 2
[61]  I2←1+I2
[62]  →(1E¯9>|(A0-A1)÷A1)/L19
[63]  →(A0≥A1)/L10
[64]  →(N3≤0)/L11
[65]  N3←N3+1
[66]  A3←(A1-A0)÷E1
[67]  A4←(A2-A1)÷E2
[68]  A3←0.25+0.3÷0.17+((A3-A4)÷A4)*2
[69]  →L12
[70] L11:N3←2×A3←1
[71] L12:I0←N1
[72] REP5:D[I0]←A3×D[I0]
[73]  Y[I0]←X[I0]
[74]  →((I0←I0+1)≤N1+N2-1)/REP5
[75]  I0←N1+N2-1
[76]  A1←A0+0×A2←A1
[77] L15:E2←E1
[78]  →L13
[79] L10:→(N4≠1)/L21
[80]  →(N4=2)/L19
[81]  N4←2
[82]  E0←2
[83]  SUBRB 5
[84]  →L18
[85] L21:→(N3>0)/L14
[86]  N3←1
[87]  D[I0]←-D[I0]
[88]  A2←A0
[89]  →L15
[90] L14:→(N3=1)/L19
[91]  I3←I3+1+I1←0
[92] L20:E0←4
[93]  SUBRB 5
[94]  →(I3=N0)/L3
[95]  →((N1←N1+1)≤N0)/REP2
[96]  →L4
[97] L3:N2←N0×N4←1
[98]  →L4
[99] L19:I1←I1+1+I3←0
[100] →(I1≤2×N0)/L20
[101]L16:N3←I2+N1←1+0×N2←N0
[102] SUBRB 22
[103] →0
[104]L5:I0←N1
[105]REP6:D[I0]←D[I0]÷E0
[106] →(I0<1)/IAC
[107] X[I0]←Y[I0]
[108]IAC:→((I0←I0+1)≤N1+N2-1)/REP6
[109] I0←N3-1
[110]L23:→0
[111]L22:'FINAL VALUE OF FACTOR TO BE MINIMIZED= ';A1
[112] '       X                   D'
[113] ⍉ 2 3 ρ(3↑X),3↑D
[114] '                FINAL VALUES          '
[115] '    ϵ''CALC    ϵ''''CALC   FREQUENCY  '
[116] ⍉(3,ρW)ρT,M,W
```

PROGRAM #8

for

ANALYSES FOR LIMITING VALUES OF RELAXATION TIME

```
        ∇HI[⎕]∇
      ∇ HI
[1]     ALPHA←⎕,0ρ⎕←'ENTER α''S'
[2]     TAU←⎕,0ρ⎕←'ENTER TAU''S'
[3]     S←1
[4]     'ALPHA   EXP(A/2)   TAOE12   TAU1E12   TAU2E12   '
[5]    L5:ALP←ALPHA[S],ι0
[6]     T0←TAU[S]
[7]     TLMTNEW
[8]     S←1+S
[9]     →(S≤ρALPHA)/L5
[10]    →0
      ∇
        ∇TLMTNEW[⎕]∇
      ∇ TLMTNEW
[1]     FACT←0.1
[2]     RHS←(3○((○1÷4)×(1-ALP)))
[3]     →((+/ALP≥0.01)=ρALP)/2+⌶26
[4]     →0,ρ⎕←' α VALUE TOO SMALL '
[5]     A←(37.6×ALP)*0.5
[6]    L7:LHS←(2÷A)×¯3○(5○A÷2)
[7]     →((+/(|DIFFN←(LHS-RHS))≤0.001)=ρALP)/END
[8]     →((+/(DIFFN<0))=ρALP)/L12
[9]     A←A×(1+FACT)
[10]    →L7
[11]   L12:A←A÷(1+FACT)
[12]    FACT←FACT÷10
[13]    →(FACT≤1E¯5)/END
[14]    →L7
[15]   END:AE←*(A÷¯2)
[16]    EA←*(A÷2)
[17]    ⎕←PARAMETERS←ALP,EA,T0,(T0×AE),T0×EA
      ∇
```

APPENDIX II

DIELECTRIC CONSTANTS AND LOSSES FOR SEVERAL ALIPHATIC BROMIDES AND AMINES IN DILUTE SOLUTIONS AT 25°C

(Calculated values are in terms of Cole-Cole distribution unless otherwise stated)

Frequency(GHz)	ϵ'measured	ϵ'calculated	ϵ''measured	ϵ''calculated
n-Bromooctane in cyclohexane f_2 = 0.07075				
141	2.061	2.043	0.0312	0.0299
70.6	2.065	2.057	0.0503	0.0465
35.1	2.093	2.081	0.0663	0.0674
24.0	2.112	2.101	0.0807	0.0786
16.2	2.131	2.126	0.0888	0.0876
9.32	2.159	2.167	0.0894	0.0923
2.45	2.258	2.250	0.0731	0.0640
1.95	2.262	2.259	0.0696	0.0569
1.45	2.280	2.268	0.0567	0.0483
0.002	2.2992		(A = 0.0010962)	
2-Bromooctane in cyclohexane f_2 = 0.06969				
141	2.052	2.041	0.0380	0.0308
70.6	2.064	2.053	0.0540	0.0540
35.1	2.090	2.081	0.0854	0.0880
24.0	2.119	2.108	0.1067	0.1077
16.2	2.155	2.146	0.1277	0.1231
9.32	2.207	2.209	0.1258	0.1260
2.45	2.323	2.309	0.0719	0.0658
1.95	2.327	2.316	0.0612	0.0554
0.002	2.3370		(A = 0.0003744)	

Frequency(GHz)	ϵ'measured	ϵ'calculated	ϵ''measured	ϵ''calculated
4-Bromooctane in cyclohexane f_2 = 0.06999				
141	2.053	2.041	0.0342	0.0226
70.6	2.056	2.047	0.0483	0.0429
35.1	2.068	2.066	0.0751	0.0781
24.0	2.097	2.088	0.1009	0.1027
16.2	2.125	2.124	0.1266	0.1267
9.32	2.187	2.194	0.1426	0.1411
2.45	2.327	2.315	0.0756	0.0719
1.95	2.336	2.322	0.0604	0.0593
0.002	2.3382		(A = 0.0003149)	
n-Bromodecane in cyclohexane f_2 = 0.07034				
141	2.059	2.051	0.027	0.023
70.6	2.066	2.061	0.037	0.037
35.1	2.082	2.079	0.054	0.057
24.0	2.103	2.095	0.071	0.069
16.2	2.117	2.117	0.082	0.080
9.32	2.160	2.156	0.089	0.090
2.45	2.238	2.243	0.067	0.067
1.95	2.253	2.252	0.061	0.059
1.45	2.261	2.262	0.060	0.050
0.002	2.2930		(A = 0.0003505)	

Frequency(GHz)	ϵ'measured	ϵ'calculated	ϵ''measured	ϵ''calculated
n-Bromododecane in cyclohexane $f_2 = 0.06976$				
141	2.058	2.055	0.0225	0.0193
70.6	2.064	2.062	0.0320	0.0314
35.1	2.076	2.078	0.0457	0.0487
24.0	2.093	2.091	0.0584	0.0595
16.2	2.107	2.109	0.0731	0.0702
9.32	2.135	2.142	0.0815	0.0806
2.45	2.224	2.225	0.0630	0.0653
1.95	2.227	2.235	0.0568	0.0588
1.45	2.243	2.245	0.0553	0.0504
0.002	2.2790		(A = 0.0002207)	
n-Bromohexadecane in cyclohexane $f_2 = 0.06979$				
141	2.066	2.059	0.0233	0.0213
70.6	2.072	2.068	0.0370	0.0334
35.1	2.087	2.085	0.0459	0.0498
24.0	2.100	2.098	0.0576	0.0598
16.2	2.110	2.116	0.0713	0.0697
9.32	2.139	2.148	0.0817	0.0796
2.45	2.228	2.230	0.0674	0.0683
1.95	2.238	2.241	0.0643	0.0626
1.45	2.254	2.253	0.0582	0.0549
0.002	2.2960		(A = 0.0003988)	

Frequency(GHz)	ϵ'measured	ϵ'calculated	ϵ''measured	ϵ''calculated
n-Bromooctadecane in cyclohexane f_2 = 0.07007				
141	2.067	2.062	0.0208	0.0175
70.6	2.068	2.070	0.0300	0.0282
35.1	2.079	2.083	0.0395	0.0436
24.0	2.098	2.094	0.0521	0.0535
16.2	2.104	2.110	0.0644	0.0636
9.32	2.130	2.140	0.0767	0.0747
2.45	2.225	2.220	0.0609	0.0656
1.95	2.241	2.241	0.0546	0.0522
0.002	2.2798	(A = 0.0002593)		
1,10-Dibromodecane in cyclohexane f_2 = 0.06998				
141	2.097	2.095	0.0502	0.0355
70.6	2.121	2.106	0.0820	0.0635
35.1	2.135	2.136	0.1010	0.1081
24.0	2.176	2.166	0.1284	0.1376
16.2	2.211	2.212	0.1632	0.1662
9.32	2.296	2.299	0.1898	0.1869
2.45	2.490	2.472	0.1166	0.1139
1.95	2.504	2.486	0.0995	0.0969
1.45	2.523	2.499	0.0849	0.0776
0.002	2.5271	(A = 0.0020059)		

Frequency(GHz)	ϵ' measured	ϵ' calculated	ϵ'' measured	ϵ'' calculated
n-Butylamine in p-dioxane f_2 = 0.1478				
142	2.314	2.272	0.1174	0.0983
70.5	2.376	2.337	0.1480	0.1550
35.1	2.489	2.445	0.1774	0.1797
16.2	2.564	2.555	0.1542	0.1388
9.32	2.606	2.597	0.1080	0.0950
2.45	2.648	2.627	0.0371	0.0300
1.95	2.655	2.628	0.0361	0.0242
1.45	2.657	2.629	0.0261	0.0185
0.002	2.6319		(A = 0.0028174)	
n-Butylamine in cyclohexane f_2 = 0.0960				
145	2.089	2.068	0.0771	0.0745
70.4	2.122	2.122	0.0749	0.0750
35.1	2.153	2.158	0.0483	0.0497
24.0	2.142	2.167	0.0337	0.0361
16.2	2.174	2.171	0.0312	0.0251
9.32	2.186	2.174	0.0208	0.0147
2.45	2.177	2.175	0.0075	0.0039
1.95	2.176	2.175	0.0065	0.0031
1.45	2.177	2.175	0.0058	0.0023
0.002	2.1753		(A = 0.0002032)	

Frequency (GHz)	ϵ' measured	ϵ' calculated	ϵ'' measured	ϵ'' calculated
n-Butylamine in cyclohexane $f_2 = 0.1445$				
145	2.124	2.118	0.1180	0.1120
70.4	2.191	2.192	0.1009	0.1105
35.1	2.232	2.245	0.0840	0.0816
24.0	2.242	2.263	0.0642	0.0637
16.2	2.276	2.274	0.0530	0.0476
9.32	2.296	2.282	0.0374	0.0304
2.45	2.298	2.289	0.0129	0.0096
1.95	2.294	2.289	0.0111	0.0079
1.45	2.294	2.290	0.0092	0.0061
0.002	2.2914		(A = 0.0006850)	
n-Butylamine in cyclohexane $f_2 = 0.1908$				
145	2.090	2.126	0.1456	0.1540
70.4	2.254	2.245	0.1485	0.1758
35.1	2.304	2.340	0.1151	0.1276
24.0	2.333	2.367	0.0935	0.0948
16.2	2.373	2.381	0.0844	0.0668
9.32	2.390	2.390	0.0528	0.0394
2.45	2.398	2.394	0.0207	0.0105
1.95	2.388	2.394	0.0146	0.0083
1.45	2.393	2.384	0.0122	0.0062
0.002	2.3940		(A = 0.0030647)	

Frequency (GHz)	ϵ' measured	ϵ' calculated	ϵ'' measured	ϵ'' calculated
n-Hexylamine in p-dioxane $f_2 = 0.1549$				
142	2.221	2.256	0.0604	0.0669
70.5	2.317	2.296	0.1196	0.1120
35.1	2.367	2.374	0.1443	0.1436
24.0	2.406	2.426	0.1312	0.1413
16.2	2.488	2.472	0.1227	0.1237
9.32	2.527	2.514	0.0882	0.0883
2.45	2.559	2.546	0.0440	0.0285
1.95	2.566	2.548	0.0289	0.0231
0.002	2.5513		(A = 0.0009012)	
n-Hexylamine in cyclohexane $f_2 = 0.1005$				
145	2.071	2.062	0.0653	0.0645
70.3	2.115	2.109	0.0779	0.0780
35.1	2.158	2.155	0.0570	0.0633
24.0	2.187	2.170	0.0565	0.0497
16.2	2.179	2.180	0.0382	0.0367
9.32	2.183	2.186	0.0247	0.0227
2.45	2.205	2.190	0.0105	0.0066
1.95	2.200	2.191	0.0089	0.0053
1.45	2.204	2.191	0.0072	0.0040
0.002	2.1912		(A = 0.0002330)	

Frequency (GHz)	ϵ' measured	ϵ' calculated	ϵ'' measured	ϵ'' calculated
n-Hexylamine in cyclohexane $f_2 = 0.1521$				
145	2.110	2.089	0.0850	0.0832
70.3	2.161	2.151	0.1078	0.1096
35.1	2.236	2.220	0.0944	0.0952
24.0	2.266	2.245	0.0785	0.0762
16.2	2.265	2.261	0.0618	0.0567
9.32	2.263	2.272	0.0363	0.0351
2.45	2.272	2.278	0.0138	0.0100
1.95	2.272	2.278	0.0117	0.0080
1.45	2.275	2.279	0.0096	0.0060
0.002	2.2791		(A = 0.0002420)	
n-Hexylamine in cyclohexane $f_2 = 0.2012$				
145	2.123	2.104	0.1405	0.1340
70.3	2.216	2.201	0.1461	0.1570
35.1	2.301	2.290	0.1263	0.1276
24.0	2.349	2.321	0.1103	0.1014
16.2	2.318	2.341	0.0876	0.0759
9.32	2.351	2.356	0.0495	0.0480
2.45	2.380	2.366	0.0177	0.0145
1.95	2.376	2.367	0.0149	0.0117
1.45	2.380	2.367	0.0121	0.0089
0.002	2.3682		(A = 0.0009244)	

Frequency (GHz)	$\epsilon'_{measured}$	$\epsilon'_{calculated}$	$\epsilon''_{measured}$	$\epsilon''_{calculated}$
n-Nonylamine in p-dioxane $f_2 = 0.1481$				
141	2.248	2.240	0.0749	0.0710
35.1	2.336	2.347	0.1146	0.1207
24.0	2.369	2.386	0.1164	0.1183
16.2	2.450	2.423	0.1144	0.1068
9.32	2.476	2.461	0.0839	0.0827
2.45	2.512	2.501	0.0286	0.0329
1.95	2.517	2.506	0.0241	0.0218
0.002	2.5134		(A = 0.0005512)	
n-Nonylamine in cyclohexane $f_2 = 0.1005$				
145	2.104	2.093	0.0602	0.0597
70.5	2.131	2.129	0.0681	0.0673
35.1	2.144	2.166	0.0609	0.0628
24.0	2.177	2.183	0.0562	0.0562
16.2	2.201	2.197	0.0511	0.0480
9.32	2.211	2.212	0.0345	0.0363
1.45	2.222	2.232	0.0101	0.0110
0.002	2.2373		(A = 0.0002439)	

Frequency (GHz)	$\epsilon'_{\text{measured}}$	$\epsilon'_{\text{calculated}}$	$\epsilon''_{\text{measured}}$	$\epsilon''_{\text{calculated}}$
n-Nonylamine in cyclohexane f_2 = 0.1594				
145	2.142	2.128	0.0809	0.0793
70.5	2.192	2.179	0.1001	0.1002
35.1	2.218	2.238	0.0979	0.1012
24.0	2.269	2.268	0.0950	0.0927
16.2	2.298	2.293	0.0871	0.0797
9.32	2.307	2.318	0.0562	0.0596
1.45	2.347	2.349	0.0172	0.0163
0.002	2.3554		(A = 0.0003248)	
n-Nonylamine in cyclohexane f_2 = 0.2007				
145	2.179	2.162	0.1046	0.1008
70.5	2.239	2.226	0.1299	0.1332
35.1	2.315	2.308	0.1390	0.1393
24.0	2.344	2.350	0.1299	0.1286
16.2	2.382	2.386	0.1189	0.1108
9.32	2.427	2.421	0.0819	0.0823
1.45	2.457	2.462	0.0224	0.0215
0.002	2.4698		(A = 0.0002991)	

Frequency (GHz)	ϵ' measured	ϵ' calculated	ϵ'' measured	ϵ'' calculated
n-Decylamine in p-dioxane $f_2 = 0.1526$				
142	2.268	2.283	0.0782	0.0795
70.5	2.343	2.327	0.1257	0.1164
35.1	2.381	2.396	0.1400	0.1476
24.0	2.399	2.442	0.1444	0.1561
16.2	2.508	2.492	0.1689	0.1554
9.32	2.562	2.557	0.1281	0.1386
2.45	2.653	2.651	0.0715	0.0728
1.95	2.658	2.659	0.0655	0.0629
0.002	2.6954		(A = 0.0028050)	
n-Decylamine in cyclohexane $f_2 = 0.0935$				
145	2.091	2.098	0.0521	0.0459
70.2	2.092	2.132	0.0660	0.0682
35.1	2.145	2.180	0.0575	0.0651
24.0	2.165	2.200	0.0533	0.0531
16.2	2.183	2.210	0.0510	0.0395
9.32	2.200	2.218	0.0335	0.0240
1.45	2.211	2.213	0.0144	0.0359
0.002	2.2224		(A = 0.0011009)	

Frequency (GHz)	ϵ' measured	ϵ' calculated	ϵ'' measured	ϵ'' calculated
n-Decylamine in cyclohexane $f_2 = 0.1494$				
145	2.110	2.097	0.0791	0.0661
70.2	2.152	2.143	0.0778	0.0862
35.1	2.193	2.196	0.0820	0.0826
24.0	2.229	2.220	0.0751	0.0714
16.2	2.251	2.238	0.0618	0.0573
9.32	2.266	2.253	0.0418	0.0389
2.45	2.280	2.265	0.0159	0.0130
1.95	2.280	2.266	0.0142	0.0107
0.002	2.2683		(A = 0.0005317)	
n-Decylamine in cyclohexane $f_2 = 0.2017$				
145	2.116	2.124	0.0830	0.0808
70.2	2.194	2.179	0.1056	0.1091
35.1	2.252	2.248	0.1090	0.1090
24.0	2.294	2.281	0.0974	0.0959
16.2	2.324	2.306	0.0791	0.0781
9.32	2.340	2.327	0.0565	0.0536
2.45	2.354	2.345	0.0225	0.0181
1.95	2.334	2.346	0.0187	0.0149
0.002	2.3495		(A = 0.0002471)	

Frequency (GHz)	ϵ' measured	ϵ' calculated	ϵ'' measured	ϵ'' calculated
	n-Undecylamine in cyclohexane	$f_2 = 0.1007$		
145	2.083	2.078	0.0444	0.0388
70.2	2.112	2.105	0.0455	0.0531
35.1	2.140	2.139	0.0532	0.0532
24.0	2.162	2.155	0.0479	0.0466
16.2	2.174	2.167	0.0402	0.0376
9.32	2.181	2.177	0.0270	0.0255
0.002	2.1873		(A = 0.0002114)	
	n-Undecylamine in cyclohexane	$f_2 = 0.2007$		
145	2.140	2.130	0.0688	0.0655
70.2	2.190	2.171	0.0958	0.0979
35.1	2.245	2.241	0.1035	0.1055
24.0	2.288	2.275	0.0962	0.0942
16.2	2.313	2.301	0.0813	0.0764
9.32	2.331	2.322	0.0540	0.0512
0.002	2.3400		(A = 0.0001387)	

Frequency (GHz)	$\epsilon'_{measured}$	$\epsilon'_{calculated}$	$\epsilon''_{measured}$	$\epsilon''_{calculated}$
2-Nonylamine in p-dioxane $f_2 = 0.1467$				
141	2.236	2.238	0.0443	0.0422
35.1	2.291	2.299	0.1150	0.1143
24.0	2.315	2.338	0.1266	0.1326
16.2	2.415	2.387	0.1450	0.1402
9.32	2.465	2.454	0.1231	0.1261
2.45	2.529	2.532	0.0517	0.0533
1.45	2.542	2.541	0.0413	0.0344
0.002	2.5495		(A = 0.0003331)	
2-Nonylamine in cyclohexane $f_2 = 0.0998$				
70.6	2.093	2.084	0.0673	0.0636
35.1	2.124	2.122	0.0602	0.0653
16.2	2.153	2.158	0.0539	0.0516
9.32	2.179	2.174	0.0413	0.0385
2.45	2.197	2.191	0.0191	0.0153
1.95	2.195	2.193	0.0167	0.0129
1.45	2.198	2.194	0.0141	0.0103
0.002	2.1976		(A = 0.0002971)	

Frequency (GHz)	$\epsilon'_{measured}$	$\epsilon'_{calculated}$	$\epsilon''_{measured}$	$\epsilon''_{calculated}$
2-Nonylamine in cyclohexane f_2 = 0.1483				
70.6	2.123	2.106	0.0903	0.0871
35.1	2.150	2.158	0.0877	0.0937
16.2	2.219	2.213	0.0832	0.0791
9.32	2.249	2.240	0.0637	0.0615
2.45	2.282	2.270	0.0290	0.0263
1.95	2.278	2.272	0.0253	0.0223
1.45	2.284	2.275	0.0210	0.0180
0.002	2.2826		(A = 0.0004670)	
2-Nonylamine in cyclohexane f_2 = 0.1987				
145	2.101	2.088	0.0710	0.0738
70.6	2.151	2.134	0.1240	0.1105
35.1	2.197	2.207	0.1175	0.1300
24.0	2.250	2.250	0.1210	0.1255
16.2	2.288	2.289	0.1176	0.1107
9.32	2.319	2.327	0.0868	0.0824
2.45	2.338	2.362	0.0366	0.0304
1.95	2.335	2.364	0.0300	0.0251
1.45	2.380	2.366	0.0292	0.0197
0.002	2.3715		(A = 0.0016470)	

Frequency (GHz)	ϵ' measured	ϵ' calculated	ϵ'' measured	ϵ'' calculated
5-Nonylamine in p-dioxane $f_2 = 0.1488$				
141	2,232	2.231	0.0554	0.0491
70.6	2.267	2.269	0.0952	0.0901
35.1	2.291	2.310	0.1037	0.1074
16.2	2.395	2.386	0.1069	0.1046
9.32	2.433	2.428	0.0829	0.0817
2.45	2.478	2.466	0.0295	0.0303
1.45	2.477	2.470	0.0226	0.0193
0.002	2.4745		(A = 0.0001935)	
5-Nonylamine in cyclohexane $f_2 = 0.0990$				
70.6	2.088	2.074	0.0589	0.0574
35.1	2.109	2.110	0.0556	0.0586
16.2	2.142	2.142	0.0466	0.0440
9.32	2.172	2.155	0.0331	0.0312
2.45	2.168	2.167	0.0126	0.0112
1.95	2.173	2.167	0.0109	0.0093
0.002	2.1700		(A = 0.0001873)	

Frequency (GHz)	$\epsilon'_{measured}$	$\epsilon'_{calculated}$	$\epsilon''_{measured}$	$\epsilon''_{calculated}$
5-Nonylamine in cyclohexane f_2 = 0.1506				
70.6	2.118	2.102	0.0819	0.0809
35.1	2.155	2.153	0.0828	0.0845
16.2	2.214	2.200	0.0669	0.0658
9.32	2.230	2.220	0.0509	0.0478
2.45	2.249	2.240	0.0262	0.0178
1.95	2.250	2.241	0.0151	0.0148
0.002	2.2459		(A = 0.0002350)	
5-Nonylamine in cyclohexane f_2 = 0.1985				
145	2.087	2.077	0.0692	0.0710
70.6	2.142	2.126	0.1201	0.1111
35.1	2.182	2.205	0.1095	0.1223
24.0	2.240	2.245	0.1119	0.1084
9.32	2.263	2.298	0.0560	0.0564
1.45	2.284	2.313	0.0140	0.0101
0.002	2.3140		(A = 0.0005813)	

Frequency (GHz)	$\epsilon'_{\text{measured}}$	$\epsilon'_{\text{calculated}}$	$\epsilon''_{\text{measured}}$	$\epsilon''_{\text{calculated}}$
	N-Methyl-n-octylamine in p-dioxane $f_2 = 0.1492$			
141	2.197	2.214	0.0216	0.0151
35.1	2.213	2.232	0.0581	0.0545
24.0	2.230	2.249	0.0683	0.0708
16.2	2.282	2.277	0.0974	0.0839
9.32	2.322	2.324	0.0908	0.0836
2.45	2.380	2.380	0.0335	0.0331
1.45	2.385	2.384	0.0289	0.0201
0.002	2.3867		(A = 0.00044084)	
	N-Methyl-n-octylamine in cyclohexane $f_2 = 0.0932$			
70.2	2.041	2.050	0.0197	0.0212
35.1	2.065	2.062	0.0395	0.0367
16.2	2.097	2.093	0.0447	0.0472
9.32	2.117	2.117	0.0386	0.0402
2.45	2.133	2.137	0.0162	0.0136
1.95	2.141	2.138	0.0114	0.0109
1.45	2.137	2.138	0.0115	0.0081
0.95	2.138	2.139	0.0087	0.0054
0.002	2.1391		(A = 0.0000573)	

Frequency (GHz)	$\epsilon'_{\text{measured}}$	$\epsilon'_{\text{calculated}}$	$\epsilon''_{\text{measured}}$	$\epsilon''_{\text{calculated}}$
N,N-Dimethyl-n-octylamine in cyclohexane $f_2 = 0.0998$				
145	2.018	2.022	0.00587	0.00358
35.1	2.029	2.027	0.01410	0.01333
24.0	2.036	2.031	0.01860	0.01747
9.32	2.043	2.049	0.01780	0.02145
1.95	2.058	2.065	0.00960	0.00708
1.45	2.064	2.066	0.00830	0.00534
0.95	2.064	2.066	0.00670	0.00353
0.002	2.0663		(A = 0.0000541)	
N,N-Dimethyl-n-octylamine in cyclohexane $f_2 = 0.1502$				
145	2.020	2.023	0.00787	0.00936
70.6	2.023	2.027	0.01600	0.01451
35.1	2.033	2.036	0.02030	0.02020
16.2	2.048	2.049	0.02330	0.02430
9.32	2.058	2.060	0.02210	0.02384
2.45	2.074	2.079	0.01290	0.01433
1.95	2.073	2.081	0.01210	0.01257
1.45	2.076	2.083	0.00990	0.01047
0.002	2.0888		(A = 0.0000720)	

Frequency (GHz)	$\epsilon'_{measured}$	$\epsilon'_{calculated}$	$\epsilon''_{measured}$	$\epsilon''_{calculated}$
N,N-Dimethyl-n-octylamine in cyclohexane $f_2 = 0.2011$				
145	2.026	2.027	0.0147	0.0102
35.1	2.040	2.040	0.0255	0.0267
24.0	2.049	2.048	0.0297	0.0314
16.2	2.061	2.059	0.0347	0.0346
9.32	2.089	2.076	0.0347	0.0340
2.45	2.108	2.102	0.0193	0.0179
1.95	2.107	2.104	0.0168	0.0152
1.45	2.111	2.106	0.0146	0.0122
0.002	2.1104		(A = 0.0001270)	
N,N-Diethyl-n-octylamine in cyclohexane $f_2 = 0.1941$				
146	2.042	2.041	0.0117	0.0066
35.1	2.046	2.044	0.0185	0.0195
24.0	2.051	2.048	0.0262	0.0249
16.2	2.057	2.056	0.0311	0.0308
9.32	2.070	2.071	0.0361	0.0376
2.45	2.111	2.112	0.0323	0.0316
1.95	2.114	2.117	0.0297	0.0282
1.45	2.119	2.122	0.0260	0.0238
0.002	2.1358		(A = 0.0001356)	

Frequency (GHz)	ϵ'calculated*	ϵ''calculated*
N-Methyl-n-octylamine in cyclohexane $f_2 = 0.0932$		
70.2	2.042	0.0248
35.1	2.058	0.0398
16.2	2.090	0.0459
9.32	2.110	0.0397
2.45	2.135	0.0174
1.95	2.136	0.0142
1.45	2.137	0.0109
0.95	2.138	0.0072
	($\epsilon_\infty = 2.035$)	(A = 0.0000525)

* Calculated in terms of Budo distribution. (Program # 7, Appendix I)

Frequency (GHz)	ϵ'calculated*	ϵ''calculated*
N,N-Dimethyl-n-octylamine in cyclohexane $f_2 = 0.0998$		
145	2.017	0.00555
35.1	2.026	0.01579
24.0	2.032	0.01743
9.32	2.044	0.01764
1.95	2.063	0.01046
1.45	2.064	0.00826
0.95	2.065	0.00565
	($\epsilon_\infty = 2.016$)	($A = 0.0000101$)
N,N-Dimethyl-n-octylamine in cyclohexane $f_2 = 0.1502$		
145	2.021	0.00773
70.6	2.025	0.01443
35.1	2.034	0.02184
16.2	2.049	0.02449
9.32	2.059	0.02408
2.45	2.082	0.01658
1.95	2.084	0.01408
1.45	2.086	0.01109
	($\epsilon_\infty = 2.020$)	($A = 0.0000591$)

* Calculated in terms of Budo distribution. (Program # 7, Appendix I)

Frequency (GHz)	ϵ' calculated*	ϵ'' calculated*
N,N-Dimethyl-n-octylamine in cyclohexane f_2 = 0.2011		
145	2.029	0.0087
35.1	2.043	0.0255
24.0	2.051	0.0295
16.2	2.061	0.0325
9.32	2.076	0.0341
2.45	2.105	0.0179
1.95	2.107	0.0147
1.45	2.108	0.0112
	(ϵ_∞ = 2.028)	(A = 0.0000731)
N,N-Diethyl-n-octylamine in cyclohexane f_2 = 0.1941		
146	2.037	0.0065
35.1	2.046	0.0214
24.0	2.052	0.0262
16.2	2.060	0.0302
9.32	2.072	0.0354
2.45	2.116	0.0346
1.95	2.122	0.0304
1.45	2.127	0.0247
	(ϵ_∞ = 2.036)	(A = 0.0000561)

* Calculated in terms of Budo distribution. (Program # 7, Appendix I)

Frequency (GHz)	ϵ' measured	ϵ' calculated	ϵ'' measured	ϵ'' calculated
1,4-Diaminobutane in cyclohexane $f_2 = 0.02024$				
145	2.045	2.042	0.0179	0.0180
70.6	2.052	2.052	0.0193	0.0186
35.1	2.060	2.062	0.0167	0.0166
24.0	2.058	2.066	0.0131	0.0147
16.2	2.068	2.069	0.0132	0.0125
0.002	2.0806		(A = 0.0000199)	
1,4-Diaminobutane in p-xylene $f_2 = 0.01976$				
145	2.284	2.290	0.0206	0.0197
70.6	2.296	2.305	0.0267	0.0276
35.1	2.320	2.323	0.0247	0.0247
24.0	2.317	2.330	0.0184	0.0198
16.2	2.336	2.334	0.0118	0.0146
9.32	2.333	2.337	0.0119	0.0089
0.002	2.3381		(A = 0.0000419)	
1,4-Diaminobutane in p-dioxane $f_2 = 0.02000$				
145	2.239	2.243	0.0251	0.0245
70.6	2.260	2.259	0.0347	0.0356
35.1	2.275	2.281	0.0414	0.0416
16.2	2.308	2.307	0.0380	0.0366
9.32	2.316	2.320	0.0251	0.0283
0.002	2.3381		(A = 0.0000305)	

Frequency (GHz)	$\epsilon'_{measured}$	$\epsilon'_{calculated}$	$\epsilon''_{measured}$	$\epsilon''_{calculated}$
1,6-Diaminohexane in cyclohexane $f_2 = 0.02090$				
145	2.048	2.046	0.0206	0.0199
70.6	2.055	2.059	0.0230	0.0240
35.1	2.070	2.074	0.0221	0.0217
24.0	2.078	2.079	0.0194	0.0184
16.2	2.085	2.084	0.0131	0.0147
9.32	2.084	2.087	0.0090	0.0100
0.002	2.0915		(A = 0.0000175)	
1,6-Diaminohexane in p-xylene $f_2 = 0.02030$				
145	2.280	2.285	0.0141	0.0134
70.6	2.292	2.294	0.0207	0.0213
35.1	2.310	2.310	0.0215	0.0228
24.0	2.317	2.317	0.0216	0.0196
16.2	2.322	2.322	0.0128	0.0151
9.32	2.324	2.326	0.0108	0.0095
0.002	2.3277		(A = 0.0000159)	
1,6-Diaminohexane in p-dioxane $f_2 = 0.01999$				
145	2.215	2.237	0.0229	0.0185
70.6	2.254	2.248	0.0290	0.0316
35.1	2.267	2.270	0.0395	0.0423
16.2	2.306	2.300	0.0382	0.0382
9.32	2.322	2.313	0.0284	0.0278
0.002	2.3256		(A = 0.0001007)	

Frequency (GHz)	$\epsilon'_{measured}$	$\epsilon'_{calculated}$	$\epsilon''_{measured}$	$\epsilon''_{calculated}$
1,9-Diaminononane in cyclohexane $f_2 = 0.01891$				
145	2.029	2.029	0.0092	0.0093
70.6	2.036	2.035	0.0111	0.0109
35.1	2.041	2.041	0.0112	0.0109
24.0	2.041	2.044	0.0097	0.0102
16.2	2.048	2.047	0.0091	0.0091
9.32	2.046	2.050	0.0070	0.0072
0.002	2.0558		(A = 0.0000045)	
1,9-Diaminononane in p-xylene $f_2 = 0.01895$				
145	2.275	2.278	0.0126	0.0122
70.6	2.282	2.287	0.0184	0.0180
35.1	2.307	2.299	0.0160	0.0186
24.0	2.305	2.305	0.0170	0.0162
16.2	2.313	2.309	0.0117	0.0129
9.32	2.310	2.312	0.0127	0.0085
0.002	2.3149		(A = 0.0000411)	
1,9-Diaminononane in p-dioxane $f_2 = 0.01890$				
145	2.269	2.273	0.0421	0.0367
70.6	2.301	2.294	0.0542	0.0575
35.1	2.320	2.331	0.0706	0.0739
16.2	2.389	2.381	0.0749	0.0719
9.32	2.415	2.410	0.0584	0.0578
2.45	2.448	2.440	0.0213	0.0236
0.002	2.4482		(A = 0.0001823)	

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