DIELECTRIC RELAXATION OF ELECTROLYTE SOLUTIONS

A thesis submitted for the degree of Doctor
of Philosophy in the University of Southampton.

by

Peter Cory Knight

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FOREWORD

The investigations described in this thesis were carried out in the Department of Chemistry of the University of Southampton between October 1964 and March 1967.

The author would like to express his sincere thanks to his supervisor, Dr. E. A. S. Cavell, for his ready guidance and constant encouragement.

The valuable assistance of workshop, glass-blowing and technical staff is acknowledged. The author wishes to express his appreciation to his colleagues, who, by their helpful advice and fellowship, have contributed to the enjoyment of his stay in Southampton.

The author is also aware that he is greatly indebted to his parents, for both their upbringing, and encouragement during the course of his studies, and he would like to take this opportunity to thank them.

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FACULTY OF SCIENCE

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by Peter Cory Knight

The Dielectric relaxation of solutions of tertiary and quaternary ammonium salts in a variety of solvents with permittivities between 2.27 and 20.7 has been investigated in the frequency range 1.2 to 3,000 MHz.

Travelling and standing wave methods, utilising coaxial line apparatus, have been described for the measurement of permittivity and loss in the frequency range 0.2 to 3.0 GHz. For measurements in the frequency range 1 to 100 MHz., a bridge method has been employed.

For solutions of tri-n-butylammonium picrate and iodide, the results are consistent with the assumption that the dielectric relaxation arises from orientational displacements of contact ion pairs. The relaxation times, which lie in the range 80 to 500 psec., increase with increasing concentration, and intrinsic relaxation times have therefore been calculated. The relaxation times are not proportional to viscosity, although it has been concluded that, in

general, ~~short~~ ion pair orientational relaxation times ~~occur~~ in solvents with low viscosities, densities and dielectric relaxation times are shorter than those in solvents having higher values of viscosity, density and dielectric relaxation time.

Solutions of tetra-n-butylammonium bromide have been investigated in ten solvents, and in addition, a number of solutions of other univalent salts has been examined. In general, the dispersion is somewhat broader than that described by the Debye-Pellat equation. Relaxation times lie in the range 70 to 600 psec., and are often rather shorter than those expected for orientational displacements of contact ion pairs, although it has been concluded that this is the principal ~~electrolyte~~ solute relaxation process. It is suggested that the shortening of relaxation times is due to additional processes, characterised by relaxation times shorter than those required by ion pair orientation. The theories of Onsager, Böttcher and Scholte have been applied to estimate ion pair concentrations.

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CHAPTER I.

REVIEW OF PUBLISHED WORK RELEVANT TO THIS THESIS.

1.1. Introduction and Aims of Present Work.

In chemical and physical relaxation methods, the system is subjected either to a sudden, or to a continuous perturbation of one of the external parameters affecting equilibrium. Examples of perturbing parameters are: temperature, pressure, electric field strength and direction, and shear stress. The process whereby the system strives to re-establish equilibrium, when either the perturbation is applied or removed, is termed relaxation, and the form of the relaxation is characteristic of the chemical and physical processes taking place within the system. Maxwell used the term "relaxation" to describe the time dependence of shear stress of viscous liquids. However the relationship between viscoelastic relaxation and molecular structure has proved difficult to elucidate.

Some years after Drude (1) and Cole (2) had detected dielectric dispersion in hydrogen bonded liquids, Debye (3) provided an acceptable molecular interpretation of this phenomenon, and this has been the basis of subsequent dielectric investigations of molecular structure. Attention has been mainly focused on pure polar liquids and on their solutions in non polar solvents. Dielectric investigations of electrolyte solutions however, have been much more limited in their scope, and it is with the object of partly remedying this deficiency that this thesis is primarily concerned.

The investigation described here was aimed at answering (or partially answering) the following questions:

a. How does electrolyte relaxation time (and its distribution if any) depend upon the electrolyte and its concentration, the solvent and the temperature?

b. How do static permittivities of solutions and solvents in solutions, depend upon electrolytes and their concentrations?

c. What is the relationship between structure and dielectric properties of electrolyte solutions?

1.2. Frequency Dependence of Ionic Conductance.

Ionic conductance is the characteristic property of electrolyte solutions. It can be measured with very great accuracy in audio-frequency ranges, but at higher frequencies, where according to the theories of Debye and Falkenhagen (4) ionic conductance should increase, much less accuracy is attainable. The increase in conductance, which is caused by the finite relaxation time required for the growth and decay of the ionic atmosphere (4), is difficult to detect both because it is small in magnitude, and because it may be masked by other processes such as dipolar relaxation of the solvent. At frequencies of measurement of 300 MHz. and 600 MHz. respectively, Little and Smith (5) and Hasted and Roderick (6) both reported increases in ionic conductance of aqueous electrolytes that were too large in magnitude to be attributed to the Debye-Falkenhagen effect. Little (5) suggested that the reason for this was that polarisation of water molecules in the third hydration shells surrounding ions, reduces the magnitude of the external field acting upon them. The conductance increases at frequencies approaching the relaxation frequency of water molecules in this shell, because the field produced by their polarisation, which opposes the applied field, is reduced.

Hills (7) has described kinetic models of ionic migration in which it is postulated that an ion "jumps" from one equilibrium position to another. For this model, ionic conductance might be expected to decrease, when the frequency of the applied field approaches the time associated with ionic movements i.e. 10^{-10} to 10^{-12} sec.

1.3. Lifetimes of Ion Pairs.

Any process occurring within an electrolyte solution that is accompanied by a change in electric polarisation ~~moment~~, can in principle give rise to dielectric absorption. The orientational motion of ion pairs is an important example of such a mechanism. At an instant of time, any electrolyte solution will contain some ion pairs resulting from random collisions. But if the average time that the ions are paired is less than their rotational relaxation time (which is an average value) little polarisation may result from them. However electrostatic attraction between ions of opposite charge, together with forces of short range, may increase the life time of ion pairs sufficiently for them to behave as ordinary dipoles.

Ion pair concentrations determined from electric polarisation measurements may be different from those determined by other methods. For example, because of the very high rates of electron transfer processes, optical and U.V. spectroscopic methods can be used to detect very short lived ion pairs. The ion pair concentration found in this way may not however, be as high as that found from methods such as conductance, because charge transfer from anion to solvated cation, by which ion pairs are spectroscopically detected, may only take place with doubly, contact, or singly solvent separated ion pairs (8), while other kinetically stable solvent separated ion pairs are not detected (8). Alternatively when ion pair concentrations are determined from measurement of ionic conductance, the concentration of ion pairs obtained depends upon which theoretical function, describing the relationship between conductance and concentration of charge carriers, is employed.

Ion pair association and dissociation reactions involve a change in volume, and have been studied both by the pressure step and ultrasonic relaxation techniques. Eigen and Tamm (9) proposed a three step association and dissociation mechanism to account for the three ultrasonic relaxation times found for 2.2 salts in aqueous solution (9, 10):

$$M(aq.) + A(aq.) \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} M(WW)A \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} M(W)A \underset{k_{43}}{\overset{k_{34}}{\rightleftarrows}} M\ A,$$

where W represents a water molecule trapped between the ions. Atkinson and Petrucci (10) reported values for stepwise rate constants, and compared their values with those reported by Eigen and Tamm for magnesium sulphate in water. These are given in table 1.1. together with dissociation constants K.

Table 1.1. Kinetic parameters for magnesium sulphate association in water at 25°C.

	Eigen and Tamm	Atkinson and Petrucci
k_{12}, M^{-1}. sec^{-1}.	4.6×10^{10}	2.8×10^{10}
k_{21}, sec^{-1}.	8×10^{8}	5.6×10^{8}
K_{12}, M.	0.017	0.020
k_{23}, sec^{-1}.	1×10^{9}	7.2×10^{7}
k_{32}, sec^{-1}.	5×10^{8}	3.7×10^{7}
K_{23}	0.5	0.51
k_{34}, sec^{-1}.	1×10^{5}	1.4×10^{5}
k_{43}, sec^{-1}.	8×10^{5}	8.0×10^{5}
K_{34}	7.5	5.8
Overall association constant	197	165
K_A (from conductance)	169	169

In solutions of tetrabutylammonium bromide in a nitrobenzene-carbontetrachloride mixture with a permittivity of sixteen, which are particularly relevant to the present investigation, Atkinson and Petrucci (11) found a single step dissociation association process with rate constants: $k_{12} = 13.1 \times 10^{10}$ M^{-1} sec^{-1}. and $k_{21} = 7.9 \times 10^{7}$ sec^{-1}. For this system, the life time of ion pairs is about 10^{-8} sec., which is appreciably longer than rotational relaxation times of ion pairs which are about 10^{-10} sec. (19 and chapter 4).

Rapid chemical processes can also in principle be investigated dielectrically, although the dielectric dispersion produced by association-dissociation reactions is small, and tends to be masked by ionic conductance. Gilkerson and Nanney (12) investigated the dissociation field effect in solutions of tetrabutylammonium picrate in benzene-p-dichlorobenzene mixtures and in chlorobenzene, which are favourable systems for study because of the lower ionic conductance, and because the dispersion is moved to lower frequencies. An earlier report of the dissociation field effect in aqueous boric acid solutions (13), proved to be spurious (14, 15).

1.4. Dipole Moments of Ion Pairs.

The dipole moments of quaternary and tertiary ammonium salts, which lie in the range 7 to 20 D., were first determined in dilute benzene solutions by Hooper and Kraus (16) and Geddes and Kraus (17). Later work by Maryott (18), Davies and Williams (19), Gilkerson and Srivastava (20), Bauge and Smith (21, 22) and others (23 to 28) was in some ways more sophisticated in its analytical approach, but emphasized the accuracy of the original determinations. Table 1.2 summarizes determinations of dipole moments of electrolytes, and some notes on it are given in Appendix 4.3. From the character of the relationship between permittivity and electrolyte concentration, an assessment of the extent of association to form complexes larger than ion pairs is possible (16, 17, 18, 26, 27). More information can be gained however, if the electrolyte relaxation times are determined (19, 23, 24, 25, 29, 30), because their magnitudes and their distributions indicate the sizes of the relaxing entities and their degree of complexity (19).

1.5. Detection of Ion Pairs in Polar Electrolyte Solutions by Dielectric Measurements.

On account of their larger physical size and moment, ion pairs can be expected to have larger relaxation times than solvents. Cavell (31, 32), attributed dielectric dispersion observed to occur between 300 MHz. and 3 GHz. in electrolyte solutions in acetone and 1,2-dichloroethane to the presence of ion pairs. Of the systems investigated by Cachet, Epelboin and Lestrade (33), only those of tetrabutylammonium iodide showed any evidence of ion pair formation.

Table 1.2. Dipole moments of electrolytes (in Debye units) reported by various authors. Key: a = ref. 16, b = ref. 28, c = ref. 18, d = ref. 30.

Electrolyte	Smith and Bauge	Geddes and Kraus	Richardson and Stern	Davies and Williams	Gilkerson and Srivastava	Others
Am_4NBr						>14 a
Am_4NSNC	15.4	15.4				
Am_4NPi		18.3				19.4 a
Bu_4NBr	12.2	11.6	13.9 (11.2)		13.5, 11.9	
Bu_4NI	12.7					
Bu_4NClO_4	17.2	14.1				
Bu_4NPi	15.3	17.8	20.8 (16.6)	15.1	15.70,13.8 16.8, 14.4, 14.3	
Bu_4NBPh_4					17.3	
Am_3NHPi						13.9 a 12.1 d 11.9 c
Bu_3NHPi	11.79	13.1		11.4		11.7 b 11.9 c
Bu_3NHI		8.09		7.7		
Bu_3NHBr	8.50	7.61				
Et_3NHPi	11.67					11.7 c

Pottel (34) found that aqueous solutions of 2,2 salts showed dielectric behaviour very different from that of typical univalent electrolytes, which he attributed principally to relaxation of ion pairs separated by one and two water molecules.

Hasted, Ritson and Collie (35), Hasted Haggis and Buchanan (36), Lane and Saxton (37), Hasted and El Sabeh (38) and others (39) have investigated aqueous solutions of univalent electrolytes. These investigations were extended to include 2, 1 and 3,1 salts by Hasted et al (6, 35,36) and Harris and O'Konski (40). Even at very high electrolyte concentrations (34, 40), there is little evidence for an additional dielectric dispersion region attributable to ion pairs, although it is possible that investigations have not been made at sufficiently low frequencies for this conclusion to be established beyond doubt. Increases in ionic conductance (section 1.2, 5, 6) could be attributed to ion pair formation (6).

1.6. The Effect of Electrolytes upon the Dielectric Relaxation Times of Solvents.

The author is unaware of investigations of the effect of electrolytes upon the relaxation times of liquids other than those on water and alcohols. A selection of data from literature is given in tables 1.3 and 1.4. Hasted (6) from measurements at a single frequency found that the relaxation times of alcohols ~~is~~ are reduced by electrolytes (table 1.3), whereas more recently Cachet has reported that their

Table 1.3. Data on alcoholic electrolyte solutions from ref. (6) at 20°C.

alcohol	salt	conc. (M)	static permittivity ε_o'	wavelength of maximum absorption λ_m (cms)
MeOH	—	—	33.64	10.0
MeOH	NaI	0.5	18.8	6.94
		1.0	11.7	4.56
	LiCl	0.5	20.3	8.13
		1.0	16.1	6.97
EtOH	—	—	25.07	22.0
EtOH	NaI	0.27	13.7	15.8
	$MgCl_2$	0.5	17.7	18.1
	$LaCl_3$	0.33	19.2	20.1

relaxation times are little changed (33).

Salts with metallic cations reduce the relaxation time of water (6, 35, 36, 37, 40, table 1.4), the change being approximately pro-portional to the electrolyte concentration. This is further evidence for the structure breaking effect of ions, proposed by Frank and Evans (41). Alkylammonium cations, on the other hand, increase the relaxation time of water (table 1.4), which is in keeping with modern ideas of structure promotion by these cations (42).

Table 1.4. Data on aqueous electrolyte solutions at 25°C.

Salt	conc. (M)	static permittivity ε'_o	wavelength of maximum absorption λ_m (cms)	α_{cole}	ref.
Water		78.54	1.55	0.00	155
LiCl	0.5	71.2	1.55	0.00	35
	2.0	51.0	1.45	0.00	35
	8.0	39	4.3	0.5	40
	12.0	35	8.0	0.57	40
LiBr	2.0	51.8	1.34	0.00	40
	10.0	39	7.2	0.53	40
KF	0.33	74.0	1.53	0.00	36
	1.0	67.0	1.47	0.00	36
	1.0	70.0	1.60	0.00	40
	12.0	57	19	0.58	40
$MgCl_2$	0.468	71.0	1.56	0.00	35
	0.935	64.5	1.53	0.00	35
	3.0	44.3	1.70	0.37	40
$LaCl_3$	0.52	71.0	1.54	0.00	35
	1.04	64.0	1.50	0.00	35
Et_3NHCl	0.5	72.4	1.67	0.00	36
	1.04	67.0	1.77	0.00	36
Pr_3NHCl	0.33	73.0	1.60	0.00	36
	1.0	64.5	1.70	0.00	36
Et_4NCl	0.2	73.6	1.61	0.00	36
	0.6	65.6	1.75	0.00	36
Me_4NI	0.125	75.8	1.58	0.00	36
	0.25	73.8	1.61	0.00	36

When the electrolyte concentration exceeds about 4M., the dielectric relaxation time of water probably does not continue to decrease with increasing concentration. According to Harris et al (40), for a number of salt solutions it increases (table 1.4), although Pottel (34) reported it then remained approximately constant for lithium chloride solutions. The physical meaning of relaxation times of electrolyte solutions in water at concentrations greater than about 1 M. is less clear, because the relaxation cannot now be adequately represented by the Debye (3) expression for a single relaxation time. Never the less, data can be satisfactorily represented by the empirical circular arc expression of Cole and Cole (43). That the Debye equation fails for aqueous solutions having electrolyte concentrations exceeding 1M. is perhaps to be expected, because at such concentrations, the ions are separated on average by about $9.4\ A^{o}$ (44), or only about two water molecular diameters.

1.7. Effect of Electrolytes on Static Permittivities of Solvents.

The static permittivity of almost all polar solvents investigated (not necessarily the permittivity of the electrolyte solution as a whole) is reduced by the presence of electrolytes. Examples of this are given in tables 1.3, 1.4, 1.5, and in chapter 4.

In aqueous solutions, the reduction in permittivity can be accounted for by assuming that the first layer of water molecules

Table 1.5. Static permittivity of acetone in tetrabutylammonium bromide solutions at 25°C from ref. (31).

conc (M)×10	Static permittivity of acetone
0.000	20.70
0.425	19.8
1.51	19.1
3.20	17.95
3.96	17.65

around monovalent ions are partially or wholly irrotationally bound (35, 36). The anionic and cationic contributions to the lowering of the solvent static permittivity have been estimated by Hasted (35, 36) by assuming, on the basis of a model, that cations are considerably more effective in this respect than anions. As an alternative method, Harris (40) assumed that because equimolar solutions of salts of the anions: iodide, bromide, chloride, have the same permittivity decrement, the effect of these anions is negligible. Cationic hydration numbers found from permittivity decrements are in agreement with those obtained from other methods (34 to 36).

Little (45) has used an electrostatic force method to measure permittivities at 2 KHz. of aqueous solutions of some univalent metal chlorides, in the concentration range 10^{-4} to 10^{-2} M. For identical concentrations the permittivity is reduced by about the same amount by all the salts investigated, the size of the reduction depending upon the square root of the salt concentration. Little's measurements apparently diverge from those obtained at much higher concentrations by other investigators. Hasted (46) has suggested that this divergence may be due to the existence of two dispersion mechanisms.

The static permittivity of alcoholic electrolyte solutions is considerably lower than the value for the pure solvent (6, 33 and table 1.3). To account for the observed change in terms of the concept of solvent molecules irrotationally bound to ions would require the existence of more than one solvation shell surrounding ions (6). Hasted (6) preferred to attribute the observed lowering in permittivity partly to ionic solvation, and partly to a breaking down of the hydrogen bonded structure of the alcohols concerned. Gluekauf's treatment (47) however, when applied to alcoholic electrolyte solutions accounts for the reduction in permittivity without invoking breaking of a chain structure (48). His theory is also applicable to a wide variety of aqueous electrolyte solutions (49).

CHAPTER 2.

DIELECTRIC THEORY.

2.1. Fundamental Relationships.

Maxwell defined permittivity as the proportionality factor in the relation between electric displacement D and field strength E.[1]

$$D = \varepsilon'_o E \; . \qquad 2.1$$

For fields which vary with time, equation 2.1 cannot be used if D and E are not in phase, although when rewritten in complex form it again becomes valid (50):[2]

$$\hat{D} = \hat{\varepsilon}\,\hat{E} \; . \qquad 2.2$$

If the displacement lags behind the applied field with a phase difference δ, then it follows (50) that real (ε') and imaginary (ε'') permittivities may be defined by:

$$\varepsilon' = \frac{D_o \cos\delta}{E_o} \; , \qquad 2.3$$

$$\varepsilon'' = \frac{D_o \sin\delta}{E_o} \; , \qquad 2.4$$

where D_o and E_o are the amplitudes of electric displacement and field strength respectively.

A lossy dielectric may be represented as a capacitance C shunted by a resistance 1/G. Measurements on it can be made by measuring the flow of electrons in an external circuit. If a

---

[1] ε'_o is the static permittivity.

[2] $\hat{\varepsilon}$ is defined as $(\varepsilon' - j\varepsilon'')$, where $j = \sqrt{-1}$. $D = D_o e^{j(\omega t - \delta)}$, $E = E_o e^{j\omega t}$.

sinusoidal potential $V_o e^{j\omega t}$ is applied to the dielectric, then the current (i) flowing in the external circuit is given using Ohm's law by:[1]

$$i = (j\omega C + G)\ V_o e^{j\omega t} \quad . \qquad 2.5$$

In addition, since a condenser filled with such a dielectric has a capacity $\hat{\varepsilon} C_o$, its charge (q) at a time (t) is given by:[2]

$$q = \hat{\varepsilon} C_o\ V_o e^{j\omega t} \quad .$$

The variation of its charge with time must correspond to the current flowing in the external circuit, which is given by:

$$i = \frac{d}{dt} (\hat{\varepsilon} C_o V_o e^{j\omega t}) = (\varepsilon' - j\varepsilon'')\ C_o V_o j\omega e^{j\omega t} \qquad 2.6$$

$$= (\varepsilon' C_o j\omega + \varepsilon'' C_o \omega)\ V_o e^{j\omega t}.$$

Hence by comparison of 2.5 with 2.6, it follows that:

$$\varepsilon' = C/C_o \text{ and } \varepsilon'' = G/\omega C_o . \qquad 2.7 \text{ and } 2.8$$

The permittivities (ε') and (ε'') can therefore be found experimentally by measuring the capacitance and conductance of the dielectric filled condenser. From equations 2.3 and 2.4, ε' is proportional to the displacement in phase with the applied field and ε'' is proportional to the displacement in quadrature with the applied field.

---

[1] ω is the frequency in radians per sec. and t is time in sec.

[2] C_o is the capacity of the empty condenser.

For any condenser, the conductance G is related to the specific conductance κ by (3):

$$G = 9 \times 10^{11} \times 4\pi C_o \, \kappa \, , \qquad 2.9$$

where κ is in cm/ohm and G and C_o are in e.s.u. Substitution of 2.9 into 2.8 yields:

$$\varepsilon'' = \frac{1.8 \times 10^{12} \, \kappa}{f} \, , \qquad 2.10$$

where f is $\omega/2\pi$.

Permittivity and loss can also be found by measuring the attenuation coefficient α and the phase constant β of a plane electromagnetic wave travelling within the material. On the assumption that propagation involves a pure travelling wave only, the electric field strength E as a function of time at a point within the dielectric at a physical distance x in the direction of propagation from a fixed point is given by:

$$\hat{E} = E_o \, e^{-(\alpha+j\beta)x} \, e^{j\omega t} \, . \qquad 2.11$$

Equation 2.11 defines α and β. From the relation[*] $\varepsilon = n^2$, which is valid when D and E are in phase, a modified relationship:

$$\hat{\varepsilon} = \hat{n}^2 \qquad 2.12$$

can be defined in cases for which permittivity is complex. If both $\hat{\varepsilon}$ and $\hat{n}$ are written in terms of their real and imaginary parts, one has:

---

[x] n is the refractive index and $\hat{n} = n' - jn''$.

$$\varepsilon' = (n')^2 \left[1 - \left(\frac{n''}{n'}\right)^2\right] \quad , \qquad 2.13$$

$$\text{and } \varepsilon'' = 2(n')^2 . \left(\frac{n''}{n'}\right) \quad . \qquad 2.14$$

To relate n' and n" to α and β it is necessary to consider only the electric field component of a plane polarised wave propagating with transverse components of electric and magnetic field only. Böttcher (50) gives the expression for the electric field component, assuming magnetic permeability of the dielectric to be unity:

$$\hat{E} = A\, e^{j\omega(t - \frac{\hat{n}}{c}x)} = A\, e^{-j\omega(\frac{n'x}{c} - \frac{jn''x}{c})} . e^{j\omega t} \quad , \qquad 2.15$$

where c is the velocity of light. Böttcher (50) identified n' as the ratio of the velocity of the electromagnetic wave in a vacuum to that in the medium, so that it can be found from an experimental measurement of λ_a/λ_m, where λ_a is the free space wavelength and λ_m is the wavelength of the electromagnetic wave within the medium. From a comparison of equations 2.11 and 2.15 it follows that:

$$\alpha = \frac{n''\omega}{c} \qquad 2.16$$

$$\text{and} \quad \beta = \frac{n'\omega}{c} = \frac{2\pi}{\lambda_m} \quad . \qquad 2.17$$

Substitution for n' and n" in equations 2.13 and 2.14, using equations 2.16 and 2.17 and the definition $n' = \lambda_a/\lambda_m$, gives:

$$\varepsilon' = \left(\frac{\lambda_a}{\lambda_m}\right)^2 \left[1 - \left(\frac{\alpha}{\beta}\right)^2\right] \quad , \qquad 2.18$$

$$\varepsilon'' = 2\left(\frac{\lambda_a}{\lambda_m}\right)^2 . \left(\frac{\alpha}{\beta}\right) \quad . \qquad 2.19$$

2.2. The Frequency Dependence of Permittivity and Loss.

a. The Debye-Pellat Equation.

Dielectric polarisation P, is by definition, the dipole moment per unit volume induced by the electric field E. At very low frequencies it is related to D and E by:

$$P = \frac{D-E}{4\pi} = \frac{\varepsilon'_o - 1}{4\pi} E \quad . \qquad 2.20$$

Now the total polarisation can be divided into a dipole orientation component P_d, and a combined atomic and electronic component P_∞, i.e.

$$P = P_d + P_\infty \quad . \qquad 2.21$$

If E is changed at an instant $t = 0$, the final value of P_∞ will be attained in less than 10^{-12} seconds, whilst P_d by its nature must take a longer time to reach its equilibrium value. It can be assumed that in a non equilibrium state the rate at which P_d changes with time at any time t, is proportional to the difference between the equilibrium value of dipolar polarisation ${}^{f}P_d$ and the instantaneous value P_d at that time, i.e.

$$\frac{dP_d(t)}{dt} = \frac{1}{\tau}\left[{}^{f}P_d - P_d(t)\right] \quad . \qquad 2.22$$

In equation 2.22, τ is the macroscopic relaxation time, which is a reciprocal rate constant. Equation 2.22 shows that polarisation attains its equilibrium value exponentially with time.

For small values of τ, it is convenient to make measurements with alternating electric fields. Solution of equation 2.22 for this case gives (3, 50, 51, 83) for the frequency dependence of $\hat{\varepsilon}$:

$$\hat{\varepsilon} = \varepsilon'_\infty + \frac{\varepsilon'_o - \varepsilon'_\infty}{1 + j\omega\tau} \quad , \qquad 2.23$$

where ε'_∞ is the part of the permittivity arising from P_∞ and ε'_o is the static permittivity of the medium. If equation 2.23 is separated into its real (ε') and imaginary (ε'') parts, $(\omega\tau)$ may be eliminated, leading to the following relation between ε' and ε'':

$$\left(\varepsilon' - \frac{\varepsilon'_o + \varepsilon'_\infty}{2}\right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon'_o - \varepsilon'_\infty}{2}\right)^2 \quad . \qquad 2.24$$

This is the equation of a circle of radius $(\varepsilon'_o - \varepsilon_\infty)/2$, whose centre lies on the abscissa, and which intersects the abscissa at ε'_∞ and ε'_o. Cole and Cole have suggested (43) that such plots are a useful way of analysing experimental data. In equation 2.24, the temperature dependence of ε' and ε'' appears implicitly, since $(\varepsilon'_o - \varepsilon'_\infty)$ and τ are both functions of temperature.

b. Other Representations.

When dielectric data are plotted on a Cole-Cole diagram (Cole diagram for brevity), they sometimes take the form of a circular arc whose centre lies below the abscissa. According to Cole and Cole (43) the frequency dependence of the complex permittivity is then given by:

$$\hat{\varepsilon} = \varepsilon'_\infty + \frac{\varepsilon'_o - \varepsilon'_\infty}{1 + (j\omega\tau_o)^{1-\alpha}} , \qquad 2.25$$

where α is the Cole "distribution" parameter, the value of which lies between zero and one and is independent of frequency. τ_o in equation 2.25 is $1/\omega_o$, where ω_o is the angular frequency for which loss is a maximum. Equation 2.25 can be regarded as an empirical representation of a system of superposed Debye relaxation processes governed by a distribution of relaxation times. Explicit forms of the function $c(\tau)$ in equation 2.26 can be found, which enable equation 2.26 to approximate to equation 2.25.

$$\hat{\varepsilon} = \varepsilon'_\infty + (\varepsilon'_o - \varepsilon'_\infty) \int_o^\infty \frac{c(\tau)\, d\tau}{1 + j\omega\tau} . \qquad 2.26$$

The parameter τ_o in equation 2.25 may be regarded as the average relaxation time. Cole and Cole (43) however, have considered that both the breadth and the form of the distribution of relaxation times required to approximate equation 2.26 to 2.25 is difficult to understand.

Sometimes data plotted on a Cole diagram take the form of a left skewed arc (52). According to Cole and Davidson (52) such data are represented by the equation:

$$\hat{\varepsilon} = \varepsilon'_\infty + \frac{\varepsilon'_o - \varepsilon'_\infty}{(1 + j\omega\tau)^\beta} \quad , \qquad 2.27$$

where β, which is independent of frequency, lies between one and zero. If β is less than one, the frequency for which loss is a maximum is higher than the frequency corresponding to τ in equation 2.27, i.e. $1/2\pi\tau$ (52).

When the axes of polar groups are unsymmetrically located with respect to the molecular moment and when the polar groups are not rigidly located within the molecule, distinct relaxation processes are possible. If two distinct relaxation processes occur simultaneously, and if each is characterised by a Debye type dispersion, the overall result can be represented by the relation:

$$\hat{\varepsilon} = \varepsilon'_\infty + (\varepsilon'_o - \varepsilon'_\infty) \left[\frac{C_1}{1 + j\omega\tau_1} + \frac{C_2}{1 + j\omega\tau_2}\right] \quad , \qquad 2.28$$

where $C_1 + C_2 = 1$.

However Smyth (53) has pointed out that when two relaxation times τ_1 and τ_2 are close together, it becomes difficult to distinguish equation 2.28 from a Cole-Cole distribution (equation 2.25). Smyth (53) has reviewed the results of analysing suitable experimental data into its two component relaxation times.

Higasi and Matsumoto (54) have shown that the distribution function proposed by Fröhlich (55) can be made to approach closely to the Cole-Cole distribution. In Fröhlich's formulation, the integration of the function c(τ) is restricted to certain limiting values τ_1 and τ_2, which are determined by a distribution of potential energy barriers governing molecular rotation and varying between H and $H + v_o$. The function c(τ) has the properties:

$$c(\tau) = \frac{kT}{v_o}\frac{1}{\tau} \qquad \text{if } \tau_1 \leqslant \tau \leqslant \tau_2 , \qquad 2.29$$

$$c(\tau) = 0 \qquad \text{if } \tau < \tau_1 \text{ and } \tau > \tau_2 . \qquad 2.30$$

Higasi, Bergman and Smyth (56) and Vaughan, Lovell and Smyth (57) have employed Frölich's theory to analyse data for alkyl halides. According to Matsumoto and Higasi (58), if the Fröhlich distribution function (equations 2.29 and 2.30) is modified to:

$$c(\tau) = \frac{1}{A}\frac{1}{\tau^n} \qquad \text{if } \tau_1 \leqslant \tau \leqslant \tau_2 , \qquad 2.31$$

$$c(\tau) = 0 \qquad \text{if } \tau < \tau_1 \text{ and } \tau > \tau_2 , \qquad 2.32$$

then with $n < 1$, left skewed arcs similar to those representable by the Cole-Davidson equation are obtained. Matsumoto and Higasi (58) have pointed out that one consequence of the form of functions 2.31 and 2.32, would be that the left skewed arcs, found by Denney (59) and Glarum (60) for alkyl halides at low temperatures, would become increasingly symmetrical as kT is increased, and this is in accord with experimental observation (58).

Glarum (60) and Cole (61) consider that in cases such as isobutyl chloride and bromide (investigated by Denney (59)) and isoamyl bromide (investigated by Denney (59) and Glarum (60)) for which the skewed arc locus is a good approximation at low temperatures, the concept of a distribution of relaxation times is inappropriate. Instead they have suggested that the locus is the result of the incorrect assumption of an exponential decay of polarisation (equation 2.22).

2.3. Molecular and Macroscopic Relaxation Times.

The problem is to relate the experimental (macroscopic) relaxation time to molecular motions. Differences between molecular relaxation times τ_μ and macroscopic relaxation times τ arise when the internal field experienced by a molecular dipole differs in magnitude and direction from the applied electric field. Equation 2.33 was obtained by O'Dwyer and Sack (62) as one of their approximations and by Powles (63), Glarum (64) and Cole (65).

$$\tau_\mu = \left(\frac{2\varepsilon'_o + \varepsilon'_\infty}{3\varepsilon'_o}\right) \tau \quad . \qquad 2.33$$

Other relations between microscopic and macroscopic relaxation times have been proposed by Debye (3) who gave:

$$\tau_\mu = \left(\frac{\varepsilon'_\infty + 2}{\varepsilon'_o + 2}\right) \tau \quad , \qquad 2.34$$

by Cole (66) who gave:

$$\tau_\mu = \tau \quad , \qquad 2.35$$

and by Davies and Williams (19) who gave for solutions of polar molecules in non polar solvents:

$$\tau_\mu = \frac{\varepsilon'_o\ \text{(solvent)}}{\varepsilon'_o\ \text{(solution)}}\ \tau \quad . \qquad 2.36$$

Hill (71) and Miller and Smyth (68) have concluded that, from an experimental point of view, equation 2.33 is a good approximation.

2.4. Models for Dielectric Relaxation.

Two kinds of model have been proposed for dielectric relaxation in liquids. In the first, the molecular dipole is considered to approach gradually the direction of the applied field, the motion being retarded by viscous forces and/or the dielectric drag of the surrounding molecules. This is a rotational diffusion model in which the rotational motion is defined by a differential equation. In the second model, the dipole is considered to jump from one momentary equilibrium orientation to another.

According to Fröhlich (55), the first mechanism is ~~most~~ more likely to be valid when the dipole is fixed fairly rigidly with respect to its neighbours. In this case, jumps will occur very infrequently, because rotation of a given dipole necessarily involves rearranging the positions of its immediate neighbours. The second mechanism

(55) obtains if surrounding molecules remain comparatively fixed during rotation of a molecular dipole. The situation is then rather as it is in solids and the dipole jumps between equilibrium positions separated by an energy barrier.

Kauzmann (69) claims that both models can lead to equations of the Debye-Pellat form. To distinguish between the models, information from other sources is necessary. For example, according to Powles (70), the size of dipole jumps can be found from the ratio of relaxation times from ^{1}H n.m.r. spectra and dielectric measurements. For water in the temperature range 0 to 75^{o}C. small jumps (less than about 15^{o}) are indicated.

a. Debye's Rotational Diffusion Model (3).

Debye has employed the theory of Brownian motion to describe the rotational motion of a molecular dipole. He obtained for the process of molecular relaxation the relationship:

$$\tau_{\mu} = \xi/2kT , \qquad 2.37$$

where ξ is a constant measuring the frictional resistance between the rotating molecular dipole and its surroundings. Debye has pointed out (3) that for mathematical reasons it was assumed in his theory that the molecular dipole does not undergo large fluctuations and that his theory is inapplicable in very high frequency fields.

Debye considered the dipolar molecules to be all equivalent, and represented them as spheres of radius $\underline{a}$. He then tentatively evaluated ξ from Stokes' law.

$$\text{i.e.}\quad \xi = 8\pi\eta a^3 \quad . \tag{2.38}$$

If the viscosity of the liquid is substituted for η in equation 2.38, values of τ_μ obtained from it are often much larger than the experimental values. It can be considered that the effective microscopic viscosity, for rotation of individual molecules, is less than the bulk viscosity of the medium. According to Hill (71), relaxation times of liquids which do not lose their rotational freedom in the solid phase should not be expected to be closely related to the viscosity of the liquid.

Assuming the dipolar molecule to be a sphere of volume V, equation 2.37 becomes, on substitution of equation 2.38:

$$\tau_\mu = \frac{4\pi\eta a^3}{kT} = \frac{3V\eta}{kT} \quad . \tag{2.39}$$

Equation 2.39 can be used to relate relaxation times to the volumes V of non spherical molecules. Both Meakins (72) and Nelson and Smyth (73) have concluded from investigations of solutions of polar molecules in non polar solvents, that if in equation 2.39 the viscosity of the solution is substituted for η, then equation 2.39 becomes roughly applicable as the volume of the polar solute molecules approaches three times the volume of the solvent molecules. Hill (67) has emphasized that in such investigations of polar solute molecules B, dissolved in a non polar solvent A, the viscosity of the solution should be replaced by a "mutual" viscosity η_{AB}. This measures the interaction between the solute B and the solvent A. Hill has shown that η_{AB} can be evaluated from the change in viscosity of the mixture as the concentration of B is increased. She has obtained for τ_μ:

$$\tau_\mu = \frac{Z}{kT} K^2_{AB}\sigma_{AB}\eta_{AB} \quad , \qquad 2.40$$

where Z is a numerical factor, K is the radius of gyration for the molecular pair AB, and σ is a mean molecular radius.

To take account of the shape of the molecular dipole, Fischer (74) has represented the molecule as an ellipsoid with semiaxes a, b, c and has used for τ_μ:

$$\tau_\mu = \frac{4\pi\eta(abc)s}{kT} \quad . \qquad 2.41$$

where s is a small numerical factor taking account of the direction of the dipole axis with respect to the axes of inertia. For solutions of polar molecules in benzene, Fischer has employed a microscopic viscosity in equation 2.41 that is 0.23 times as large as the viscosity of the solution or solvent. Davies (75) has reviewed the use of equations 2.39 to 2.41.

Smyth (76) and Miller and Smyth (77) have concluded that equation 2.39 is not satisfactory for pure liquids composed of small spherical molecules. Kalman and Smyth (78) found that equation

2.39 is also unsatisfactory for solutions of small polar molecules in high viscosity solvents such as nujol. Lamb has pointed out (79) however, that viscous liquids exhibit viscoelastic relaxation at those frequencies at which dielectric dispersion becomes significant, with the result that the effect of viscosity may be considerably reduced. Recently, Zwanig (80) has calculated that the contribution of drag on a rotating dipole due to dielectric relaxation of the surroundings amounts to between 10% and 20% of the total retarding force.

b. Kinetic Theories of Dielectric Relaxation.

Viscous flow can be treated as if it were a process governed by a potential energy barried H_η. Empirically one can write:

$$\eta \alpha e^{H_\eta/kT} . \qquad 2.43$$

Frölich has considered (55) that if H is the corresponding potential energy barrier for re-orientation of dipolar molecules, then for sudden re-orientations to occur rarely, $H >> H_\eta$. Provided that the pre-exponential factors for dielectric and viscous processes are similar in magnitude, this condition is most likely to be realized for low values of η and large values of τ_μ.

However according to Davies (51), commonly $H \simeq H_\eta$; an observation which apparently makes kinetic treatments of dielectric dispersion more appropriate. Application of transition state theory to dielectric relaxation (82) gives for τ_μ:

$$\tau_\mu = \frac{h}{kT}\, e^{F^{\ddagger}/RT} \quad . \qquad 2.43$$

In equation 2.43, $F^{\ddagger}$ is the molar free energy of activation. According to Schallamach (81), the factor h/kT in equation 2.43 is correct for rotational as well as for translational motion. On the assumption of a temperature independent entropy term, equation 2.43 implies a linear relation between ln.$(T\tau_\mu)$ and 1/T.

According to Kauzmann (70), Debye-Pellat behaviour can result from a dipolar "jump" model if the molecular dipoles have either a continuous distribution over different directions in space, or possess discrete orientations, subject to the conditions that jump rate $(\frac{1}{\tau_\mu})$ is independant of:

a. the original orientation of the dipole,

b. the angle through which it jumps.

Fröhlich (55) has proposed a 'two position model', in which the molecular dipole has two equilibrium orientations. He has shown that the model leads to behaviour characterised by the Debye-Pellat equations, and that the microscopic relaxation time is given by:

$$\tau_\mu = \frac{\pi}{\omega_o}\, e^{H/kT} \quad , \qquad 2.44$$

provided H >> kT. In equation 2.44, ω_o is the angular frequency with which the dipole oscillates about either of its equilibrium positions, which will be of the same order of magnitude as the "collision" frequency. Frölich points out that data obtained from measurements at frequencies approaching the collision frequency may deviate from Debye-Pellat behaviour.

c. Co-operative Models of Dielectric Relaxation.

Glarum (60) has described a one dimensional defect diffusion model, in which relaxation of a molecular dipole occurs on arrival of a defect. Relaxation of a molecular dipole is made more probable by relaxation of a dipole near it. Glarum has shown that non-exponential behaviour results and that the frequency dependence of permittivity and loss can resemble the function of Cole and Davidson (52) (equation 2.27).

CHAPTER 3.

EXPERIMENTAL METHODS.

Measurement of the permittivity and loss of solutions of electrolytes and pure solvents in the frequency range 300 to 3000 MHz. was made using coaxial line apparatus, having a characteristic impedance of 50 ohms. The liquid under investigation was contained at a convenient place within the coaxial line system. Most of the electrolyte solutions investigated could be classified as "high loss" liquids and for these a travelling wave method (84) was employed. A standing wave method (84) was used for measurements on "low loss" liquids such as pure solvents and dilute electrolyte solutions. A bridge method was used for measurements in the frequency range 1 to 100 MHz.

3.1. Coaxial Line Apparatus.

Apart from the cells, which had to be constructed specially, commercially available apparatus was employed. A Sanders Type CLC 2 4 Klystron oscillator was used as a signal source at 3 GHz. In the frequency ranges 0.9 to 2.0 GHz. and 250 to 950 MHz. respectively, General Radio Co. Type 1218A and 1209B oscillators were employed. Their output voltages could be adjusted as required. The detector consisted of a G. R. mixer rectifier, local oscillator and I. F. amplifier. The frequency of the signal from the local oscillator was set above or below the frequency of the signal oscillator in order to produce a 30 MHz. difference frequency. When necessary the first harmonic, generated within the mixer crystal, was used to beat with the higher signal frequencies. The heterodyned output from the mixer was amplified and detected by a G. R. Type 1216 A tuned I. F. amplifier. The amplitude of the difference frequency signal can be read directly in decibels to ±0.2dB. For it to be proportional to the amplitude of the high frequency input, the local oscillator voltage employed must be relatively large compared with the voltage of the high frequency signal input. When the fundamental frequency of the local oscillator is used, good linearity between meter reading and input voltage (in dB.) is obtained over the whole of the amplifier's range, provided the mixer crystal current exceeds a minimum value (quoted by the manufacturers) of 5 divisions on the output meter scale. For detection with the first harmonic, a larger crystal current is required. According to the manufacturers, a current of 1 ma. corresponds to approximately 50 scale divisions, and this was found to be convenient and satisfactory for all purposes.

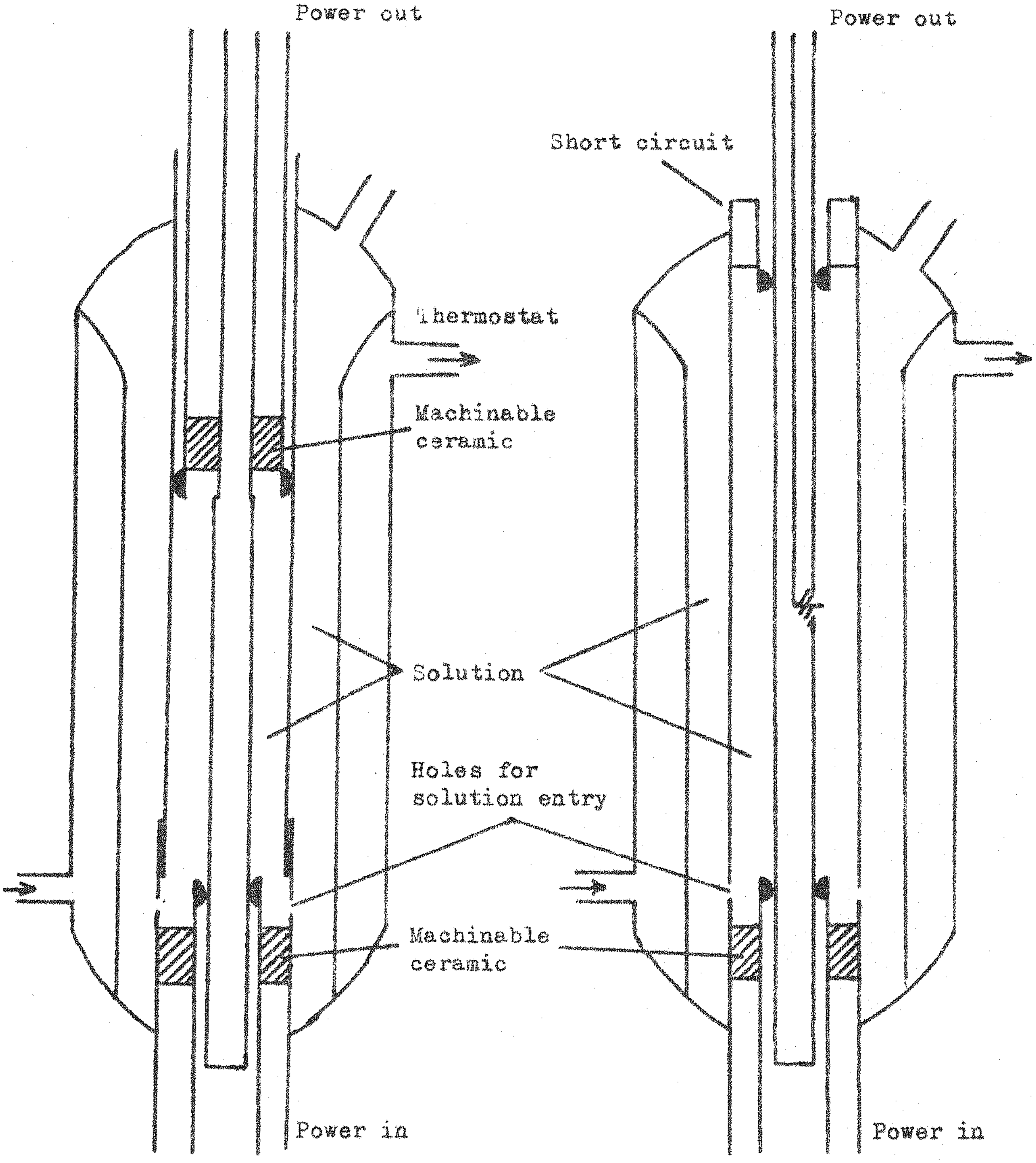
In the travelling wave method a G. R. Co. adjustable piston attenuator was employed. The accuracy of this type of attenuator is reduced by undesired capacitive coupling between input and output circuits. This can be minimised by making the voltage at the coupling point approximate to zero. This is done by terminating the input line with a stub tuner. The correct setting of this is found by substituting a coaxial "tee" for the attenuator, and then by adjusting the stub setting until a voltage minimum occurs at the coupling point. The "tee" is then replaced by the attenuator.

At each frequency of measurement the free space wavelength λ_a was measured using a G. R. Co. slotted line.

The travelling and standing wave cells are illustrated in figures 3.1 and 3.2. The travelling wave cells, used to hold the solutions under investigation, were constructed from G. R. constant impedance telescopic coaxial air lines. They were made of silver plated brass tubing, and the standing wave cell was short circuited at the upper end by a solid brass cylinder. Appropriate movement of the inner conductor of the standing wave cell, and both conductors in the case of the travelling wave cell, was measured by means of a scale and vernier attached to the top of the cell.

In both types of cell, the liquid enters the coaxial line through small holes in the outer conductor, from an external, thermostatted reservoir, coaxial with the line. With the travelling wave cell, the liquid was contained within the line between two cylindrical lengths of pyrophillite ($\varepsilon_o' = 5.2$), glued with Araldite to the inner and outer conductors in the positions indicated in figure 3.1.

With the standing wave cell, the liquid was located between a ceramic cylinder at one end, and the brass short circuit at the other. The physical length of the liquid contained within this



TRAVELLING WAVE CELL

STANDING WAVE CELL

FIGURE 3.1, 3.2.

cell was approximately 30 cms.

The ceramic cylinders behave as quarter wave transformers if the permittivity of the liquid in the cell is approximately $(5.2)^2$, i.e. about 27, and if an odd number of quarter wavelengths are contained within them at the frequency of measurement. Two travelling wave cells were constructed. One was matched for use at 1 and 3 GHz., employing ceramic blocks 3.3 cms long. The other was matched for 670 and 2000 MHz., for which the ceramic blocks used were 4.8 cms. long. Within the travelling wave cell itself, reflections were negligible provided that the minimum length of liquid employed was sufficient to produce an attenuation of about 20 dB.

The standing wave cell was constructed so as to be matched for use at 1 and 3 GHz., and an additional matching block, 4.7 cms. in length, could be added to match the cell for use at 2 GHz. The quality of the matching is important in the standing wave cell, to avoid unnecessary distortion of the standing wave pattern within the cell by secondary reflections from the ceramic cylinder. The lower the loss of the liquid under investigation, the more significant will secondary reflections be.

The electric field within the liquid contained in the standing wave cell could be sampled by means of a movable probe, approximately 0.3 cms. in length. The probe projected into the liquid from a small hole in the inner line from which the probe is insulated with Araldite. The inner line acts as the outer conductor of the output line beyond the short circuit.

Temperature control was achieved by circulating water, from a thermostat bath, around the cell. Additionally, the cell concerned was housed in a box which could be heated, or cooled with solid carbon dioxide, as required.

3.2. Experimental Procedure for the Travelling Wave Method.

A diagram of the experimental arrangement used for the measurement of permittivity and loss by the travelling wave method is given in figure 3.3. With the variable attenuator set to a high level of attenuation, the stub tuners were adjusted to give a maximum output at the I. F. amplifier. A suitable length of liquid was introduced into the cell and the line stretcher and variable attenuator adjusted until the signals travelling along the two arms of the bridge were of equal amplitude but in antiphase. The length of the column of liquid within the cell was then increased and the cut-off attenuator adjusted until a second null balance position was attained. The increase in the length of the liquid column is equal to the wave-length λ_m of the signal within the solution and the difference in attenuator settings is the attenuation (a) of the signal, in decibels, produced by λ_m cms. of the liquid. The phase constant β is $2\pi/\lambda_m$, while the relation between

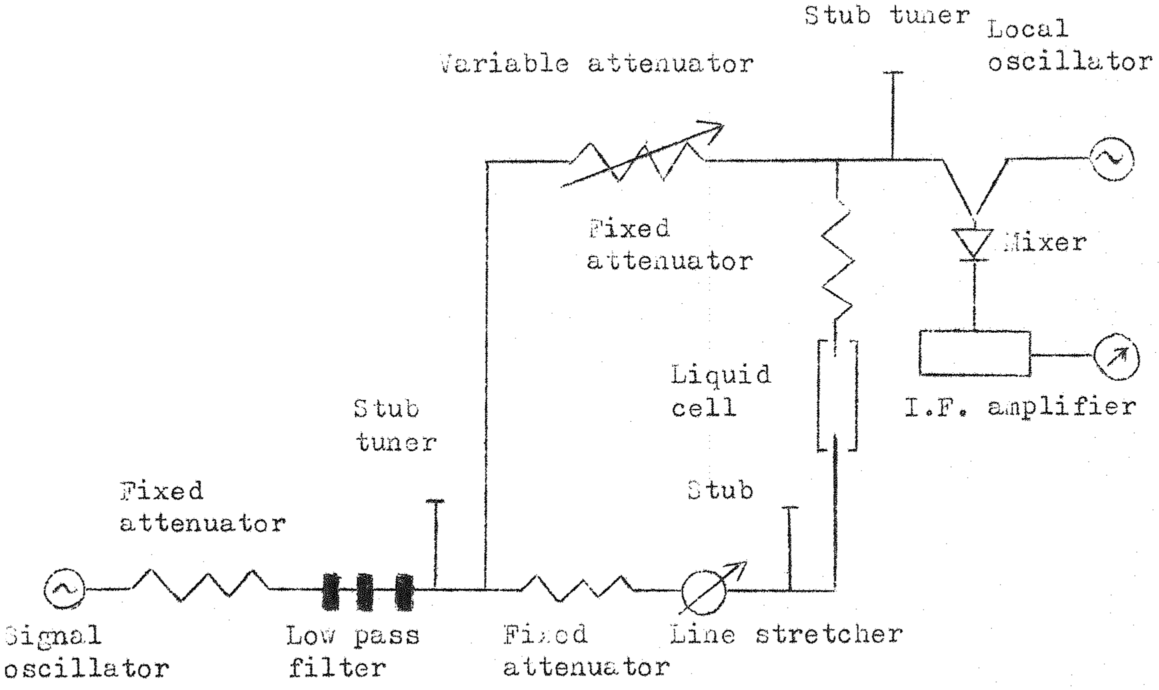


Figure 3.3. Arrangement of Coaxial Line Apparatus for the Travelling Wave Method.

the attenuation constant α and (a) is readily obtained as follows. If E_1 is the amplitude of the output voltage of the cell when it contains a column of liquid x cms. long, and E_2 is the amplitude of the output voltage when the cell contains a liquid column $(x + \lambda_m)$ cms. long, then E_1 and E_2 are related by:

$$E_2 = E_1 \exp.(-\alpha\lambda_m) \quad . \qquad 3.1$$

Equation 3.1 becomes, on taking its logarithm:

$$\log\ (E_1/E_2) = \frac{\alpha\lambda_m}{2.303} \ . \qquad 3.2$$

But by the definition of a decibel, E_1/E_2 is related to (a) by:

$$a/20 = \log.(E_1/E_2) \quad . \qquad 3.3$$

From equations 3.2 and 3.3:

$$\alpha = \frac{2.303(a)}{20\lambda_m} \quad . \qquad 3.4$$

The minimum frequency at which measurements can be made by the above method is limited by the physical length of the cell. The range was in some cases extended by using the constant impedance line stretcher to measure the change in phase produced by a column of liquid less than λ_m in length. In this case, the movement of the trombone line stretcher was measured by a cathetometer. An additional fixed attenuator was inserted between the line stretcher and the stub tuner nearest the cell.

3.3. Experimental Procedure for the Standing Wave Method.

A diagram of the experimental arrangement used for the measurement of permittivity and loss by the Standing Wave method is given in figure 3.4. The stub tuners were adjusted to give a maximum

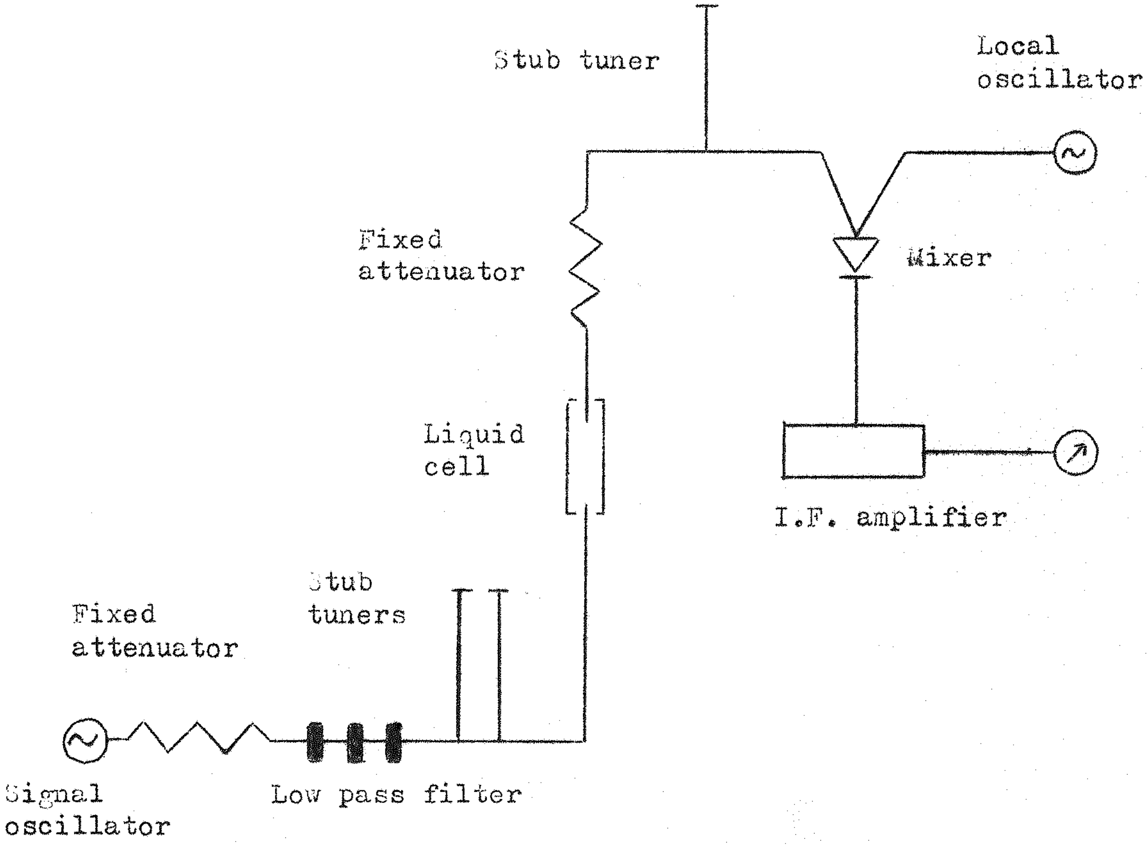


Fig. 3.4. Arrangement of Coaxial Line Apparatus for the Standing Wave Method.

output at the I.F. amplifier. A power output from the local oscillator sufficient to produce a mixer current of between 30 and 50 scale divisions on the output meter was found to be the most suitable. The local oscillator was carefully adjusted to give a maximum reading on the voltage output meter. The experimental procedure consisted of measuring the position and output of successive maxima and minima, starting from the short circuit. The probe was then moved away from the short circuit and the voltage output in decibels, and the distance of the first maximum from the short circuit recorded. The procedure was repeated for successive output minima and maxima until the minima became too indistinct for precise measurement. The attenuation constant α of the electolyte solution or solvent was calculated by means of equation 3.5, in which, according to Buchanan and Grant (84), x is the distance of a voltage minimum an odd number of half wavelengths from the short circuit, and r is the ratio of the output voltage at the minimum to that at a point at a distance x/2 from the short circuit.

$$\sinh(\alpha x/2) = r/2 \quad . \qquad 3.5$$

Provided that $\alpha^2/\beta^2 << 1$, the wavelength λ_m of the electromagnetic wave within the attenuating liquid can be found (84) by solving reiteratively equation 3.6, in which d is the distance between successive minima.

$$\lambda_m = 2d(1 + \alpha^2/\beta^2) \quad . \qquad 3.6$$

3.4. Accuracy of the Travelling and Standing Wave Methods.

Permittivity and loss are determined absolutely by the travelling and standing wave methods. The accuracy of measurement depends upon the mechanical and electrical design of the apparatus. The value of α obtained by either method represents the sum of the attenuation produced by the attenuating liquid and that of the coaxial line itself, which may not be negligible when "low loss" liquids are being investigated. In either method, if the liquid is insufficiently attenuating, reflections from the lower end of the cell may not represent a negligible fraction of the power output from the cell, in which case serious errors will result. Other potential sources of error include power dissipation resulting from propagation of energy by modes higher than the principal (TEM) mode. This may arise if the inner and outer lines are not coaxial. Variation of the characteristic impedance of the cell arising from changes in the diameter of the telescopic brass tubing used in its construction, will also contribute to the errors of measurement.

In the travelling wave method, the attenuation of the liquid column was measured by means of a G. R. piston attenuator, and this is said to measure relative attenuation to $\pm(1\% + 0.2)$ dB. The characteristic feature of a piston attenuator, is that no change in the phase of the transmitted signal accompanies changes in the degree of attenuation. The accuracy of values of total loss found by this method depends mainly on the precision of the attenuator, and are therefore probably accurate to between ± 2 and $\pm 5\%$, although the mean deviation of individual measurements from the mean value for a given experiment was often only 1%. Usually in each experiment, ten individual determinations of λ_m and (a) were made at each frequency. For λ_m, the mean deviation obtained was often less than 0.5%. Under optimum conditions the accuracy of permittivity probably approaches ±0.1%. For measurements at 3.0 GHz., however, the accuracy of permittivity and loss is considered to be somewhat lower. In the case of permittivity, the accuracy is reduced to about ±1%.

In the standing wave method, reflections from the probe and a dissipative short circuit can also reduce the precision. Both of these effects tend to make values of α determined with the probe in positions near the short circuit larger than for positions further away (84). Neither effect was apparent in the present investigation.

The accuracy of values of λ_m determined by the standing wave method depends upon the distinctness of the voltage minima. With low loss liquids, it is possible to determine permittivity to within ±0.1%. However, for most liquids, the larger loss at 3.0 GHz. reduces the precision of permittivity, quoted values of which are considered to be within ±1%. The accuracy with which α can be measured depends upon the detection and amplification system employed. The equipment used in the present investigation does not measure voltage ratios to better than ±0.2 dB., which represents an uncertainty of about ±3% in α. The accuracy of values of loss can also be estimated by comparing values calculated employing measurements made at different pairs of maxima and minima within the cell. In certain circumstances loss may be accurate to only ±5%.

For many polar liquids the static permittivity changes by about 1% for a change in temperature of one Centigrade degree, and therefore adequate thermostating is essential. At 15° and 25°C., temperature control to 0.1°C was possible and it is to these temperatures that the above estimated errors refer. At higher and lower temperatures, the estimated accuracy may be less than that quoted, because of possible temperature fluctuation during the insertion and removal of the output probe.

3.5. Transformer Ratio Arm Bridge Method of Measuring Permittivity and Loss.

Measurement of conductance and capacitance in the frequency range 1 to 100 MHz. was made by means of a Wayne Kerr transformer ratio arm admittance bridge. For this purpose, a nickel plated brass coaxial capacitor, illustrated in figure 3.5, was used as the liquid cell. It could be bolted directly to the top of the bridge. The outer dimensions of the cylinder were much larger than those of the inner electrode, in order to ensure that

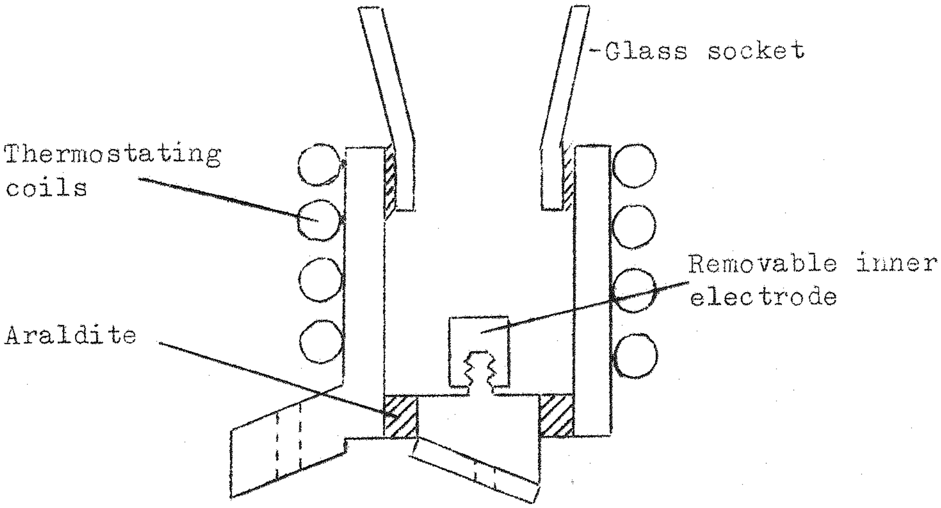


Figure 5.3. Coaxial Capacitor Cell.

capacitance was independent of the volume of liquid within the cell. Since a coaxial cell is an unbalanced admittance, the outer cylinder was earthed. Water from a thermostat was circulated through a coil of copper tubing soldered to the outside of the cell.

The liquid cell used for measurements can be represented by an inductance L in series with a capacitance C, the latter being shunted by a conductance G. C and G are related to the measured capacitance C_m and the measured conductance G_m (in parallel) by equations 3.7.

$$\omega c = b/(a^2+b^2) \quad , \qquad 3.7$$

$$G = a/(a^2+b^2) \quad ,$$

where $a = G_m/(G_m^2+\omega^2 C_m^2)$ and $b = \omega C_m/(G_m^2+\omega^2 C_m^2) + \omega L$.

The series inductance L was determined from measurements of capacitance at 5 MHz. and 100 MHz., with the liquid cell filled with pure water. It was found to be 2.3×10^{-9} Henries. The total capacitance of the liquid cell may be regarded as a parallel combination of a fixed stray capacitance and a variable working capacitance. The latter, of course, depends on the permittivity of the dielectric.

The liquids used to calibrate the cell were chosen so that their permittivities approximated to those to be measured. For electrolyte solutions in 1,2-dichloroethane, 1,2-dichloroethane itself and diethylketone were used because their static permittivities bracket those of the solutions being measured. The stray capacitance was found to be 4.4 pF. and with these two liquids, the average value of the variable capacitance with the smallest inner electrode was found to be 1.10 pF. The cell conductance constant was determined by calibration with aqueous potassium chloride solutions, using a Pye low frequency conductance bridge. With the smallest inner electrode it was found to be 0.087.

The admittance bridge is said to measure absolute values of capacitance to ±(2% + 1.5) pF. and conductance to ±(2% + 0.1) mmhos. Experiments with standard resistors and capacitors supplied with the bridge, and whose frequency dependence was known, indicated that the measured capacitance was too large at frequencies below 30 MHz., when the capacitor was shunted by a resistor of 100 ohms or less. Values of conductance are considered accurate to ±2%. With liquids of very low conductivity, permittivity is considered to be accurate to ±2%, and with more conducting liquids, it is accurate to ±2% if the frequency of measurement exceeds 30 MHz.

3.6. The Interpretation of Capacitance and Resistance Data.

The most commonly employed network which is electrically equivalent to a conductance cell is shown in figure 3.6 (85), with the cell inductance L added.

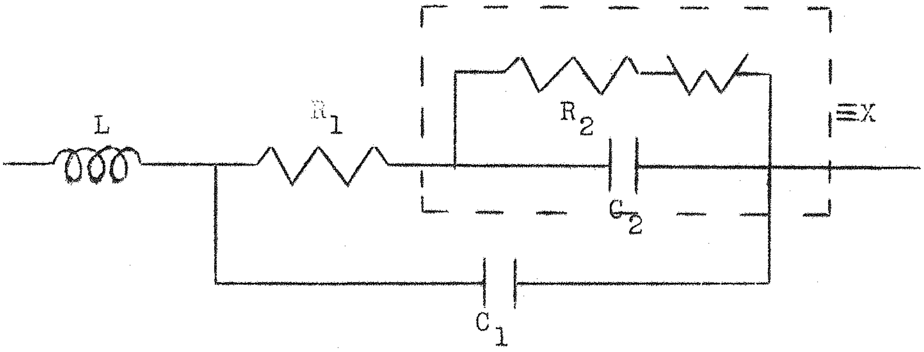


Figure 3.6. Equivalent Circuit of a Conductance Cell.

R_1 is the "homogeneous" solution resistance, and C_1 its capacitance. C_2 is the double layer capacitance which is shunted by the "Faradaic leakage". This consists of a resistance R_2 in series with a "Warburg impedance". To obtain some idea of the behaviour of the cell at different frequencies, one can select typical numerical values of the elements. For example, $C_1 \sim 1$ pF., $C_2 \sim 1\mu$F. and $R_1 \sim 10^3$ ohms. Then at a frequency of 100 MHz., the impedance of C_1 is of the same order of magnitude as R_1, while the impedance of C_2 is negligible (and so is X). Under these circumstances, the cell can be represented by the equivalent circuit described in section 3.5. At a frequency of 1 KHz. however, the impedance of C_1 is now very much larger than R_1, while C_2 is of the same order of magnitude as R_1. Because $C_2 >> C_1$, the measured capacitance is approximately the parallel equivalent of C_2 in series with R_1, which may be much larger than C_1 (and the measured resistance may be somewhat larger than R_1 because it also includes a contribution from X). To measure C_1 and R_1 successfully therefore, R_1 must be comparable in magnitude to the impedance of C_1, whilst the impedance of C_2 should be as small as possible. This may be accomplished either by making the frequency of measurement sufficiently high, or alternatively, by investigating a system with a sufficiently large value of R_1. C_2 can be maximised by using platinum black electrodes.

The equivalent circuit network shown in figure 3.6, can be used to explain why the permittivity of some electrolyte solutions investigated and analysed by means of the simple equivalent circuit given in section 3.5, appears to increase quite rapidly when the frequency of measurement is reduced below 30 MHz. The results obtained for permittivity between 50 MHz. and 100 MHz. are however considered to be reliable, partly because the values obtained show little frequency dependence, and partly because measurement of appropriate combinations of standard resistors and capacitors gave acceptable reults in this frequency range.

3.7. Measurement of Low Frequency Ionic Conductance.

For this purpose, a Pye conductance bridge catalogue number 11700 together with a dipping conductance cell was used. It is said to measure conductance to better than ±0.2%. The frequency of the bridge is preset to 5 kHz. on the 10^{-3} to 10 mhos range and to 300 Hz. on the 10^{-7} to 10^{-3} mhos range. The conductance cell constant was found by means of aqueous potassium chloride solutions. The cells employed had constants of 0.446 and 0.432.

3.8. Preparation and Purification of materials.

AnalaR grade solvents were used when obtainable. Tetrahydrofuran was first dried with sodium wire and then treated with calcium hydride. Chloroform was used immediately after removing water and alcohol from it by passage through an alumina column. All other solvents were dried and purified by vacuum distillation through a column packed with phosphorous pentoxide suspended on glass wool, followed by fractionation through a column packed with glass helices (86). Diethyl ketone and 1,1-dichloroethane were subjected to an initial fractionation before being dried in this way.

All salts were dried by heating to 100°C. in a vacuum for several hours. Throughout this thesis, the following abbreviations are made: Am = amyl, Bu = nbutyl, Pr = npropyl, Ph = C_6H_5, Pi = picrate, Et = ethyl, Me = methyl.

B.D.H. Bu_4NI was recrystallised from acetone, mp. = 146 to 147°C.

B.D.H. Pr_4NI was recrystallised from ethyl acetate, mp. = 278°C. (with decomposition).

B.D.H. Pr_4NBr was recrystallised from 1,2-dichloroethane, mp. = 276°C. (with decomposition).

Bu_4NBr was prepared by careful neutralisation of the hydroxide with purified hydrogen bromide gas, followed by vacuum drying and recrystallisation from ethyl acetate, mp. = 118 to 119°C.

Bu_4NNO_3 was prepared by neutralisation of the hydroxide with nitric acid, followed by vacuum drying and recrystallisation from benzene, mp. = 118 to 120°C.

Bu_4NClO_4 was prepared by neutralisation of the hydroxide by means of perchloric acid, followed by filtration of the product, vacuum drying, and recrystallisation from benzene, mp. = 214 to 215°C.

Bu_4NBPh_4 was precipitated on mixing aqueous solutions of Bu_4NI and $NaBPh_4$. The product obtained by filtration was recrystallised from acetone-water mixtures, mp. = 233 to 234°C.

Bu_3NHPi was prepared by mixing hot alcoholic solutions of Bu_3N and picric acid in equimolar quantities. The product was obtained by crystallisation, mp = 106°C.

Bu_3NHI was prepared from the amine and the corresponding acid in hot alcoholic solution, followed by recrystallisation from ethyl acetate, mp = 101 to 102°C.

CHAPTER 4.

RESULTS AND DISCUSSION

4.1. Elimination of the Conductive Contribution to the Measured Loss.

Since all the solutions studied possess a low frequency ionic conductance, the total measured loss (ε''_m) will contain a contribution from the ionic conductance appropriate to the frequency concerned. The "dipolar" loss (ε''_d) can be calculated from the measured loss (ε''_m) by means of:

$$\varepsilon''_d = \varepsilon''_m - \frac{1.8 \times 10^{12}\kappa}{f} , \qquad 4.1$$

where f is the frequency of measurement, and κ is the specific ionic conductance at that frequency. Throughout the present work, κ has been taken to be independent of frequency up to the highest frequency of measurement (3.0 GHz.).

However, since considerable increases in ionic conductance in aqueous electrolyte solutions have been reported by Little (5) and Hasted et al (6), and have also been found in this laboratory (87), this assumption may be a source of error. In the case of solutions of tributylammonium picrate and some of the quaternary ammonium salt solutions in solvents of low permittivity, the ionic contribution to the total loss is small for the frequencies investigated. Consequently, it is unlikely that large errors have resulted from the assumption that κ is independent of frequency. With solutions of quaternary ammonium salts in solvents such as acetone and 1,2-dichloroethane, in which κ is of the order of 10^{-3} to 10^{-2} mhos $cms.^{-1}$, a 20%

increase in κ above its low frequency value, would have the effect of reducing the value of the relaxation time by up to about 30%. In addition, the shape of the Cole-Cole plot would be altered considerably, and in certain cases, the experimental points would lie outside a Debye semicircle. Within the frequency range investigated, such unusual dielectric behaviour was not observed.

In order to provide some experimental justification for this assumption, the specific conductances of a number of representative solutions in 1,2-dichloroethane have been measured at various frequencies between 1 and 100 MHz. by means of the admittance bridge, and are given in table 4.1.

Table 4.1. Specific Conductance (in mhos cms^{-1}.) as a function of Frequency for Solutions in 1,2-dichloroethane. Temperature is 25°C.

Salt	Bu_4NBr				Bu_4NBPh_4
Conc. (M)	0.00669	0.05	0.1	0.2	0.232
freq. (MHz)	$\kappa \times 10^4$	$\kappa \times 10^3$	$\kappa \times 10^3$	$\kappa \times 10^3$	$\kappa \times 10^3$
100	0.91	0.50	0.91	1.63	2.19
60	0.96	0.47	0.87	1.59	2.12
30	0.95	0.46	0.86	1.60	2.16
10	0.91	0.46	0.85	1.61	2.16
5	0.90	0.46	0.85	1.61	2.16
1.2	0.89	0.46	0.85	1.60	2.16
5 KHz.	-	0.453	0.865	1.62	2.17
300 Hz	0.919	-	-	-	-

Within the accuracy of the results (±2%), κ is independent of frequency up to 100 MHz.

Values of permittivity and loss (ε_d'') found for all the solutions investigated are given in Appendix 1. Values of specific ionic conductance are given in Appendix 2. Mead, Fuoss and Kraus (88) measured the ionic conductance of solutions of tributylammonium picrate in 1,2-dichloroethane, and reported ionic conductances for this particular system that are slightly lower than those found in the present work.

4.2. Separation of Solvent and Electrolyte Dielectric Dispersion Regions.

Over the frequency range in which the electrolyte solutions were investigated, changes of permittivity and to a lesser extent changes of loss of many of the pure solvents are small, but are not necessarily negligible. Ideally, measurements on electrolyte solutions should be extended over a very wide frequency range, so that it would be possible to separate the electrolyte and the solvent contributions to the observed dielectric dispersion. In the present investigation, measurements have been confined to a limited frequency range, and the electrolyte contribution has been found by assuming that the permittivity and loss of the solvents are unchanged by the presence of the electrolyte. Corrected permittivities and losses, attributable to the electrolyte alone, were found by means of equations 4.2 and 4.3, where ε'_m is the measured permittivity at a frequency f, and ε''_d is the dipolar loss calculated from equation 4.1.

$$\varepsilon' = \varepsilon'_m + (\varepsilon'_o - \varepsilon')_{solvent} \quad . \qquad 4.2$$

$$\varepsilon'' = \varepsilon''_d - \varepsilon''_{solvent} \quad . \qquad 4.3$$

In equation 4.2, ε'_o is the static permittivity of the pure solvent, and $\varepsilon'_{solvent}$ and $\varepsilon''_{solvent}$ are its permittivity and loss at the frequency f. Where necessary, values of $\varepsilon'_{solvent}$ and $\varepsilon''_{solvent}$ at a frequency f, have been calculated either from data obtained in this investigation, or from the literature.

4.3. Permittivity and Loss of Solvents.

Permittivity and loss of those solvents employed, for which no data could be found in the literature, were measured by the Standing Wave method, the results obtained being given in Appendix 3. Diethyl Ketone has been studied in the frequency range 250 to 500 MHz. (89), but measurements at higher frequencies do not seem to have been made. Below 1.0 GHz., the value of permittivity of diethyl ketone (appendix A3.1) obtained, does not change with frequency, and is therefore equal to the static value. The static permittivities for various temperatures, found by taking the average of the values found at 1.0, 0.7 and 0.5 GHz., together with their deviations are:

17.57 ± 0.01 (17.44) at 15°, 16.73 ± 0.00 (16.56) at 25°, 15.99 ± 0.03 (15.71) at 35°, and 15.17 ± 0.02 (14.92) at 45°C. The small deviations suggest that the results are accurate. The numbers given in parentheses are static permittivities calculated by interpolation from the data of Cole (90), and are lower than the values found here. Because of these discrepancies, a sample of the diethyl ketone employed in the present measurements was analysed by V.P.C.; it appeared to contain less than 0.05% of impurities.

Permittivity and loss data obtained for 1,2 and 1,1-dichloroethane is given in appendices A3.2 and A3.3. The value of permittivity of 1,2-dichloroethane obtained at 1 GHz. at 25°C agrees exactly with the value (10.36) given by the National Bureau of Standards (91), but is higher than that reported by Heston, Hennelly and Smyth (92) (10.16). The loss at 3 GHz. determined by Branin and Smyth (93), by a standing wave method, is smaller than that found here by about 15%. The losses found for 1,2-dichloroethane and for diethyl ketone at frequencies below 3 GHz., are larger than those calculated from the 3 GHz. values. The difference is unlikely to be the result of experimental error, since satisfactory values of loss for 1 and 2 GHz. have been calculated from the value found at 3 GHz. in the case of 1,1-dichloroethane.

The permittivity of 1,1-dichloroethane should not change appreciably with frequency below 1 GHz., and a value of 9.98 found here, is close to an earlier literature value of 10.0 (91), although not in such good agreement with a more recent result of 9.90 (94). The sample used was carefully fractionated, and appeared to be pure by V.P.C. standards. The discrepancy may be due both to the difficulty of purifying chlorocarbons, and to the limitations of conducting V.P.C. analyses of such compounds, owing to the similarity in the retention times of halocarbons when boiling point columns such as silicone oil are employed.

The loss of dichloromethane at 3.0 GHz. is small, and the value of permittivity of 8.75 found here, which should be identical with the static value, is lower than the literature value of 9.83 (95). The data for 1,1,2,2-tetrachloroethane can be represented by the Debye-Pellat equation, and was found to have a rather large relaxation time of 33 psec. The value of static permittivity found here of 8.20, is in agreement with the literature value of 8.2 at 20°C (91).

For acetone, tetrahydrofuran, 1,1,1-trichloroethane, chlorobenzene and chloroform, permittivities and losses obtained from the literature, interpolating where necessary, are given in appendix A3.7.

4.4. Density and Molar Volume Determinations.

The densities of various electrolyte solutions in 1,2-dichloroethane, prepared by weight, were determined by pipetting and weighing 10 ml. samples of the solutions, maintained at 25°C. This method was used in preference to that involving the use of a pyknometer because with the latter, the solvent tended to boil as the solution was drawn in. From a comparison of values obtained for the pure solvent by both methods, it was estimated that densities determined in this way are accurate to at least ±0.5%. Densities were determined at three concentrations in the range 0 to 0.7 M. and were found to be proportional to electrolyte concentration. At 25°C., densities (ρ) of solutions can be represented by means of the following relation:

$$\rho = 1.2457 - \delta . c \quad , \tag{4.4}$$

where values of δ, appropriate for the electrolyte concerned, are given in table 4.2, and c is the electrolyte concentration in moles litre^{-1}.

Table 4.2.

Electrolyte	δ(g.cm^{-3}. mole^{-1})
Bu_4NBr	0.050
Bu_4NI	0.009
Bu_4NNO_3	0.089
Bu_4NClO_4	0.058
Bu_4NBPh_4	0.120
Pr_4NBr	0.019
Bu_3NHPi	0.034
Bu_3NHI	0.026

The greatest changes in density occur with solutions of tetrabutylammonium tetraphenylboride and nitrate. Molar volumes of the electrolytes were obtained by plotting specific volume against weight fraction, and extrapolating to an electrolyte weight fraction of unity. The product of the specific volume, obtained as an intercept, and the molecular weight then gives the partial molar volume (99), values of which are given in table 4.3.

Table 4.3. Molar Volumes (in cm^3 $mole^{-1}$) of various Electrolytes in 1,2-dichloroethane in the concentration range 0 to 0.7 M.

Bu_4NBr	300
Bu_4NI	317
Bu_4NNO_3	315
Bu_4NClO_4	320
Bu_4NBPh_4	550
Pr_4NBr	226
Bu_3NHPi	360
Bu_3NHI	260

The values given in table 4.3 are probably accurate to ± 2%. Any concentration dependence is obscured by the inaccuracy inherent in the density data. The values obtained here are comparable in magnitude to those reported by Gilkerson and Stewart (100). Thus they reported molar volumes of 302 and 316 ccs $mole^{-1}$ for tetrabutylammonium iodide in o-dichlorobenzene and water respectively.

4.5. Viscosity Measurements.

Viscosities of electrolyte solutions in 1,2-dichloroethane were measured by means of an Ostwald viscometer, calibrated with pure water as described in the British Standards Institution publication Number B.S.188. For most solutions, three electrolyte concentrations were examined, and the results are displayed graphically in

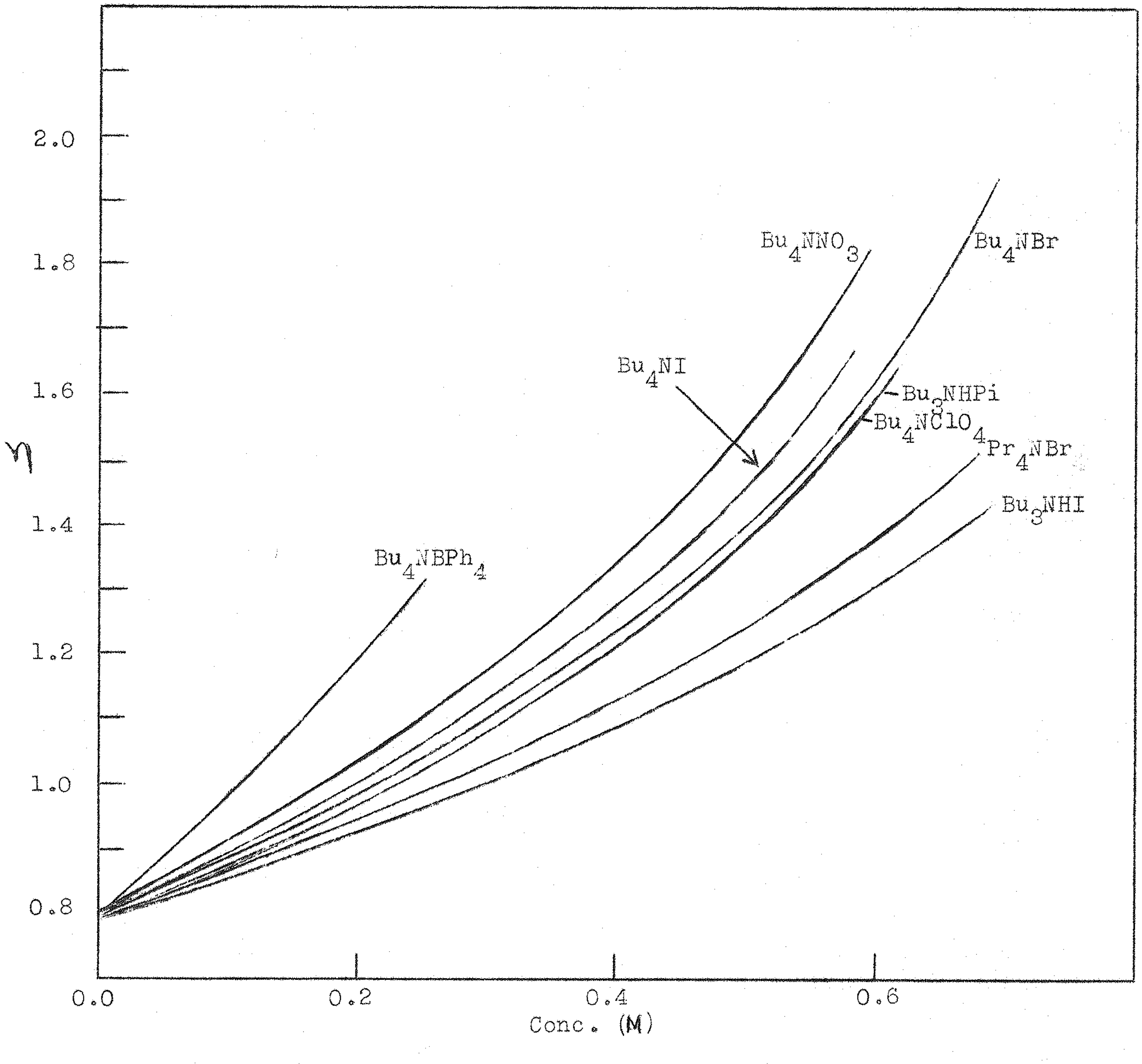


Fig. 4.1 Dependence of viscosity (in cP.) on electrolyte concentration in 1,2-dichloroethane. (at 25°C)

figure 4.1. The viscosity of solutions in 1,2-dichloroethane is increased by the addition of electrolytes, those with the smallest molar volumes having smallest effect.

4.6. Method used to find the Relaxation Time (τ_o) and the Cole-Cole distribution parameter (α).

Experimental permittivities and losses, corrected for the effects of low frequency ionic conductance and changes in solvent permittivity and loss were plotted on a Cole diagram, and the best fitting circular arc was drawn through the points concerned. The low frequency intercept on the abscissa of such a Cole-Cole plot is the static permittivity (ε_o') of the solution, if no further dielectric dispersion takes place at frequencies below those used for measurement. The high frequency intercept (ε_∞') may be regarded as the static permittivity of the solvent in the presence of electrolyte.

The Cole-Cole (43) distribution parameter (α) was found from the relationship:

$$\alpha = \theta/90^\circ \quad , \qquad 4.5$$

where θ is the angle made by the radius drawn from the centre of the Cole-Cole circle, which lies below the abscissa, to one of the points at which the plot intercepts the abscissa axis.

Relaxation time (τ_o), was found by means of (83) equation 4.6:

$$v/u = (\omega\tau_o)^{1-\alpha} \quad , \qquad 4.6$$

where v and u are the lengths of the chords between an experimental point corresponding to an angular frequency ω and the intercepts ε'_o and ε'_∞, which the circular arc makes with the abscissa. Values of τ_o, given in tables 4.5 (page 76) and 4.8 (page 98), are the means of the values calculated using equation 4.6, from experimental points for each frequency employed. The number following τ_o in these tables, is the mean deviation of individual values of τ_o from the mean value.

Examples of Cole-Cole diagrams, and details of specific systems are given in the following sections.

4.7. Reasons for Investigating Solutions of Tributylammonium Picrate and Iodide.

In this investigation, solutions of tetralkylammonium salts were studied initially, but because the interpretation of their dielectric behaviour presented certain difficulties, an investigation of tri-n-butylammonium salt solutions was undertaken. There is evidence in the literature, which is described below, to suggest that these salts exist predominantly in the form of "contact" ion pairs over a wide range of concentrations and solvents.

a. Concentration dependence of static permittivity of electrolyte solutions in non polar solvents.

Kraus (101) has connoted that investigations of electrolyte solutions in non polar solvents, give an indication of the behaviour to be expected in solvents of higher permittivity, in which association is likely to be less extensive, and consequently correspondingly simpler. Maryott (18) and Geddes and Kraus (17) have found that plots of permittivity against electrolyte mole fraction, are more nearly linear than those for other types of electrolyte. This indicates that these solutions are simpler than those of, for example, quaternary ammonium salts.

b. Cryoscopic Measurements on Electrolyte Solutions in Benzene.

Electrolyte solutions in benzene have been investigated cryoscopically by Kraus and co-workers (102 to 105), who have concluded that association is most pronounced with highly symmetrical ions. Copenhafer and Kraus (104) reported that for a concentration of 0.01 M., the association number n (the ratio of the apparent molecular weight to the formula weight) is 1.07 for tributylammonium picrate and 1.4 for the iodide. For the same concentration of quaternary ammonium salts, n is much larger. For example, for tetrabutylammonium perchlorate n is 5.0 and for the thiocyanate n is 4.2. Since for benzene solutions of tributylammonium picrate, n is less than it is for solutions of the iodide, solutions of the picrate have been the subject of the more extensive study in the present investigation.

c. Dielectric Relaxation of Electroylte solutions in non polar solvents.

Davies and Williams (19) have reported that in concentrations of 0.021 and 0.066 M., the dielectric behaviours of solutions of tributylammonium picrate in xylene can be represented by the Debye-Pellat equation, whereas those of tributylammonium iodide in mixed solvents cannot. Davies and Johansson (30) have studied benzene solutions of tri-iso-amylammonium picrate, and have found that even in solutions with concentrations approaching 0.54 M., only small Cole distribution parameters are required. Simple Debye-Pellat behaviour arising from the orientational relaxation of contact ion pairs could therefore be reasonably expected, (and has in fact been observed) with solutions of tributylammonium picrate in solvents of higher permittivity.

d. Conductance of Tributylammonium Picrate in 1,2-dichloroethane.

Mead, Fuoss and Kraus (88) determined the conductance of solutions of tributylammonium picrate in 1,2-dichloroethane up to a concentration of about 0.5 M. By assuming a value for* Δ_o of 60, they estimated its ion pair dissociation constant to be 2.10×10^{-8} litre^{-1} mole. For dissociation of triple ions into ion pairs and free ions, an equilibrium constant of 0.045 litre^{-1} mole was reported. The ion pair dissociation constant of this electrolyte is much smaller than those of quaternary ammonium salts, which usually lie in the region of 10^{-4} litre^{-1} mole (106). From its dissociation constant, it seems that between about 0.01 and 0.05% of the concentration of tributylammonium picrate in 1,2-dichloroethane

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*Δ_o is limiting ionic conductance.

is in the form of free ions in the concentration range 0.1 to 0.5 M. According to the triple ion dissociation constant, less than 0.2% of the electrolyte is in the form of triple ions at concentrations up to 0.5 M. Hence in 1,2-dichloroethane, tributylammonium picrate exists almost entirely in the form of ion pairs. However the static permittivity of the solution changes considerably in the concentration range investigated by these authors, and their data ~~is~~ are therefore re-examined in the next section.

4.8. Re-examination of Data of Mead, Fuoss and Kraus (88).

A selection of conductances reported by these authors for solutions of tributylammonium picrate in 1,2-dichloroethane are given in table 4.4. Static permittivities of solutions obtained by interpolation from the data given in table 4.5, are summarised in the third column. The expression:

$$K = K_o \, e^{-e^2/a\varepsilon_o' kT} \qquad 4.7$$

can be used to discuss the dependence of dissociation constants on static permittivities (ε_o') of the solutions. Non-coulombic forces, which are of course independent of permittivity, are amongst the factors which determine K_o. Accascina, D'Aprano and Fuoss (107) have pointed out that equation 4.7 should be modified, to include the additional electrostatic attraction between the anion and cation due to the dipole moment of the picrate ion.

Table 4.4.

conc.(M)	Λ_M ohm^{-1} cm.	ε'_o	$e^2/a\varepsilon'_o kT$	Calcd.K	$\Lambda_{calcd.}$ ohm^{-1} cm.$^{-1}$
0.2982	0.1414	17.2	6.51	1.55×10^{-6}	0.14
0.2382	0.1283	16.0	7.00	9.48×10^{-7}	0.12
0.1123	0.0973	13.2	8.48	2.15×10^{-7}	0.08
0.0448	0.0852	11.55	9.70	6.36×10^{-8}	0.07
0.00535	0.1363	10.5	10.67	2.41×10^{-8}	0.13
0.00018	0.6425	10.36	10.81	(2.10×10^{-8})	0.64

Mead et al assumed a value for K_o and obtained a value of 2.4 Å for the distance of closest approach, which is unexpectedly small (88). An 'a' value of 5Å (Appendix 4, table A4.5) calculated from its dipole moment is in reasonable agreement with that estimated from molecular models. On the assumption that the value of K given by Mead et al corresponds to a permittivity of 10.36, values of K have been calculated using equation 4.7, with 'a' = 5Å. K changes by a factor of nearly 100 over the electrolyte concentration range 0 to 0.3 M, as is shown in table 4.4. The value of K is, of course, very sensitive to the value of 'a' used in equation 4.7, for example, with 'a' = 2.4 Å, K changes by a factor of about 10^4 in the concentration range 0 to 0.3 M. Proper analysis of conductance data may only be possible when 'a' has been determined from measurements of the conductance in solvents of various permittivity, so that a plot of log. K against $1/\varepsilon'_o$ can be constructed.

For each value of K, given in table 4.4, an assessment of the degree of dissociation (γ) has been made. If the degree of dissociation (γ) is very small, then an approximate equivalent conductance ($\Delta_{Calcd.}$) can be calculated from (108):

$$\Delta_{Calcd.} = \gamma\Delta_o \quad . \qquad 4.8$$

Values of $\Delta_{Calcd.}$, so obtained, are given in table 4.4, and agree reasonably well with experimental values reported by Mead et al, and given in the second column in table 4.4.

Thus the minimum observed in the experimental phoreogram, at a concentration of approximately 0.05 M., may be the result of the permittivity dependence of K, rather than to the formation of triple ions.

4.9. Analysis of Permittivity and Loss Data of Tertiary ammonium salt solutions (data in Appendix 1).

Data for tertiary ammonium salt solutions were obtained by the Travelling Wave method, and in addition, a limited number of measurements were made with the Admittance Bridge. Corrected permittivities and losses for these electrolytes (see sections 4.1 and 4.2) when plotted as Cole-Cole diagrams, can in all cases be represented by semicircular arcs.

If α is zero, it follows from equation 4.6 that a plot of log.(v/u) against log.f should be a straight line with a slope of unity. Such a plot is illustrated in figure 4.2, for a 0.4 M. solution of tri-n-butylammonium picrate in 1,2-dichloroethane. With the exception of the low frequency point, all

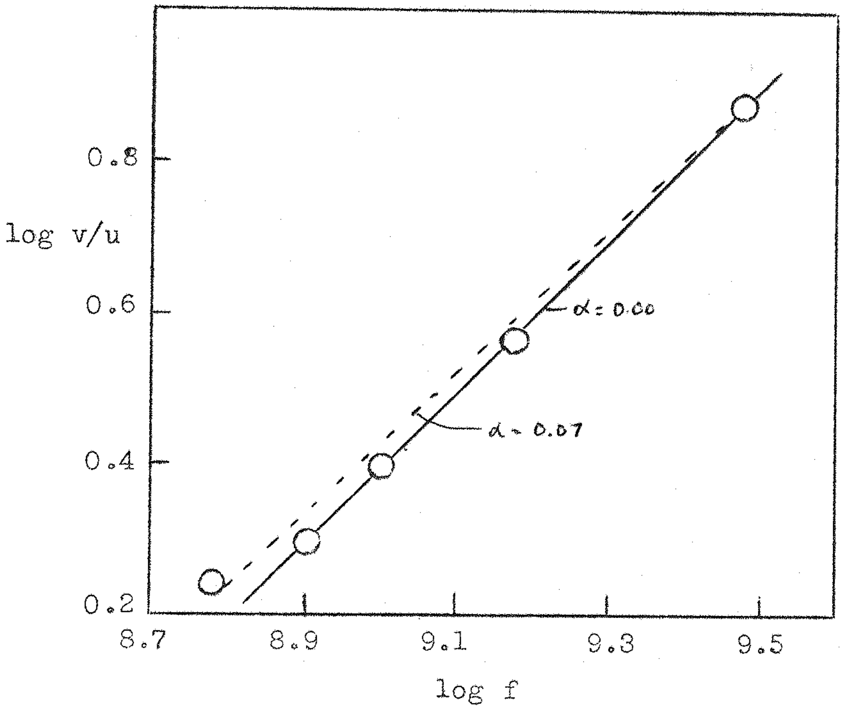


Figure 4.2. Log.(v/u) against log.f.

the points lie accurately on a straight line, with a slope of unity. This confirms that the data can be represented by the Debye-Pellat equation. Furthermore, if α is zero, then τ_0 obtained (109) from equations 4.7 and 4.8, by plotting permittivity against respectively ε''/ω and $\varepsilon''.\omega$, should have the same value from each plot, and should also agree with the value obtained from the use of equation 4.6.

$$\varepsilon' = \varepsilon'_0 - \varepsilon''(\omega\tau) \quad . \qquad 4.7$$

$$\varepsilon' = \varepsilon'_\infty + \varepsilon''/(\omega\tau) \quad . \qquad 4.8$$

Plots of equations 4.7 and 4.8, for 0.4 M. tributylammonium picrate in 1,2-dichloroethane are illustrated in figure 4.3.

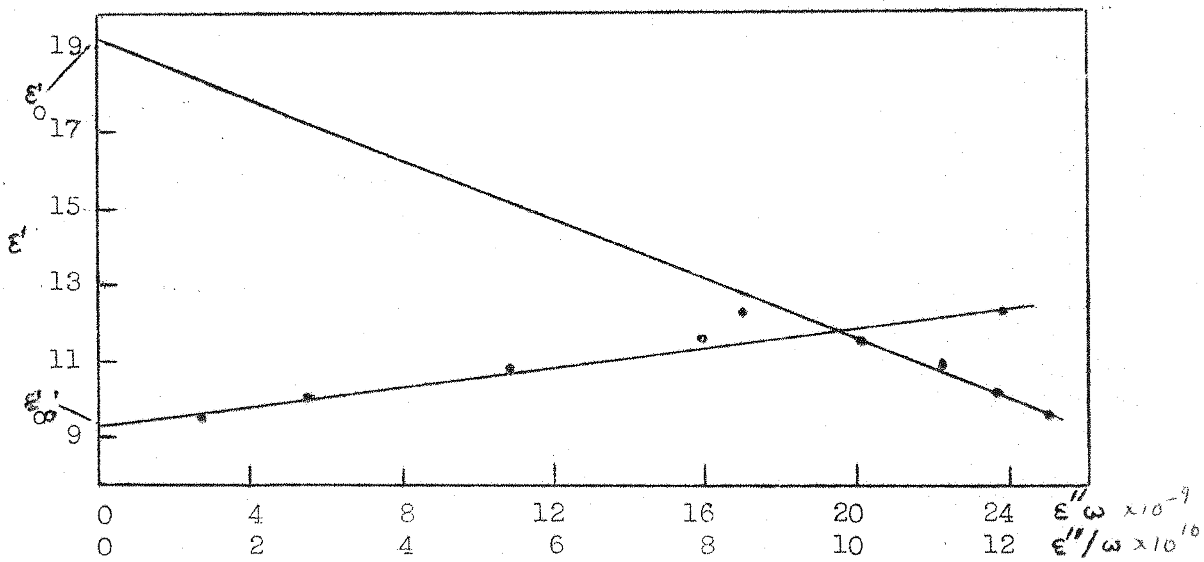


Figure 4.3. ε' against ε''/ω and $\varepsilon''\omega$.

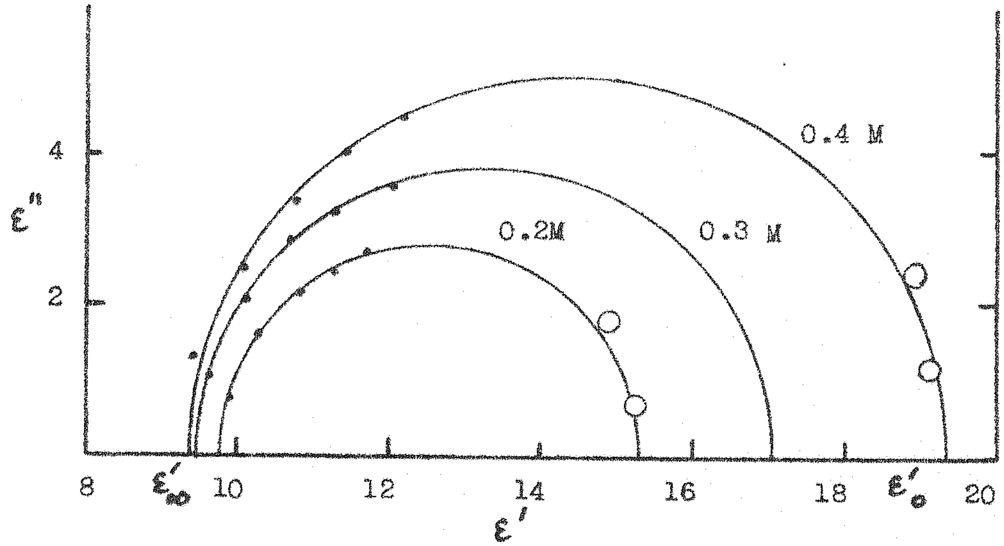


Fig. 4.4 Bu_3NHPi in 1,2-dichloroethane.

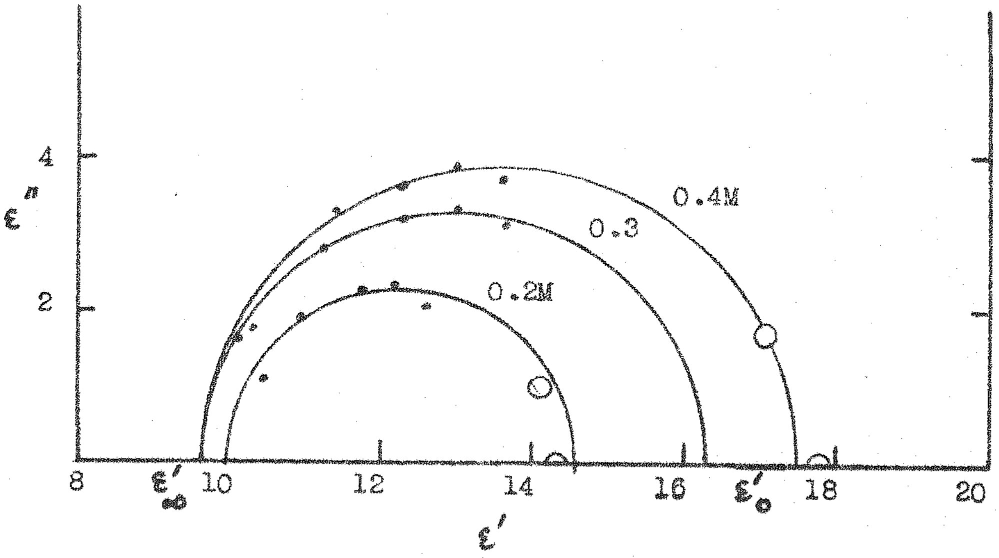


Fig. 4.5 Bu_3NHI in 1,2-dichloroethane.

Values of ε'_o and ε'_∞ obtained from the Cole diagram, shown in fig 4.4, are helpful in the construction of the linear plots corresponding to equations 4.7 and 4.8. From the ε''/ω plot, $\tau_o = 395$ psec. and from the $\varepsilon''.\omega$ plot, $\tau_o = 402$ psec. These values are in excellent agreement with each other, and also with the value of 400 psec. obtained by means of equation 4.6, and which is given in table 4.5. This agreement is further evidence that data can be represented by the Debye-Pellat equation. Cole diagrams for all the systems investigated are given in figures 4.4 to 4.15, and values of τ_o, ε'_o and ε'_∞ for each solution are given in table 4.5.

Table 4.5. Static permittivities (ε'_o), Solvent Static Permittivities (ε'_∞), and Relaxation Times (τ_o) of Tri-n-butylammonium Salts at 25°C.

Solvent	Electrolyte	Conc. (M)	ε'_o	ε'_∞	$\tau_o \times 10^{12}$ sec.
acetone	Bu_3NHI	0.4 0.3 0.2	26.6 25.3 24.0	17.8 18.25 19.2	97±8 85±6 86±9
diethyl ketone	Bu_3NHI	0.2	20.6	15.5	163±6
1,2-dichloroethane	Bu_3NHI	0.4 0.3 0.2	17.45 16.2 14.6	9.7 9.7 9.95	229±16 219±11 204±13
	Bu_3NHPi	0.4 0.3 0.2	19.35 17.1 15.3	9.35 9.5 9.8	400±10 370±6 336±12

Table 4.5. (continued).

1,1-dichloroethane	Bu_3NHI	0.4	15.6	9.45	228±15
		0.2	13.25	9.6	183±17
	Bu_3NHPi	0.4	18.95	9.05	318±24
		0.2	14.8	9.55	291±27
dichloromethane	Bu_3NHPi	0.4	18.85	8.0	259±14
		0.2	14.7	8.45	245±13
tetrahydrofuran	Bu_3NHPi	0.4	17.55	7.1	313±11
		0.2	13.0	7.3	262±5
1,1,1-trichloroethane	Bu_3NHPi	0.4	16.0	7.4	427±25
		0.2	11.6	7.5	350±12
chloroform	Bu_3NHI	0.4	12.0	4.8	282±39
		0.2	9.0	4.6	218±18
	Bu_3NHPi	0.4	14.9	4.8	401±12
		0.2	10.2	4.85	351±11
trichloroethylene	Bu_3NHPi	0.4	11.2	3.7	441±29
		0.2	7.0	3.5	298±23

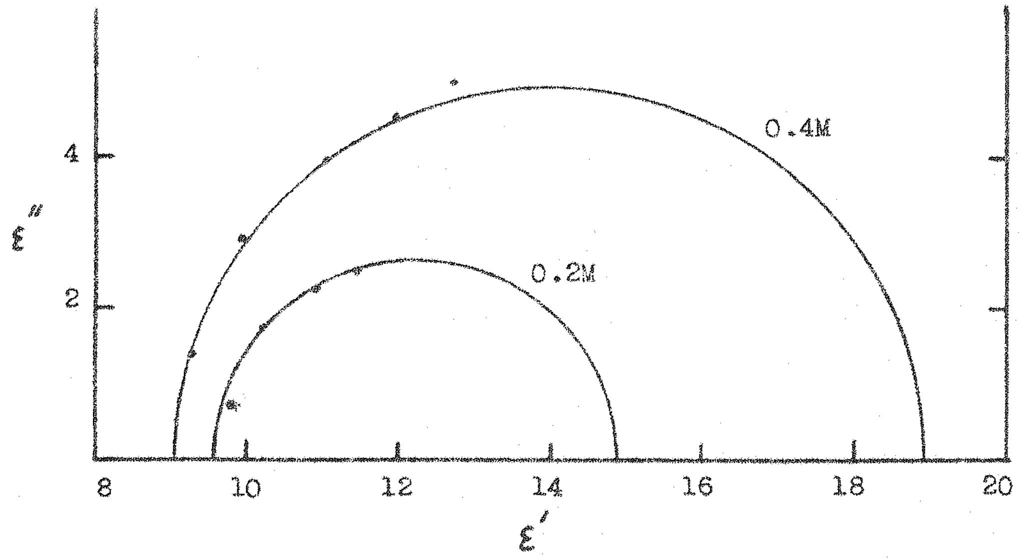


Fig. 4.7 Bu_3NHPi in 1,1-dichloroethane.

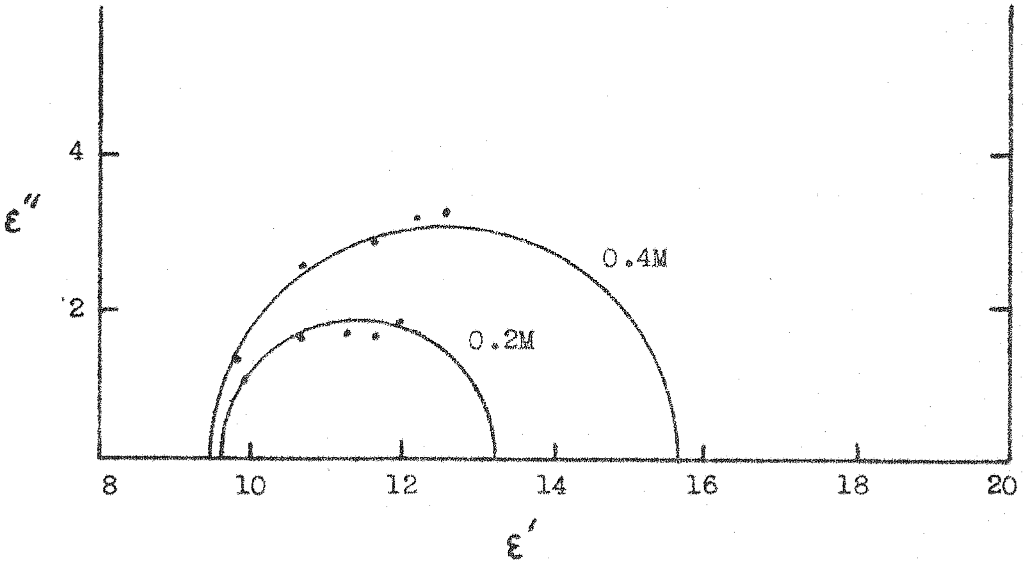


Fig. 4.6 Bu_3NHI in 1,1-dichloroethane.

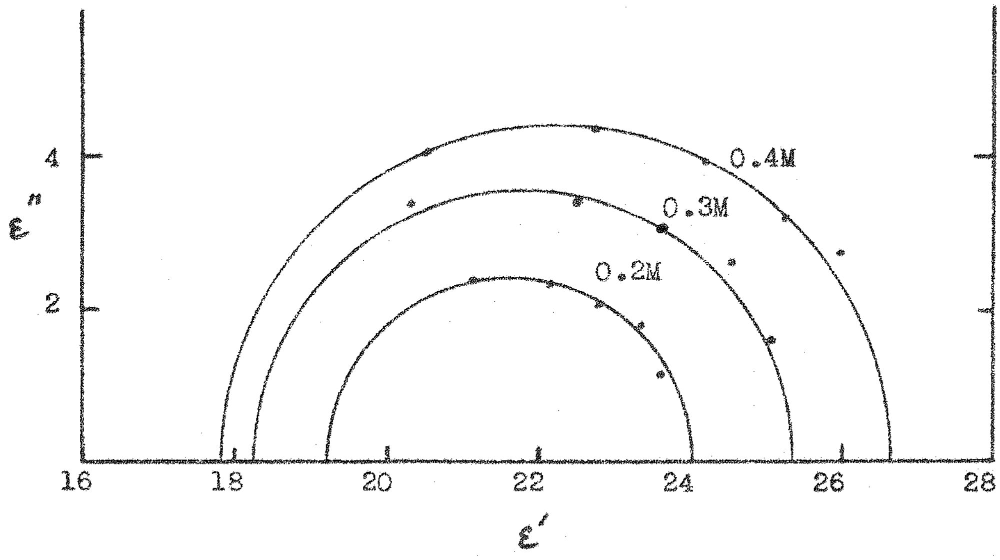


Fig. 4.8 Bu_3NHI in Acetone.

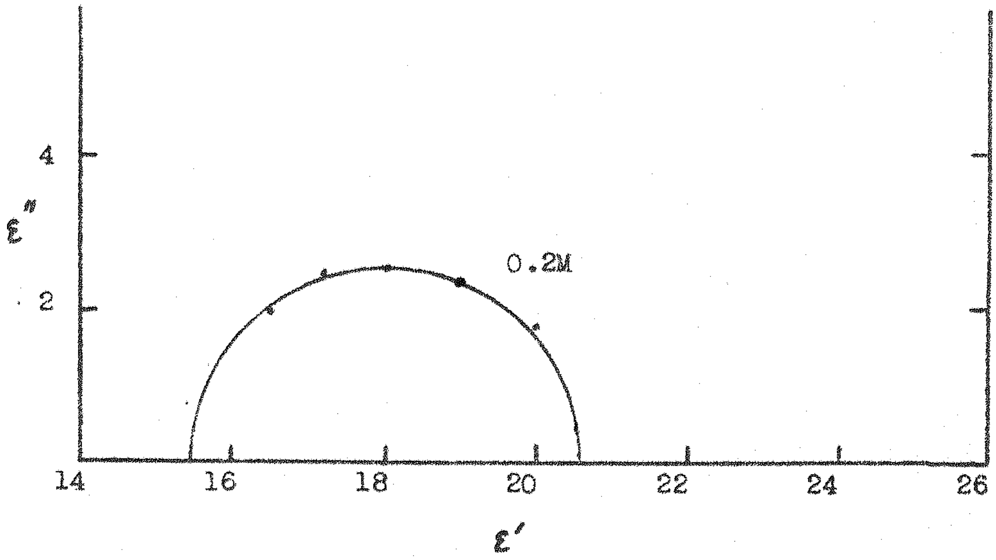


Fig. 4.9 Bu_3NHI in Diethyl ketone.

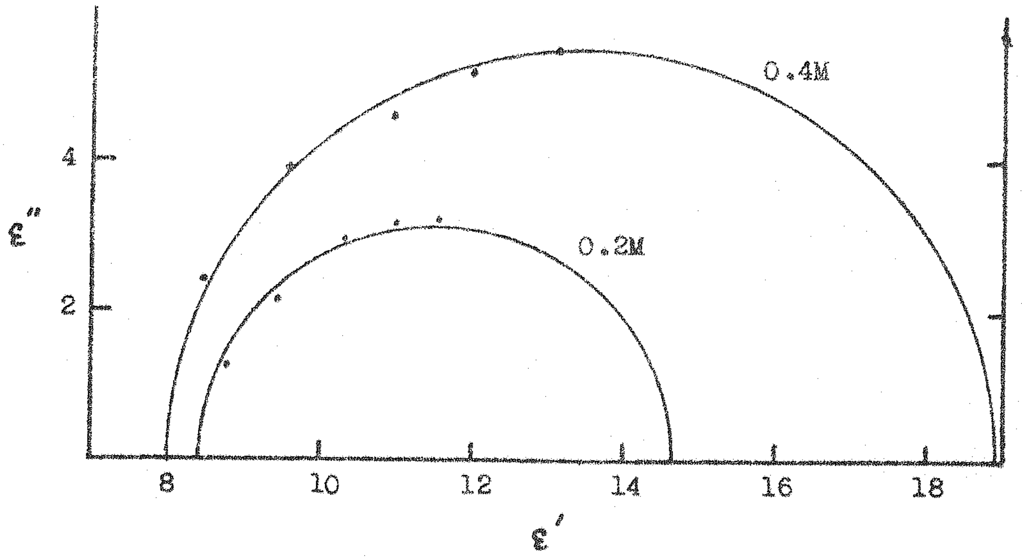


Fig. 4.10 Bu_3NHPi in Dichloromethane.

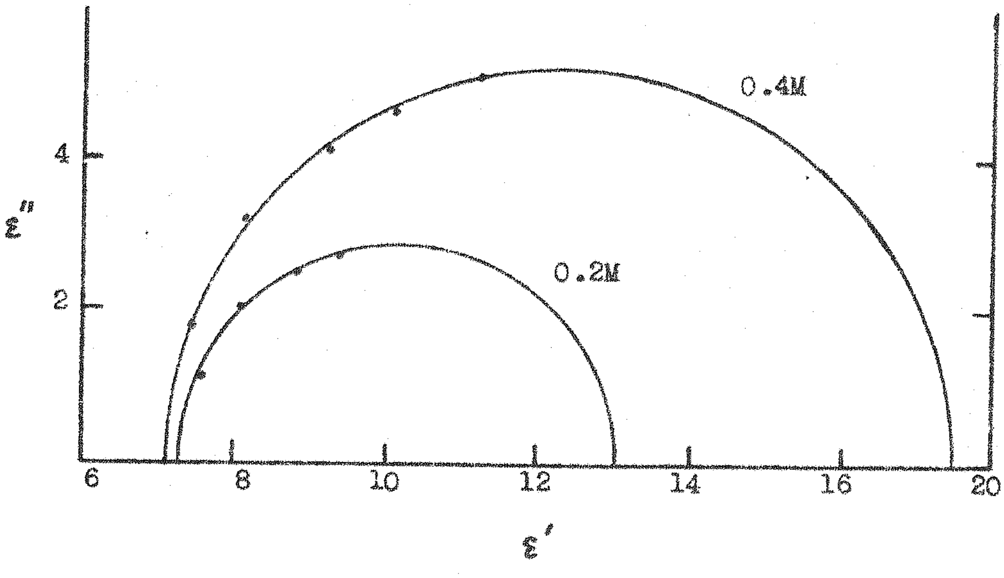


Fig. 4.11 Bu_3NHPi in Tetrahydrofuran.

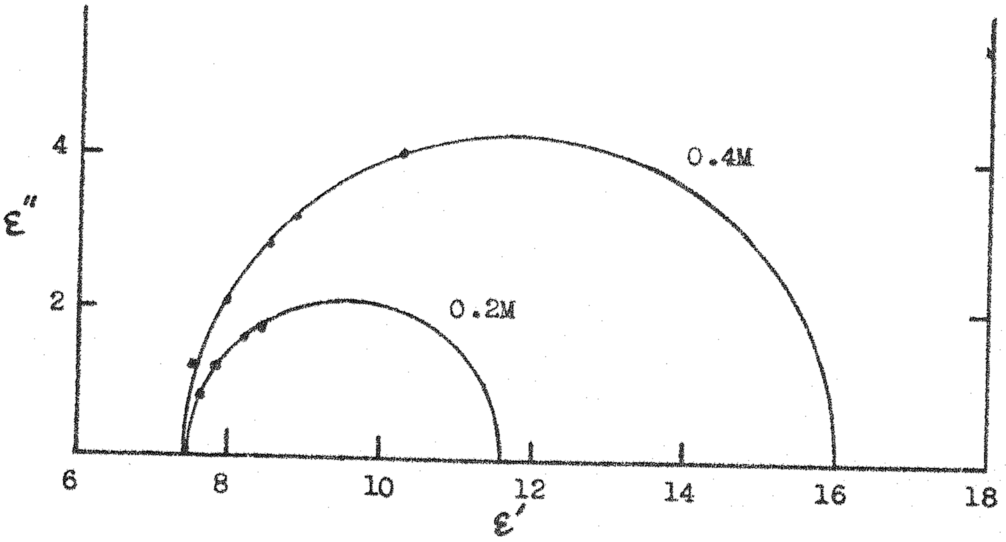


Fig. 4.12 Bu_3NHPi in 1,1,1-trichloroethane.

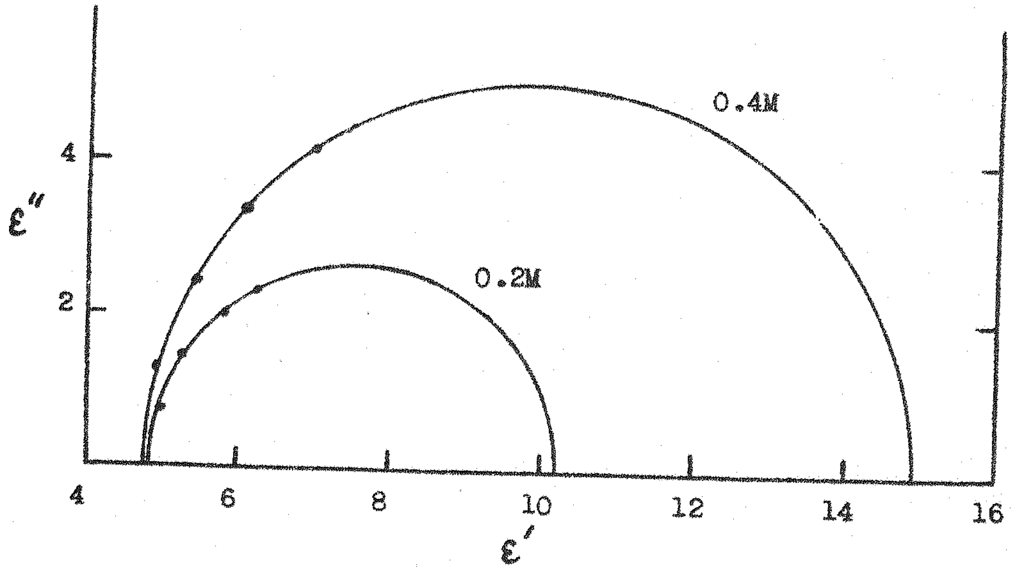


Fig. 4.13 Bu_3NHPi in chloroform.

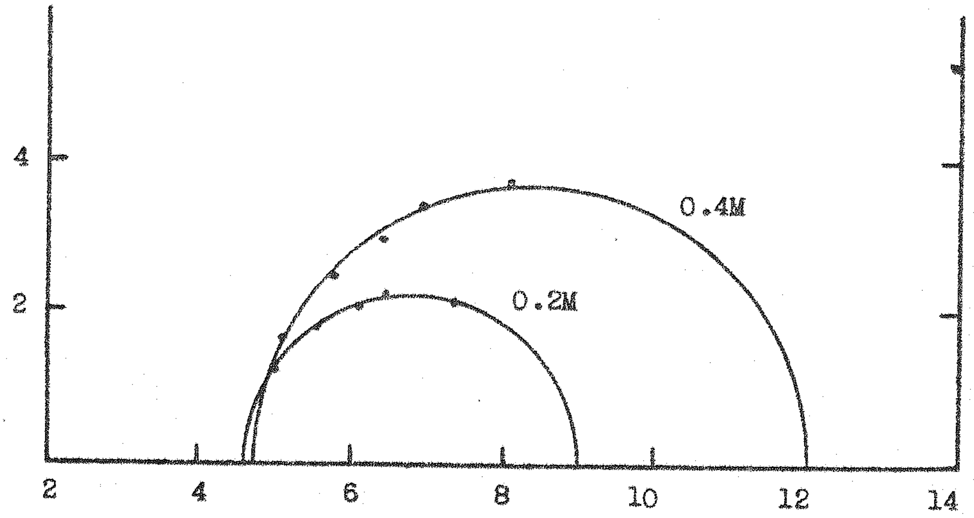


Fig. 4.14 Bu_3NHI in Chloroform.

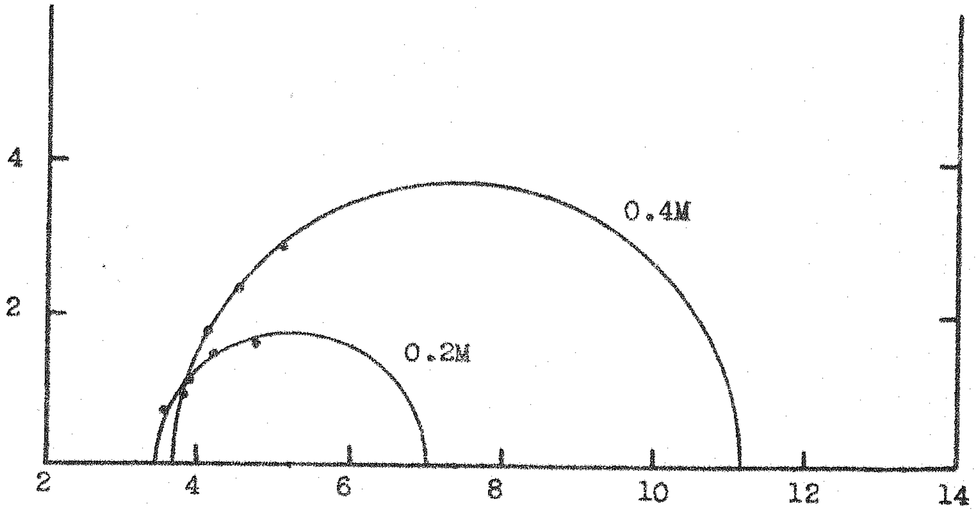


Fig. 4.15 Bu_3NHPi in Trichloroethylene.

4.10. Calculation of Intrinsic Relaxation Times.

Values of τ_o (see table 4.5) are quite concentration dependent, particularly in solvents of low permittivity. This suggests that the observed concentration dependence of the macroscopic relaxation time (τ_o), may be the result of an "internal field" effect. Powles (63) gave the expression:

$$\tau_p = \frac{2\varepsilon'_o + \varepsilon'_\infty}{3\varepsilon'_o} \cdot \tau_o \quad , \qquad 4.9$$

connecting a microscopic relaxation time τ_p, which may be the average relaxation time of a molecule, with the experimental relaxation time τ_o. This expression has been used to calculate τ_p from τ_o, by substituting the values of ε'_o and ε'_∞, given in table 4.5, into equation 4.9. According to Glarum (64), this procedure is correct if the relaxation time characterising the dispersion of one component of a system, is very much longer than that of the other component.

Values of τ_p are given in table 4.6, together with static permittivities, dielectric relaxation times, densities and viscosities of pure solvents. With the exception of solutions of tributylammonium picrate in dichloromethane, for which τ_p is the same at both concentrations studied, τ_p like τ_o is still concentration dependent. However, with some higher permittivity systems, the concentration dependence of τ_p is not very pronounced. The greater sensitivity of τ_p to concentration observed in lower permittivity systems, may be partly due to factors described in the next sections, and partly due to the inadequacy of equation 4.9. Miller and Smyth (68) concluded that the Powles correction slightly under corrects, and their conclusion seems confirmed by the results obtained here.

Davies and Williams (19) found that the relaxation time of tributylammonium picrate in xylene solutions was very dependent upon its concentration. They found that the empirical expression

$$\tau_{DW} = \frac{\tau_o \, \varepsilon'_o \text{ (Solvent)}}{\varepsilon'_o \text{ (Solution)}} \quad , \qquad 4.10$$

gave values of τ_{DW} that were reasonably independent of concentration. Davies and Johansson (30) studied benzene solutions of triisoamylammonium picrate up to a concentration of 0.54 M. The authors found that τ_{DW}, calculated from equation 4.10, was about 150 psec., and was reasonably concentration independent. Equation 4.9 is not satisfactory for the data relating to solutions of tributylammonium picrate in trichloroethylene. This solvent has the lowest permittivity of those investigated here. In this respect, therefore, the conclusions regarding the suitability of the Powles' equation are in harmony with those of Davies and his collaborators. When equation 4.10 is applied to the data obtained for solutions in trichloroethylene, values of τ_{DW} of 133 psec. and 143 psec for concentrations

Table 4.6. Properties of Solvents and Microscopic Relaxation Times of Tri-n-butylammonium Salts at 25°C. a = ref. 110, b = 92, c = 96, d = 97, e = 11, f = 112.

Solvent and its Properties					Electrolyte	Conc (M)	τ_P psec.	τ_{DW} psec.
	ε'_o	τ psec.	ρ gm/cc	η (c.p.)				
acetone	20.70	3.2a	0.785	0.309	Bu_3NHI	0.4	86	75
						0.3	77	70
						0.2	80	74
diethyl ketone	16.73	6.1	0.81	0.444	Bu_3NHI	0.2	149	132
1,2-dichloroethane	10.36	6.95b	1.245	0.787	Bu_3NHI	0.4	195	136
						0.3	190	140
						0.2	182	145
					Bu_3NHPi	0.4	331	215
						0.3	315	225
						0.2	296	228
1,1-dichloroethane	9.98	5.8	1.167	0.466	Bu_3NHI	0.4	198	146
						0.2	166	125
					Bu_3NHPi	0.4	263	168
						0.2	257	197
dichloromethane	8.75	2.4	1.33	0.41	Bu_3NHPi	0.4	209	120
						0.2	210	146
1,1,2,2-tetrachloroethane	8.20	33.	1.59	1.64	-	-	-	-
tetrahydrofuran	8.04	2.7c	0.883	0.480	Bu_3NHPi	0.4	251	144
						0.2	224	162

Table 4.6. (continued).

1,1,1-trichloroethane	7.04	5.2d	1.44	0.78	Bu_3NHPi	0.4 0.2	351 309	188 212
chlorobenzene	5.63	10.8e	1.10	0.76	-	-	-	-
chloroform	4.82	5.2f	1.48	0.54	Bu_3NHI	0.4 0.2	226 182	113 117
					Bu_3NHPi	0.4 0.2	310 289	130 166
trichloroethylene	3.37	6.	1.46	0.550	Bu_3NHPi	0.4 0.2	343 248	133 143

of 0.4 M and 0.2 M respectively (see table 4.6) are obtained. These values are similar in magnitude to the values of τ_{DW} of about 150 psec. reported by Davies et al (30).

Values of τ_{DW} obtained for solutions of tertiary ammonium salts, are listed in table 4.6. For a given solvent, τ_{DW} is as satisfactorily independent of electrolyte concentration as is τ_P. Davies and Johansson have stressed the empirical nature of equation 4.10, but the fact that it is successful provides good reason for its retention. Never the less, the present author continues to regard equation 4.9 as approximately correct in so far as it goes. Its apparent failure may in fact be the result of other relevant factors such as dipolar interactions, or changes in the state of the electrolyte, both of which are functions of permittivity and concentration.

4.11. Dependence of Electrolyte Relaxation Times on Properties of Solvents.

From inspection of figure 4.1, it can be seen that in 1,2-dichloroethane, viscosity increases considerably with increasing concentration of electrolyte. Similar changes have also been observed with solutions of triamylammonium picrate in benzene (30), and probably occur with most of the electrolyte solutions studied here. The increase in values of τ_o or τ_P could therefore be attributed to increases in solution viscosities, but for reasons discussed below, this does not seem very likely.

If relaxation time is closely controlled by viscosity, then the increase in either τ_o or τ_P with electrolyte concentration could reasonably be expected to be most pronounced for solutions in a solvent such as acetone, which on account of its own low viscosity, ought to exhibit the greatest changes when electrolytes are dissolved in it. In fact, for solutions of tributylammonium iodide in acetone, τ_o changes by about 10% when the concentration is increased from 0.2 M to 0.4 M, while τ_P changes only slightly. For similar changes in concentration with solvents having larger viscosities, the corresponding changes in both τ_o and τ_P are generally larger. Secondly, the relaxation times (τ_o or τ_P) of equimolar solutions of the same electrolyte in different solvents, do not exhibit the linear dependence on viscosity as proposed by Debye. In the case of tributylammonium iodide, τ_o and τ_P are larger for solutions in diethyl ketone than for solutions in acetone, and the difference is probably larger than would have been predicted from the difference in solution viscosities. Relaxation times of both tributylammonium iodide and picrate are only slightly lower in 1,1-dichloroethane than they are in 1,2-dichloroethane, in spite of the fact that with this pair of solvents, the difference in solvent viscosities is greater than that for acetone and diethyl ketone. Despite the large size of an ion pair as compared with that of a solvent molecule, the Debye-Stokes relation does not seem to be obeyed at all well. This is interesting, because for solutions of electrolytes in acetone, 1,2 and 1,1-dichloroethane, limiting ionic conductances obey Walden's rule quite well (106).

For a variety of solvents, the relaxation times (τ_o or τ_P) of tributylammonium picrate are about 50% larger than those of tributylammonium iodide. One fact which is probably relevant in the present comparison, is that the molar volume is also about 50% greater than that of the iodide (see table 4.3). The relaxation time of tributylammonium picrate in dichloromethane is quite short and in magnitude is equivalent to the relaxation time of the iodide in diethyl ketone. The relaxation time of the picrate in tetrahydrofuran is a little shorter than that for the same electrolyte in either of the dichloroethanes. Relaxation times of ion pairs in other solvents, are all fairly similar in magnitude, although those for 0.4 M solutions in 1,1,1-trichloroethane and trichloroethylene are significantly longer than those in other solvents.

The correlation between ion pair relaxation times and solvent relaxation times is in some ways closer than that between ion pair relaxation times and solvent viscosities. Thus acetone, dichloromethane and tetrahydrofuran have short relaxation times, and ion pair relaxation times are also short in these solvents. The difference between the relaxation time of acetone and diethyl ketone is proportionately larger than that between the viscosities, whilst for the pair of solvents 1,1 and 1,2-dichloroethane, the converse is true. It seems, therefore, that ion pair relaxation times correlate at least as closely with solvent relaxation times as they do with their viscosities.

Examination of table 4.6 reveals that solvent density also influences electrolyte relaxation times. It may be concluded that in solvents with small densities, low viscosities and short dielectric relaxation times, ion pairs can be expected to have short relaxation times, and the converse naturally applies.

4.12. Conclusions drawn from the results of the present investigation of Solutions of Tertiary Ammonium Salts.

Plots of $(\varepsilon'_o - \varepsilon'_\infty)$ against electrolyte concentration are illustrated in figures 4.16 and 4.17. For equimolar solutions of different electrolytes in the same solvent, $(\varepsilon'_o - \varepsilon'_\infty)$ is greater for tributylammonium picrate than for the iodide. This may be expected, since the dipole moment of the picrate is about 12D. (see table 1.2) compared with 8D. for the iodide, but the slopes of the curves are not proportional to the squares of the dipole moments. The plot obtained for solutions of tributylammonium iodide in acetone is the most nearly linear. This is consistent with the conclusion that in this solvent, tributylammonium iodide is mainly in the form of ion pairs. The experimental point for a 0.2 M solution of this electrolyte in diethyl ketone lies just above the curve for acetone solutions, which suggests that this electrolyte has a similar structure in both ketones.

The plots illustrated in figure 4.17, for solutions of tributylammonium picrate in 1,2 and 1,1-dichloroethane, dichloromethane, tetrahydrofuran and chloroform are similar in shape, which again indicates a general similarity in solution structure. Probably in these cases therefore, the electrolyte is principally in the form

Key: ● $Cl_2C{:}CHCl$, ▵ $CHCl_3$, □ Cl_3CCH_3, ▽ THF, ○ CH_2Cl_2, D $ClCH_2CH_2Cl$

X Cl_2CHCH_3, A $(CH_3)_2CO$, V $(C_2H_5)_2CO$.

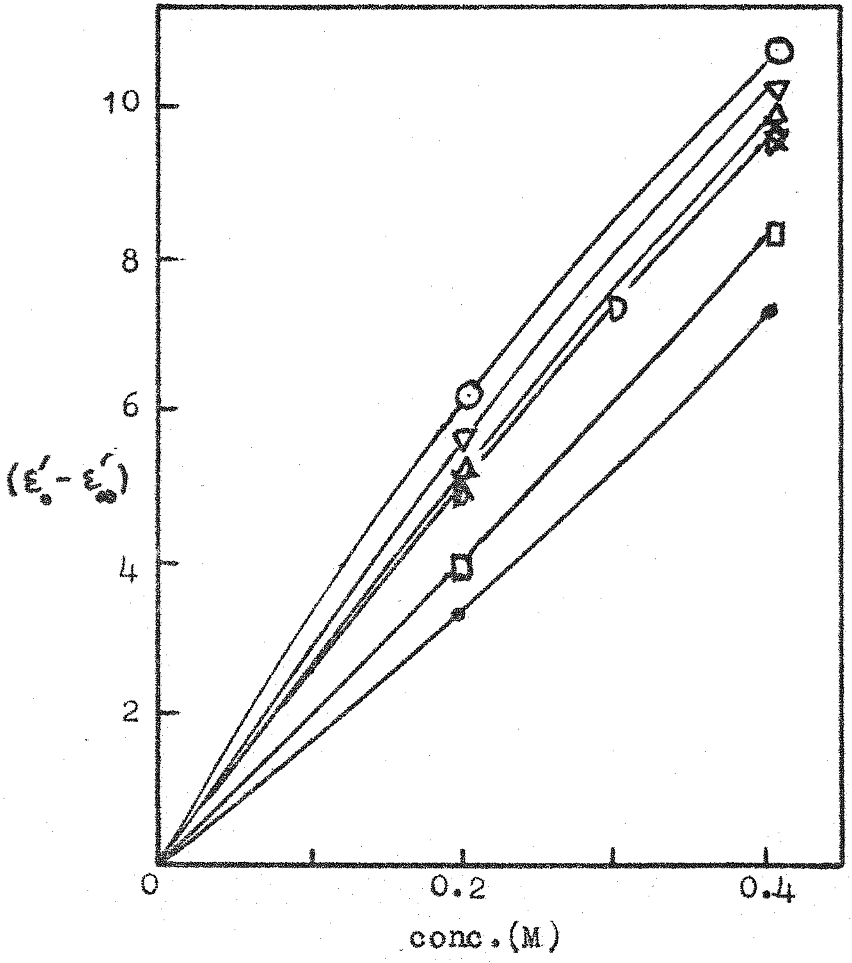


Fig.4.17 Bu_3NHPi

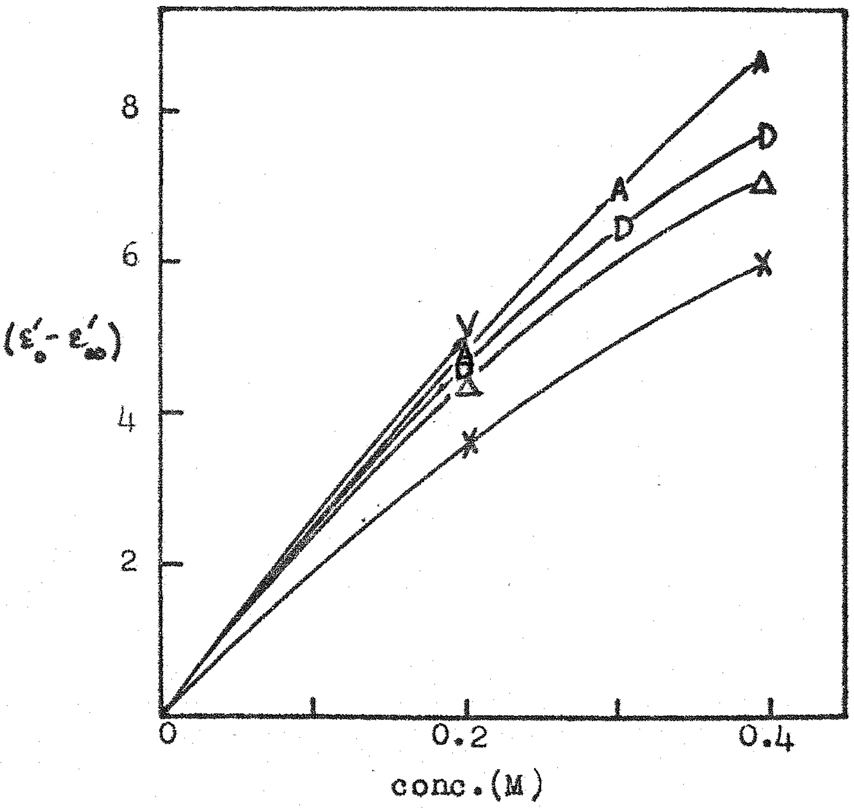


Fig.4.16 Bu_3NHI

of contact ion pairs. Plots for solutions of tributylammonium iodide in 1,2 and 1,1-dichloroethane and in chloroform, are more curved than are those for solutions in acetone and diethyl ketone. Further, it is worth noting that for equimolar solutions, the magnitudes of the amplitudes ($\varepsilon'_0 - \varepsilon'_\infty$) in different solvents vary in the same manner for different electrolytes.

Dipole moments calculated from measurements in non polar solutions, often depend on the solvent used (113). It seems reasonable therefore, to attribute the variation in amplitudes of the five similarly shaped plots in figure 4.17, to a "solvent effect". The differences in the plots shown in figure 4.16, on the other hand, are greater. These are probably due to more extensive ionic aggregation beyond the ion pair stage. It is interesting that, despite the higher static permittivity of solutions in 1,1-dichloroethane, those in chloroform appear to be less complex from the point of view of these plots. In contrast to this behaviour, solutions of tetrabutylammonium bromide and nitrate in 1,1 and 1,2-dichloroethane seem to be structurally similar. The evidence for this is discussed below. Solutions of quaternary ammonium salts in chloroform also seem to have unusual properties, and their behaviour is more characteristic of solvents of greater polarity.

Rothrock and Kraus (102) have suggested that in benzene solutions of tributylammonium iodide, both linear and antiparallel quadrupole ions are formed. If it is accepted that τ_p represents a molecular relaxation time, and that its value depends on the size of the relaxing dipole, then any increase in τ_p with increasing concentration might be attributed to contributions from relaxation of chainwise associated species. Alternatively, such species might be detected from the variation with concentration of the ratios of relaxation times for equimolar solutions of tributylammonium picrate and iodide in the same solvent. These ratios, which are given in table 4.7, should indicate the relative extents to which linear polar species, larger than ion pairs, are formed in equimolar solutions of the two electrolytes.

Table 4.7.

Solvent	Conc. (M)	$\frac{\tau_o \text{ (Picrate)}}{\tau_o \text{ (Iodide)}}$	$\frac{\tau_p \text{ (Picrate)}}{\tau_p \text{ (Iodide)}}$
1,2-dichloroethane	0.4	1.75	1.70
	0.3	1.69	1.66
	0.2	1.65	1.63
1,1-dichloroethane	0.4	1.39	1.33
	0.2	1.59	1.55
chloroform	0.4	1.42	1.37
	0.2	1.61	1.59

The ratios of relaxation times τ_p, change appreciably (0.22) with electrolyte concentration in the solutions in 1,1-dichloroethane and chloroform, but to a lesser extent (0.07), and in the opposite sense, with solutions in 1,2-dichloroethane. This does seem to give some support for the idea that polar aggregates, of larger size than ion pairs, are formed in certain tributylammonium iodide solutions, to a greater extent than occurs in the corresponding picrate solutions. Clearly, much more information of the type listed below is necessary to make these proposals more definitive:

a. Data are required over a wider concentration range. This would establish the form of the functional dependence of both $[\tau_p \text{ (Picrate)}]/[\tau_p\text{(Iodide)}]$ and of $(\epsilon'_o - \epsilon'_\infty)$ on concentration.

b. Data are required for solutions of both electrolytes in more solvents.

c. Data are required over a wider frequency range, particularly at lower frequencies, so that uncertainty in values of both τ_o and $(\epsilon'_o - \epsilon'_\infty)$ may be reduced.

Solutions of tributylammonium picrate in trichloroethylene and methylchloroform, are characterised by plots of $(\epsilon'_o - \epsilon'_\infty)$ against concentration, that are slightly concave upwards (see figure 4.17). In addition values of τ_p and τ_o obtained for these systems, particularly for solutions in trichloroethylene, show the greatest concentration dependence. This behaviour is consistent with that reported by Davies and Johansson (30) for solutions of triamylammonium picrate in benzene. Values of $(\epsilon'_o - \epsilon'_\infty)$ interpolated from the data of these authors are 9.2 for a 0.4 M. solution, and

4.0 for a 0.2 M. solution. For the same concentrations, relaxation times τ_o of 700 psec. and 400 psec. respectively can be obtained by interpolation. Thus in benzene solution, both τ_o and $(\varepsilon'_o - \varepsilon'_\infty)$ exhibit a greater dependence on concentration than is observed with solvents studied here. It seems possible that the upward curvature of plots of $(\varepsilon'_o - \varepsilon'_\infty)$ against electrolyte concentration, and the large increases in relaxation time with concentration in these low polarity solvents, are caused by the production of "linear" quadrupoles. The formation of non polar quadrupoles may, of course, also take place, but since such quadrupole ions do not contribute to dielectric dispersion they are more difficult to detect.

Except for solutions of tributylammonium picrate in tetrahydrofuran, for which conductances are higher than expected, at the concentrations investigated here, specific conductance (see Appendix 2) depends upon the static permittivity of the solution. The considerable increase in conductance, observed here, in changing the concentration from 0.2 to 0.4 M., has been noted by other workers (30, 114) in low permittivity solvent systems. It could partly be the natural result of the increase in static permittivity of the solution.

4.13. Analysis and Discussion of Permittivity and Loss Data of Quaternary Ammonium Salt Solutions.

a. Benzene Solutions.

Data for solutions (0.2 M. and 0.4 M.) of tetrabutylammonium bromide in benzene are given in Appendix A.1.30. Measurements over the frequency range 0.4 to 3.0 GHz. were made using the Standing Wave Method. In this frequency range, the loss remains approximately constant and proportional to electrolyte concentration, although permittivity itself changes slightly with frequency. Measurements in the frequency range 5 to 100 MHz. were made using the admittance bridge, and are therefore less accurate. The results obtained suggest that there is an absorption maximum within the frequency range 0.1 to 0.4 GHz., although the small increase in loss observed at 0.1 GHz, may in fact arise from the limitations of the bridge. These results are similar to those of Davies and Williams (19), who studied the same system in the concentration range 0.013 to 0.019 M. These authors reported a loss maximum at 6.8 MHz, with a 0.013 M. solution, which moved to lower frequencies as the concentration was increased.

b. Trichloroethylene Solutions.

Data for solutions of tetrabutylammonium bromide in trichloroethylene were obtained by the Travelling Wave method in the frequency range 1.0 to 3.0 GHz., by the Standing Wave method in the frequency range 0.35 to 1.0 GHz., and by the admittance bridge in the frequency range 0.03 to 0.1 GHz. Corresponding Cole-Cole diagrams are illustrated in figure 4.18. The data cover the frequency range of the dispersion, but are considered to be of low accuracy. Never the less, a considerable concentration dependence of τ_o is apparent (see table 4.8). The distribution parameter (α) for these solutions, although subject to considerable error, seems to be

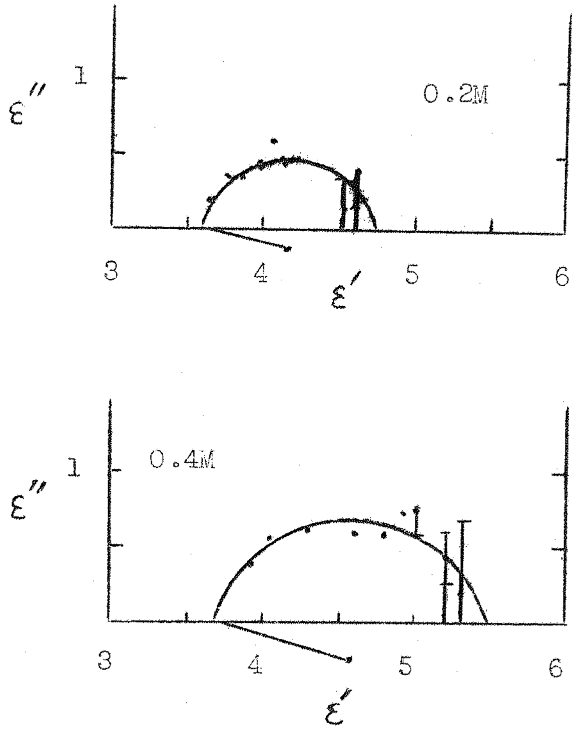


Fig. 4.18 Bu_4NBr in Trichloroethylene.

Table 4.8.

Static Permittivities (ε'_o), solvent static permittivities (ε'_∞), relaxation times (τ_o) and distribution parameters (α), characterising the dispersion of quaternary ammonium salts (at 25°C unless otherwise stated).

Solvent	Electrolyte	Conc.(M)	ε'_o	ε'_∞	α	τ_o psec.	
diethyl ketone	Bu_4NBr	0.4	19.2	12.9	0.12	146±6	45°
		0.3	19.0	13.2	0.16	141±13	45°
		0.2	18.3	14.3	0.07	138±7	45°
		0.4	19.8	13.85	0.08	162±4	35°
		0.3	19.9	14.0	0.14	158±8	35°
		0.4	21.1	13.7	0.17	179±9	25°
		0.3	20.9	14.4	0.13	177±7	
		0.2	20.25	15.2	0.11	163±11	
		0.1	19.2	15.8	0.12	210±46	
		0.05	18.2	16.1	(0.19)	161±15	
		0.01	17.0	16.4	-	-	
		0.3	21.9	15.1	0.14	191±16	15°
		0.2	20.9	15.7	0.10	190±13	15°
1,2-dichloroethane	Bu_4NBr	0.4	14.15	8.8	0.06	194±6	35°
		0.3	13.85	9.25	0.03	186±8	35°
		0.2	13.1	9.4	0.00	180±11	35°
		0.4	14.5	9.25	0.07	211±5	25°
		0.3	14.45	9.6	0.07	217±11	
		0.2	14.2	9.7	0.05	235±2	
		0.1	13.1	9.9	0.06	225±4	
		0.05	12.0	10.0	(0.06)	264±44	
		0.00493	10.55	10.45	-	-	
		0.4	15.3	9.65	0.06	243±17	15°
		0.3	14.9	9.8	0.07	247±7	15°
		0.2	14.55	10.4	0.05	234±2	15°
		0.4	16.1	10.2	0.05	327±16	1°
		0.3	15.8	10.5	0.05	306±7	1°

	Bu_4NNO_3	0.4 0.2	14.75 14.0	8.95 9.7	0.14 0.10	183±1 203±4
	Bu_4NClO_4	0.4 0.2	14.25 14.0	9.0 9.5	0.10 0.14	168±3 191±7
	Bu_4NI	0.4 0.2	14.7 13.95	9.05 9.55	0.11 0.11	202±2 219±12
	Bu_4NBPh_4	0.232	12.6	9.1	0.18	337±21
	Pr_4NBr	0.4 0.2	15.7 14.7	9.75 10.1	0.07 0.07	189±7 201±8
	Pr_4NI	0.2	14.1	9.9	0.03	186±6
1,1-dichloroethane	Bu_4NBr	0.4 0.2	13.9 13.6	8.7 9.1	0.09 0.09	192±7 213±14
	Bu_4NNO_3	0.4 0.2	13.8 13.25	8.7 9.2	0.13 0.10	165±8 168±8
dichloromethane	Bu_4NBr	0.4 0.2	13.3 12.6	8.2 8.35	0.00 0.00	149±11 141±7
1,1,2,2-tetrachloroethane	Bu_4NBr	0.4 0.2	10.8 10.7	6.7 7.3	(0.0) (0.0)	608±48 558±51
tetrahydrofuran	Bu_4NNO_3	0.4 0.2	10.6 10.0	7.15 7.35	0.11 0.11	177±16 207±15
1,1,1-trichloroethane	Bu_4NBr	0.4 0.2	10.2 9.9	6.7 7.1	0.27 0.21	392±14 509±28
chlorobenzene	Bu_4NBr	0.33	7.9	5.5	0.24	323±16

TABLE 4.8 (continued)

chloroform	Bu_4NBr	0.4	8.5	4.55	0.10	226±10
		0.3	8.4	4.6	0.13	235±3
		0.2	8.0	4.4	0.16	212±9
		0.1	7.6	4.8	0.00	233±4
	Bu_4NNO_3	0.4	9.6	4.6	0.31	178±41
		0.3	9.25	4.6	0.32	239±68
		0.2	9.2	4.8	0.25	296±18
		0.1	7.65	4.7	0.19	314±34
trichloroethylene	Bu_4NBr	0.4	5.5	3.7	0.18	252±28
		0.2	4.75	3.6	0.13	406±39

greater for the more concentrated solution. In general, it seems that for all the quaternary ammonium salt solutions investigated, τ_o decreases or remains constant, while α increases or remains constant (within estimated errors), with increasing electrolyte concentration. These effects are most marked with solvents of low permittivity.

There is a marked difference in dielectric behaviour between solutions in benzene and those in trichloroethylene. Low frequency conductances, too, are considerably higher for trichloroethylene solutions (Appendix 2). This may be, at least partly, due to the difference in permittivity of the solvents (benzene: $\varepsilon'_o = 2.27$, trichloroethylene: $\varepsilon'_o = 3.37$).

c. Chloroform Solutions.

Measurements were made using the Travelling Wave method. For measurements made at frequencies below 1.0 GHz., the total lengths of the liquid columns available were such that a phase change of less than 2π radians was produced. In these circumstances, it was necessary to compensate for the phase change produced by a given length of liquid by making an appropriate adjustment to the overall length of the "trombone" line stretcher. Cole diagrams for solutions of tetrabutylammonium bromide and nitrate in chloroform are illustrated in figures 4.19 and 4.20.

The loci obtained for both electrolytes are arcs. For the bromide solutions, the disposition of the experimental points is such that they can be satisfactorily described by the Cole-Cole (43) equation. Although the experimental points for the nitrate solutions lie on a circular arc, their disposition is such that they are not satisfactorily represented by a single Cole-Cole equation. This is indicated by the fact that mean deviations between average relaxation times and those calculated from experimental points, are larger than would have been caused by experimental uncertainty. In all cases with the nitrate, values of τ_o calculated from low frequency experimental points, are lower than those calculated from high frequency points.

With the bromide solutions, τ_o is nearly independent of concentration, within the range 0.1 to 0.4 M. This contrasts with the

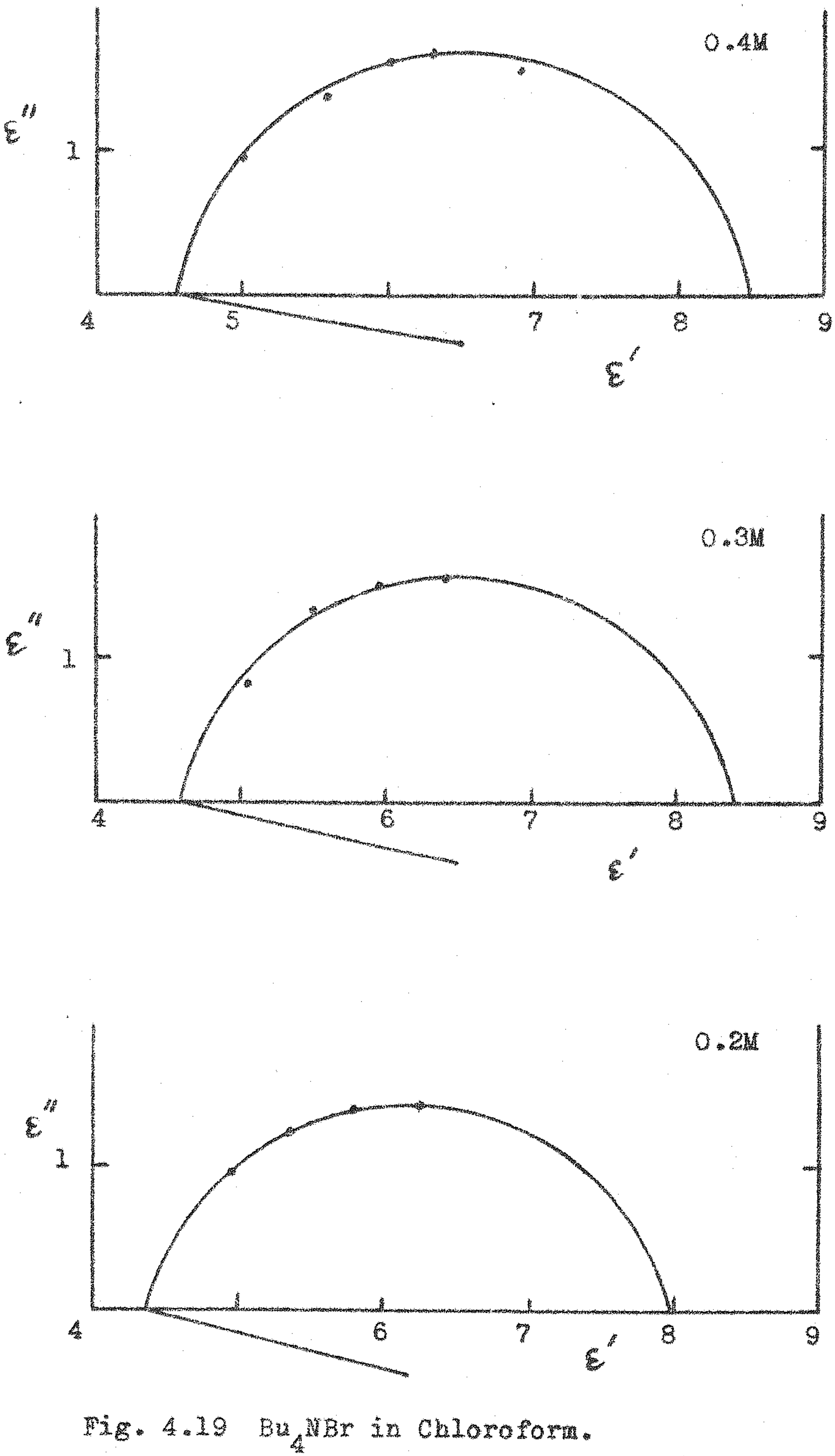


Fig. 4.19 Bu_4NBr in Chloroform.

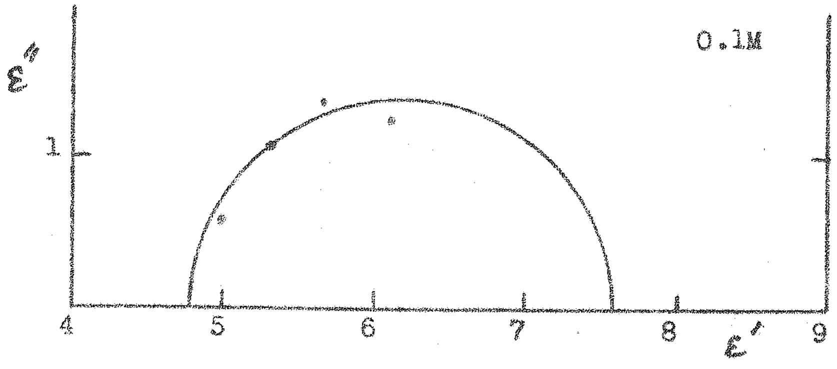


Fig. 4.19 Bu_4NBr in Chloroform.

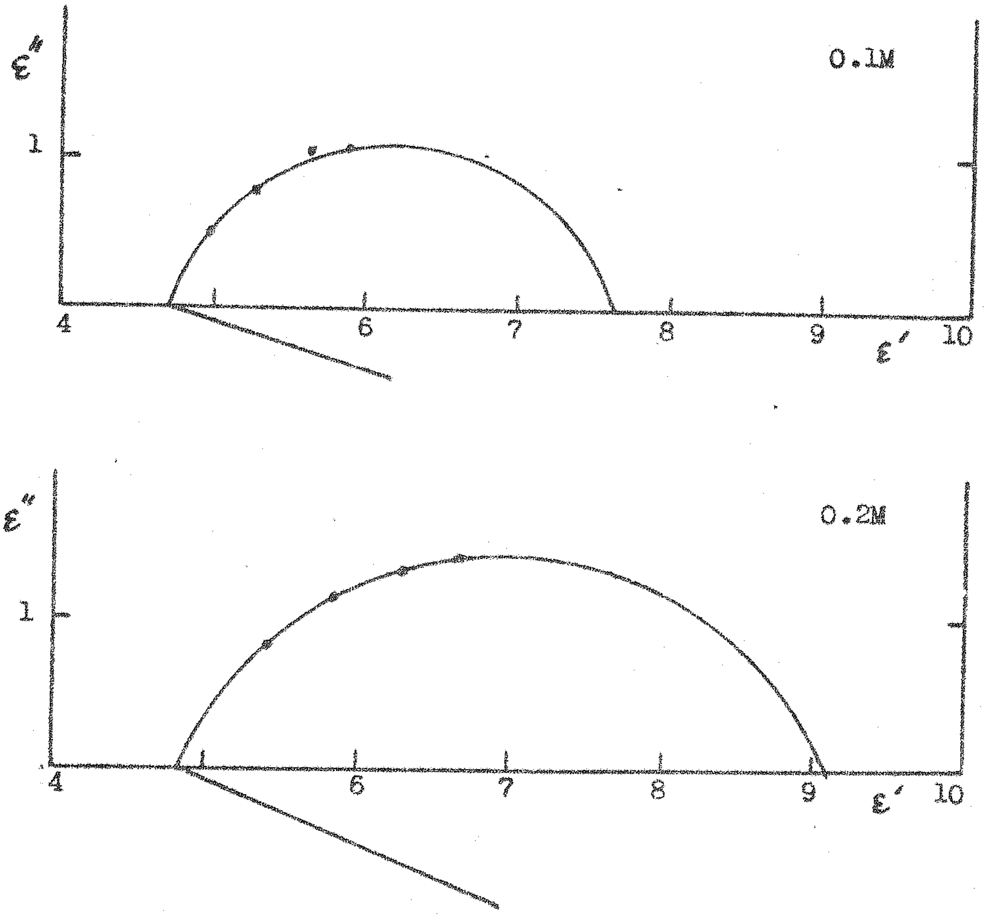


Fig. 4.20 Bu_4NNO_3 in Chloroform.

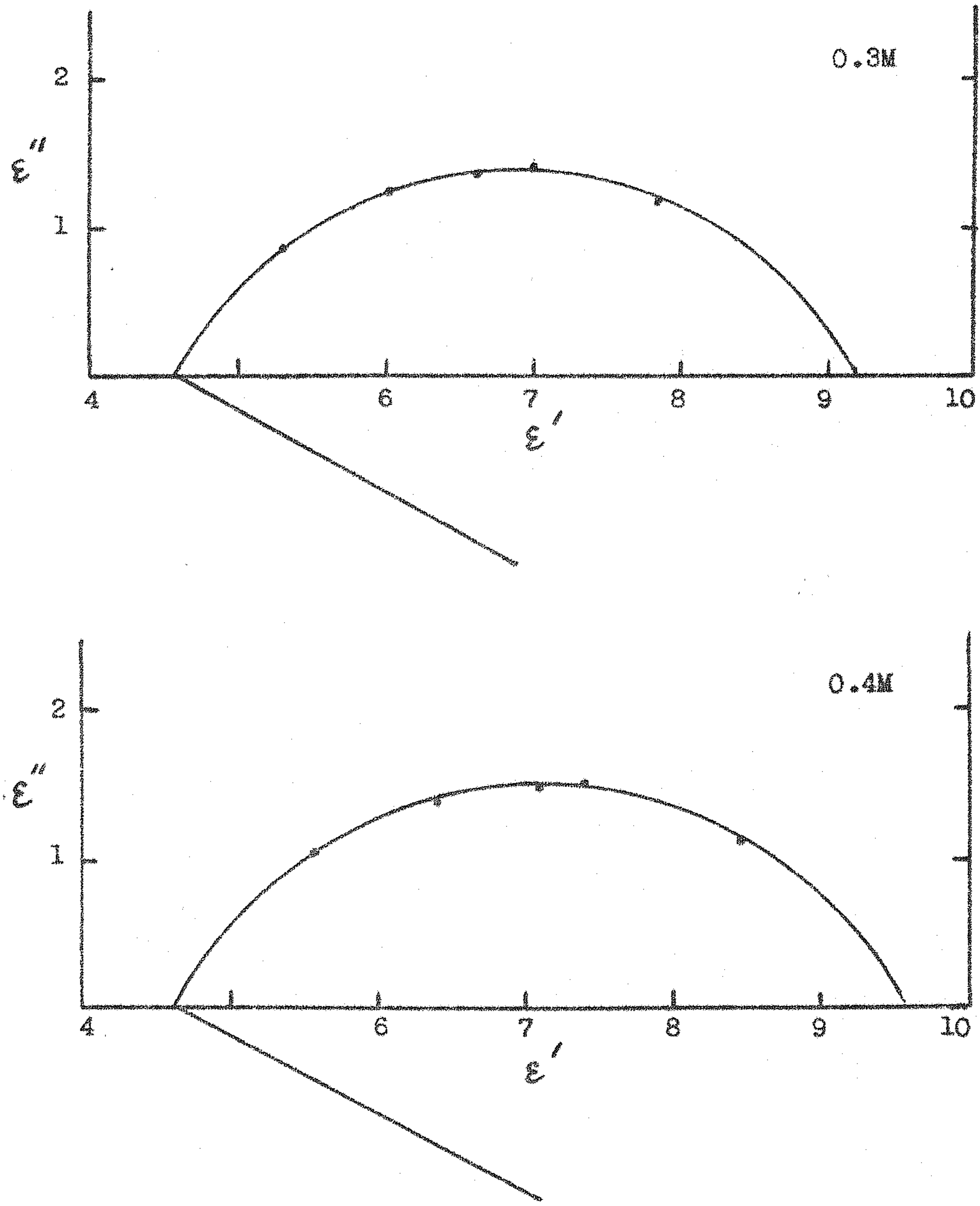


Fig. 4.20 Bu_4NNO_3 in Chloroform.

behaviour of the nitrate, for which τ_o decreases significantly with increasing electrolyte concentration. Since this is accompanied by a considerable broadening of the dielectric dispersion, it seems likely that as the electrolyte concentration is increased, processes characterised by shorter relaxation times contribute appreciably to the dielectric dispersion. From the point of view of dipole moment and molar volume, the rotational relaxation time of a tetrabutylammonium bromide or nitrate ion pair, can be expected to lie between those for tributylammonium iodide and picrate. For chloroform solutions of tributylammonium iodide and picrate, τ_p lies between 180 and 310 psec., whereas in the case of a 0.4 M. solution of tetrabutylammonium bromide, τ_p is 191 psec. Here it has been assumed, that the Powles (63) expression can be applied in cases where dispersion is not characterised by the Debye-Pellat equation. Since a slightly larger rotational relaxation time might have been expected for a tetrabutylammonium bromide ion pair, there seems to be reasonable grounds for assuming that there are contributions from more rapid processes. In the case of a 0.4 M. solution of tetrabutylammonium nitrate τ_p is 147 psec., although the value increases to 247 psec. when a concentration of 0.1 M is employed. In the more concentrated solution therefore, there seems to be a considerable contribution from processes having smaller relaxation times than that for ion pair rotational displacements.

With data for electrolyte solutions in 1,2-dichloroethane, Cole distribution parameters are smaller, and these have been analysed, by assuming that two processes contribute to the observed dispersion. It seems that for chloroform solutions also, contributions made by processes characterised by shorter relaxation times are more important for solutions of tetrabutylammonium nitrate than for solutions of the bromide.

Conductances of nitrate solutions are lower than those of equimolar bromide solutions, which is the reverse of the situation obtaining in 1,1 and 1,2-dichloroethane (See Appendix 2). An explanation for this is that chloroform molecules do not specifically solvate (see the next section) nitrate ions ~~are~~ as strongly as they do bromide ions.

The shape, and structure of the chloroform molecule, makes it easy to visualise a solvent separated ion pair, with the proton of the chloroform molecule directed toward the anion, and with the cation positioned symmetrically between its chlorine atoms. Even for a decimolar solution of tetrabutylammonium nitrate, the Cole distribution parameter and τ_o are quite large. The reason for this could be that solvent separated ion pairs contribute to the dispersion. However, the lower conductances of nitrate solutions in chloroform probably indicate that nitrate is solvated less strongly than bromide. Hence solvent separated ion pairs should be formed to a lesser extent. One can speculate that the disc like structure of nitrate (see Appendix 4), assists the formation of linear quadrupole ions, and these cause increases in values of τ_o.

However with solutions of tetrabutylammonium bromide, the Cole distribution parameters are smaller, and the correspondence of the relaxation times with those for tertiary ammonium salts, suggests that the principal process governing the dielectric properties of these solutions is orientation of contact ion pairs.

d. Solutions in Chlorobenzene and 1,1,1-trichloroethane.

Data for solutions of tetrabutylammonium bromide in chlorobenzene and in 1,1,1-trichloroethane were obtained by means of the travelling wave method in the frequency range 1.0 to 3.0 GHz., by the standing wave method in the frequency range 0.25 to 1.0 GHz., and by the admittance bridge method in the frequency range 0.03 to 0.1 GHz.

Although the static permittivities of both chlorobenzene and 1,1,1-trichloroethane are higher than that of chloroform (see table 4.6), conductances of equimolar solutions of tetrabutylammonium bromide are lower. Prue (115) has drawn attention to the importance of specific solvent effects in determining the magnitude of electrolytic conductance. For example, he has pointed out that whereas aluminium bromide is a weak electrolyte in nitrobenzene (ε'_o = 34.8), it must be regarded as a strong electrolyte in dilute solution in pyridine ($\varepsilon_o' = 12.0$). Prue has attributed this difference in behaviour to solvation of the aluminium ion by pyridine molecules. Such an explanation may reasonably be extended to include chloroform solutions of tetrabutylammonium salts, by assuming that the high conductances in these solutions are due to solvation of anions by chloroform molecules. In this connection, it is notable that the conductances of solutions of tributylammonium picrate in chloroform are no higher than would be expected on the basis of solvent permittivity, although conductances of tributylammonium iodide solutions are. It appears, therefore, that the picrate ion, possibly on account of its "protected" nature, is not appreciably solvated by chloroform molecules. Never the less, as is described in section 4.12, relaxation times and dispersion amplitudes of tributylammonium picrate in chloroform differ in character from those in methyl chloroform. They are similar in character to those observed in solvents of somewhat higher permittivity.

Corrected values of permittivity and loss for solutions in chlorobenzene and 1,1,1-trichloroethane are illustrated by means of Cole diagrams in figures 4.21 and 4.22. Values of loss at low frequencies are inaccurate, so that the representation of the data by circular arcs is probably justified. The data for frequencies of 0.5 GHz. and above can be satisfactorily represented by the function of Cole and Cole (43). The relatively large Cole distribution parameters emphasise the complexities of these solutions. In view of the relaxtion time, density, and viscosity of chlorobenzene (see table 4.6), and also relaxation times of tertiary ammonium salts, the relaxation time of a 0.33 M. solution of tetrabutylammonium bromide in chlorobenzene (323 psec.) is probably approximately that which would be expected for orientation of contact ion pairs.

The relaxation time of a 0.2 M. solution of the quaternary ammonium bromide in 1,1,1-trichloroethane is larger than those of solutions of tributylammonium picrate in the same solvent. From a consideration of tributylammonium picrate solutions, the relaxation times of contact ion pairs derived from tetrabutylammonium bromide might be expected to be somewhat less than 350 psec. The value of τ_o decreases considerably when the concentration is increased from 0.2 to 0.4 M. A number of possible interpretations are available when the measured relaxation time is greater than that expected for contact ion pair orientational displacements. The relaxation time may be associated with processes such as: orientation of polar ionic aggregates larger in size than contact ion pairs, orientation of solvent separated ion pairs, and dissociation and association of ionic aggregates.

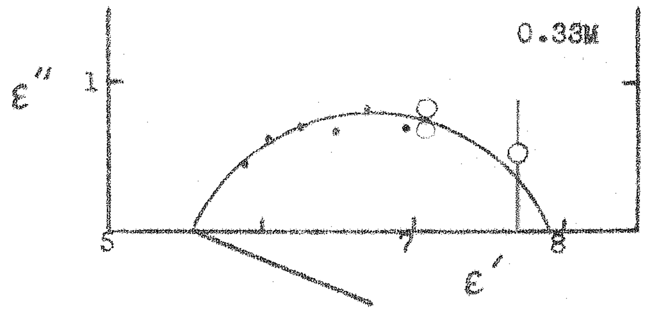


Fig. 4.21 Bu_4NBr in Chlorobenzene.

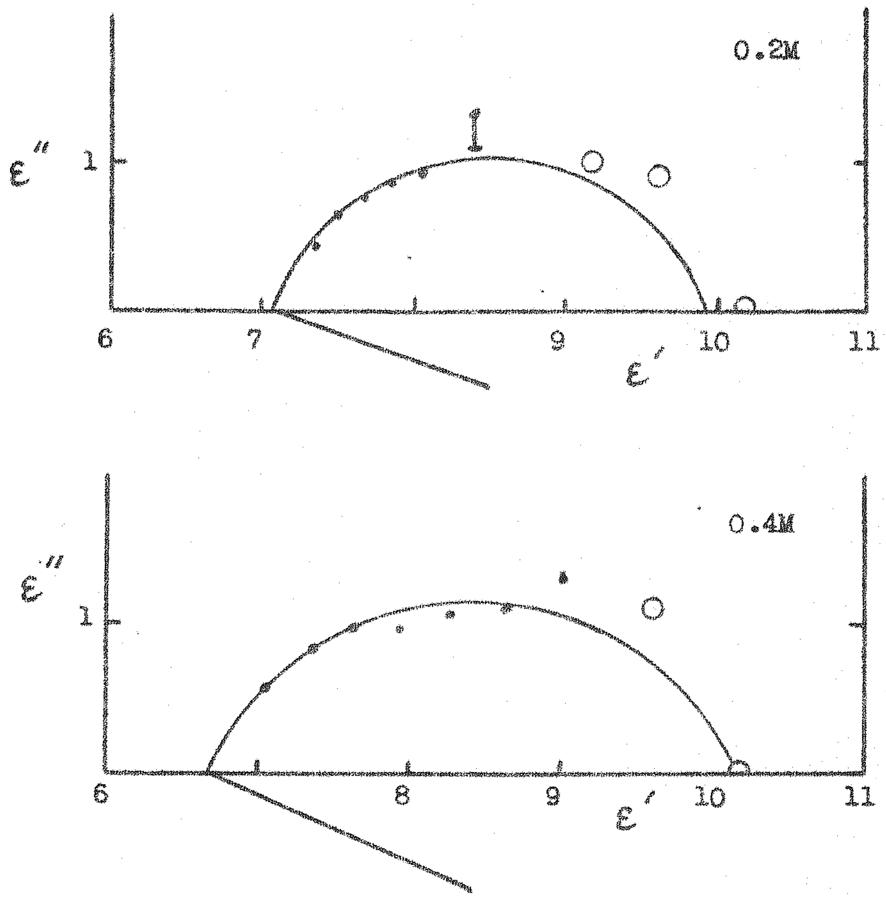


Fig. 4.22 Bu_4NBr in 1,1,1-trichloroethane.

e. Solutions of Tetrabutylammonium Nitrate in Tetrahydrofuran.

Tetrabutylammonium bromide is not sufficiently soluble in tetrahydrofuran for the purposes of this investigation, consequently only solutions of the nitrate were examined. Data were obtained by means of the travelling wave method. Measurements of permittivity and loss at 0.5 GHz. were made by using the "trombone" line stretcher to determine the change in phase produced by an alteration in the length of the liquid column within the cell. The data define the absorption maximum quite well, and they can be adequately represented by the Cole-Cole (43) function. Data are plotted on a Cole diagram in figure 4.23.

Values of τ_p (see table 4.6) for solutions of tributylammonium picrate in this solvent, lie in the range 224 to 251 psec. In comparison, respective values of τ_p for 0.4 and 0.2 M solutions of tetrabutylammonium nitrate are 158 and 189 psec. The observed relaxation times are therefore approximately those which would be expected for ion pair orientation. The small Cole distribution parameters and the concentration dependence of τ_o, again indicate the existence of contributions from processes with relaxation times shorter than that for ion pair orientation.

Conductances of Bu_4NNO_3 in this solvent are, on the basis of solvent permittivity, compatible with those of other systems. They emphasise further the anomalously large values of conductance found for solutions of quaternary ammonium salts in chloroform.

Carvajal, Tölle, Smid and Szwarc (116) have concluded from studies of electrolytic conductance, that triisoamylbutylammonium tetraphenylboride forms contact ion pairs in tetrahydrofuran at room temperature, whereas Chang, Slates and Szwarc (117) have reported that solvent separated ion pairs are also formed in some solutions of sodium salts of aromatic radical ions. It seems likely that tetrabutylammonium nitrate should fall into the class of electrolytes which co-ordinate weakly with tetrahydrofuran, and this supports the conclusion that the dielectric dispersion, observed here, is mainly attributable to contact ion pairs.

f. Solutions of Tetrabutylammonium Bromide in 1,1,2,2-tetrachloroethane.

For a 0.4 M. solution, the measured loss at 3.0 GHz., after correction for ionic conductance, is less than the loss of the pure solvent. The dipolar loss attributable to the electrolyte would therefore appear to be negative. In order to avoid this particular difficulty, it was assumed that the relaxation of the solvent could still be described by the Debye-Pellat equation, and that the relaxation time is unchanged by the electrolyte. Permittivity (ε') and loss (ε'') of the solvent in an electrolyte solution could then be calculated for a given frequency from the corresponding permittivity ($\varepsilon'_{Solv.}$) and loss ($\varepsilon''_{Solv.}$) of the pure solvent by means of equations 4.11.

$$\varepsilon' = 2.85 + (\varepsilon'_{\text{Solv.}} - 2.85)\left(\frac{\varepsilon'_{\infty} - 2.85}{8.20 - 2.85}\right) \quad . \qquad 4.11$$

$$\varepsilon'' = \varepsilon''_{\text{Solv.}}\left(\frac{\varepsilon'_{\infty} - 2.85}{8.20 - 2.85}\right) \quad . \qquad 4.11$$

8.20 is the static permittivity (see Appendix A3.5) of tetrachloroethane, and 2.85 is the high frequency "limit" of permittivity. $(\varepsilon' - 2.85)$ can be regarded as the amplitude of the dispersion of the solvent in the presence of electrolyte. The value of ε' employed in equations 4.11, was found reiteratively from the Cole diagrams, illustrated in figure 4.24.

Data were obtained by means of the travelling wave method, utilising the trombone line stretcher for phase measurement at 0.5 GHz. The data do not cover a sufficiently wide frequency range for the most appropriate representation to be decided. Consequently, they have been represented in the simplest possible way, namely by means of the Debye semicircular arc. The relaxation time is about 600 psec., for both solutions investigated. If the data should be more satisfactorily represented by a Cole-Cole circle, then the relaxation time, calculated from these data, would be correspondingly longer.

Long electrolyte relaxation times are to be expected for solutions in this solvent, in view of its own large relaxation time and high density (see table 4.6). The magnitude of the dispersion

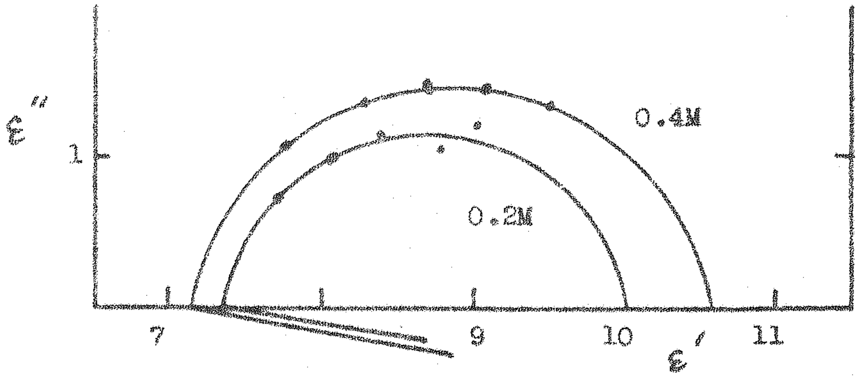


Fig. 4.23 Bu_4NNO_3 in Tetrahydrofuran.

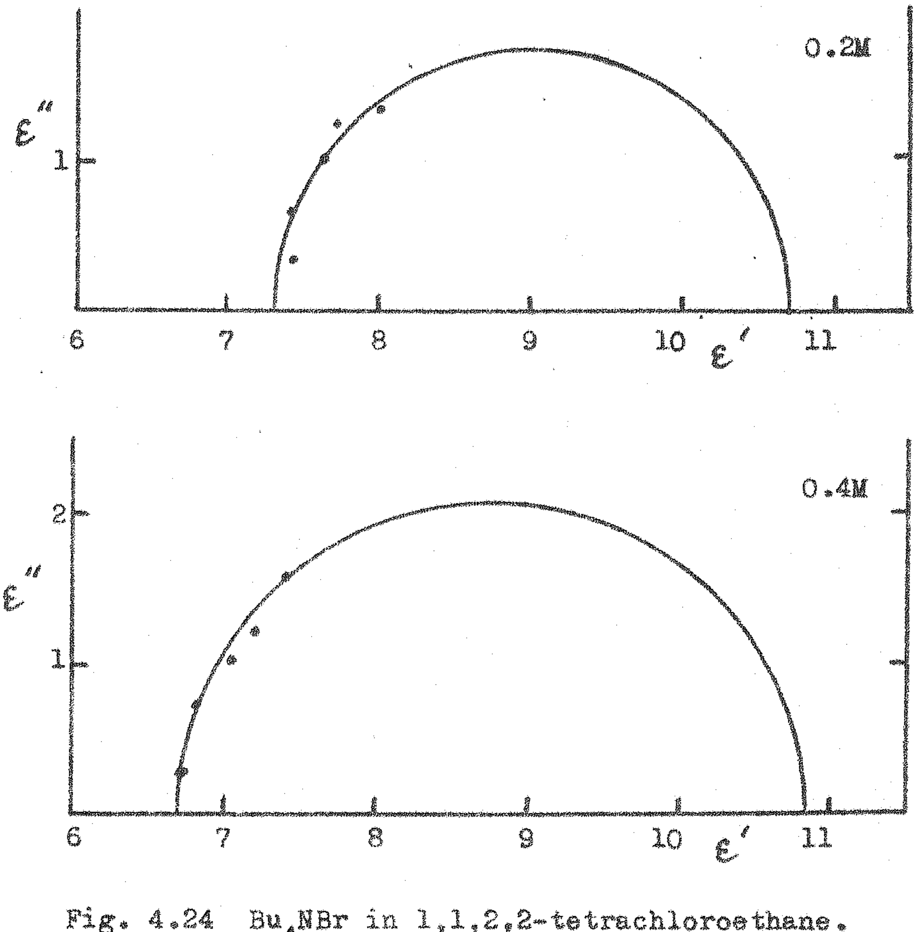


Fig. 4.24 Bu_4NBr in 1,1,2,2-tetrachloroethane.

amplitude is consistent with the solvent permittivity.

g. Solutions of Tetrabutylammonium Bromide in Dichloromethane.

Data were obtained by means of the travelling wave method. Corrected permittivity and loss plotted on a Cole diagram, can be adequately represented by a semicircular arc, as can be seen from inspection of figures 4.25. Respective relaxation times for 0.2 and 0.4 M. solutions, are 141 and 149 psec. (see table 4.8). For the same solutions, corresponding values of τ_p are 125 and 130 psec. In comparison, values of τ_p for tributylammonium picrate solutions are about 210 psec. Hence, values of τ_p for solutions of tetrabutylammonium bromide in dichloromethane are consistent with the assumption that in this solvent, the dielectric dispersion arises principally from the orientational motion of contact ion pairs. The value of the Cole distribution parameter is zero, within experimental error. Of all the non aqueous solutions of tetrabutylammonium bromide so far investigated, only those in acetone (31) and in this solvent, have zero distribution parameters. In this connection, it is probably relevant that the shape and structure of molecules of dichloromethane and acetone, are obviously similar.

Relaxation times are shorter in this solvent than those in other solvents investigated, and this is probably due to both its low relaxation time and its low viscosity.

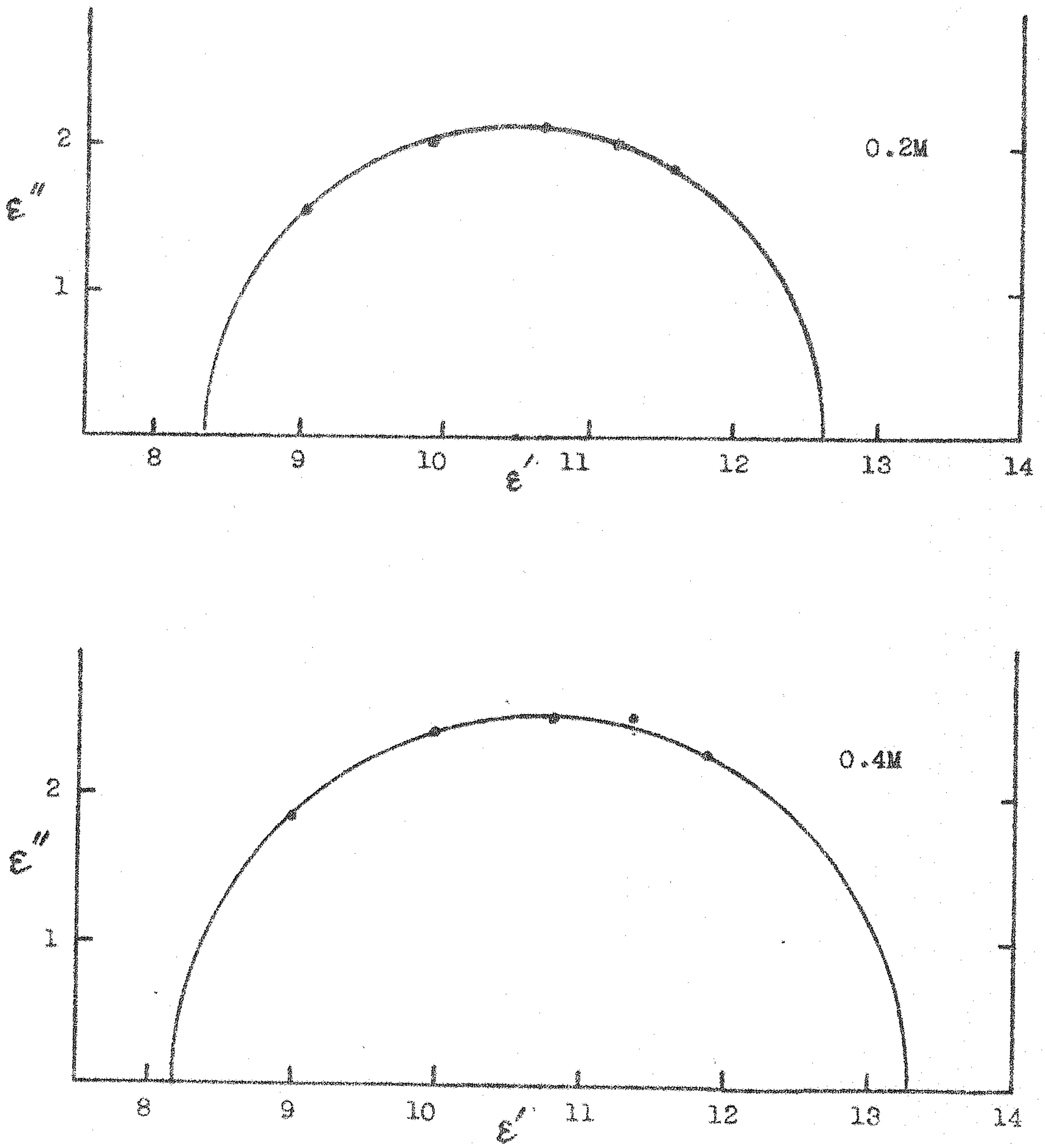


Fig. 4.25. Bu_4NBr in Dichloromethane.

Blandermer, Gough and Symons (118) have studied the U.V. absorption spectra of various solutions of quaternary ammonium and alkali metal iodides, including solutions in tetrahydrofuran and dichloromethane. The authors have interpreted the absorption spectra in terms of transitions described as "charge transfer to solvent", and have concluded that solvent separated ion pairs are formed in solvents such as dichloromethane and tetrahydrofuran. Blandamer et al (119) have, however, considered that in carbon tetrachloride solutions, contact ion pairs are formed. Before considering that the conclusions of these authors, regarding solvent separated ion pairs, differ from the present ones, it must be noted that the concentrations employed in the U.V. investigations were lower than those used in this work. It could be that contact ion pairs are only formed in more concentrated solutions.

h. Solutions of various Univalent Electrolytes in 1,1 and 1,2-dichloroethane.

Experimental measurement of permittivity and loss of solutions of univalent electrolytes in 1,1 and 1,2-dichloroethane was made by means of the travelling wave method. In addition, a limited number of measurements were made using the admittance bridge. Cole diagrams for solutions investigated are illustrated in figures 4.26 to 4.35.

The procedure used to analyse all corrected data was as follows.

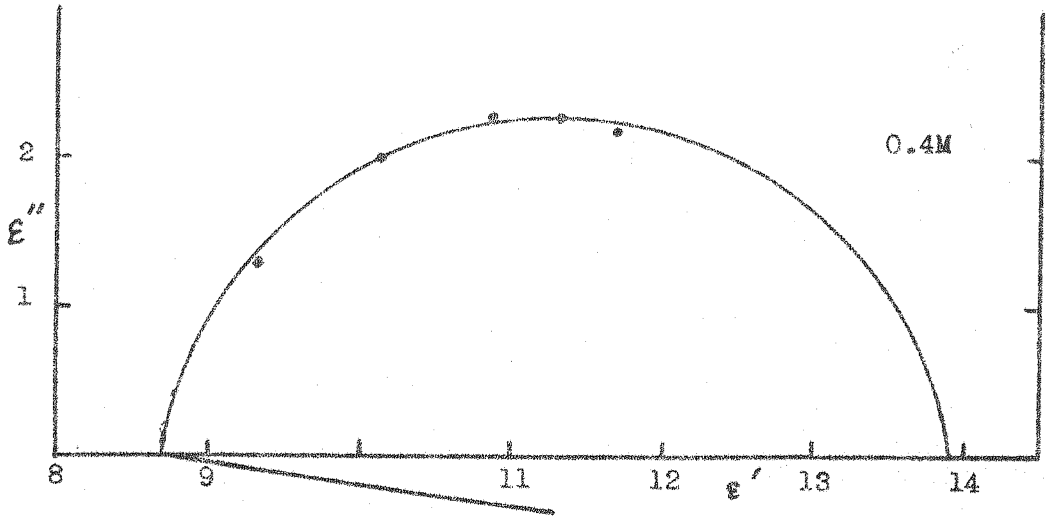


Fig. 4.26 Bu_4NBr in 1,1-dichloroethane.

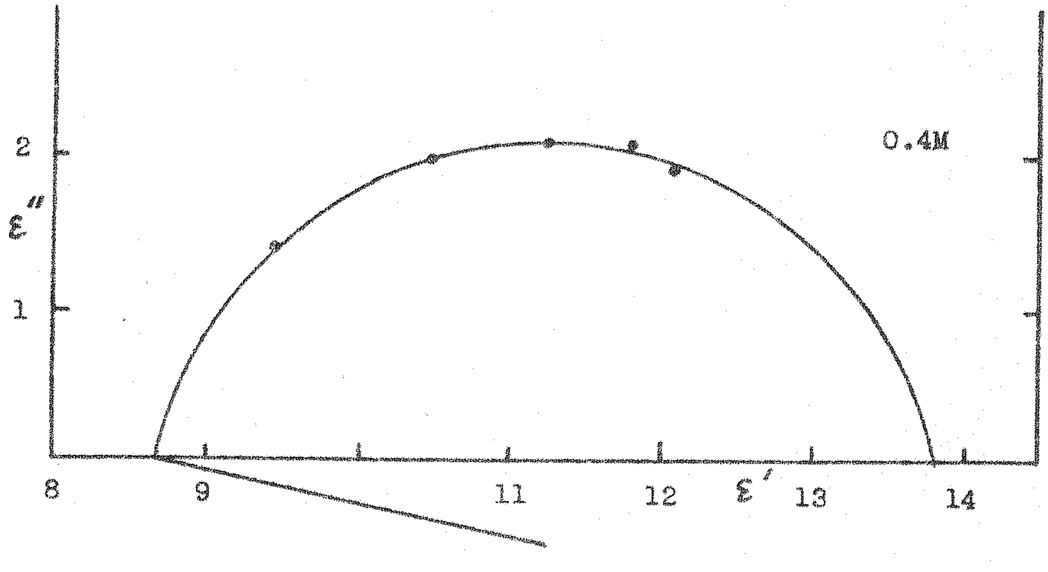


Fig. 4.27 Bu_4NNO_3 in 1,1-dichloroethane.

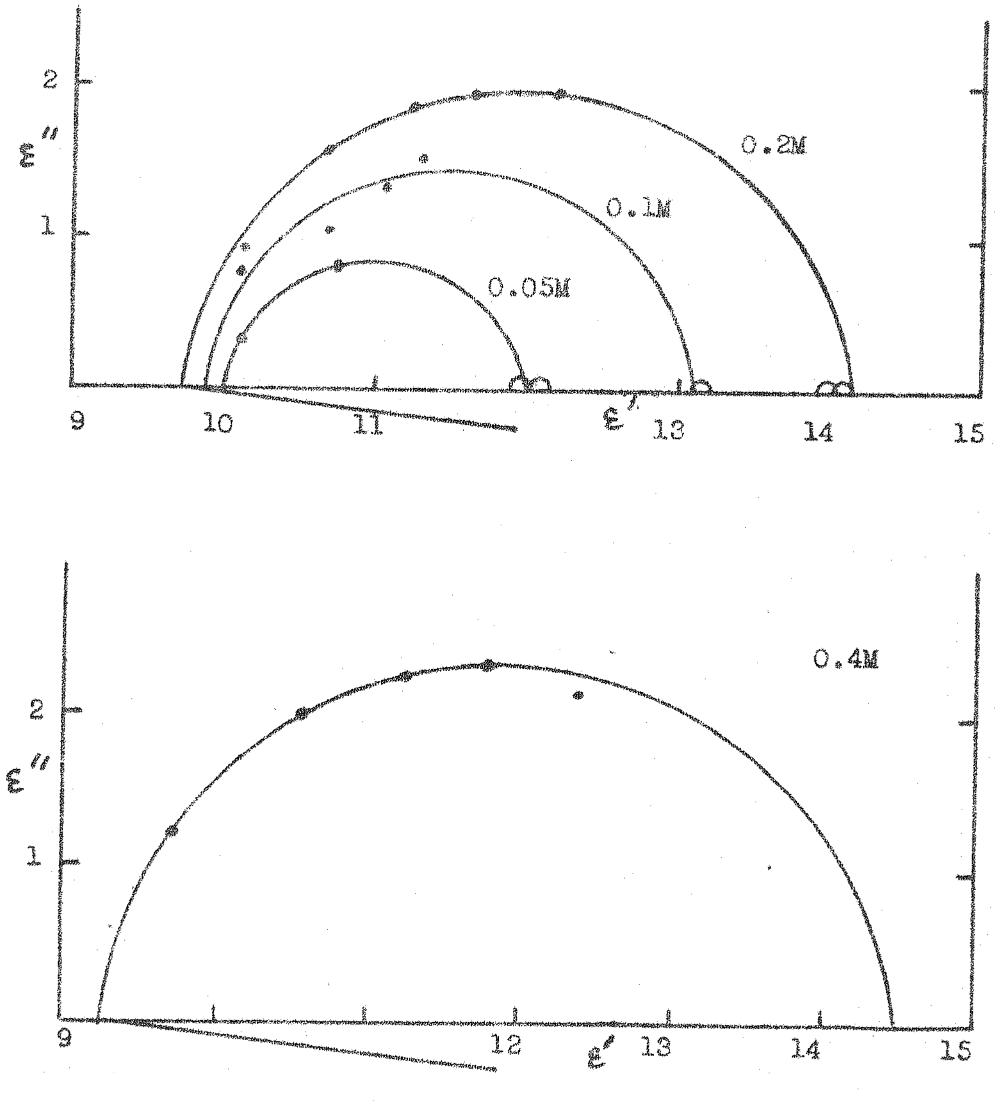


Fig. 4.28 Bu$_4$NBr in 1,2-dichloroethane.

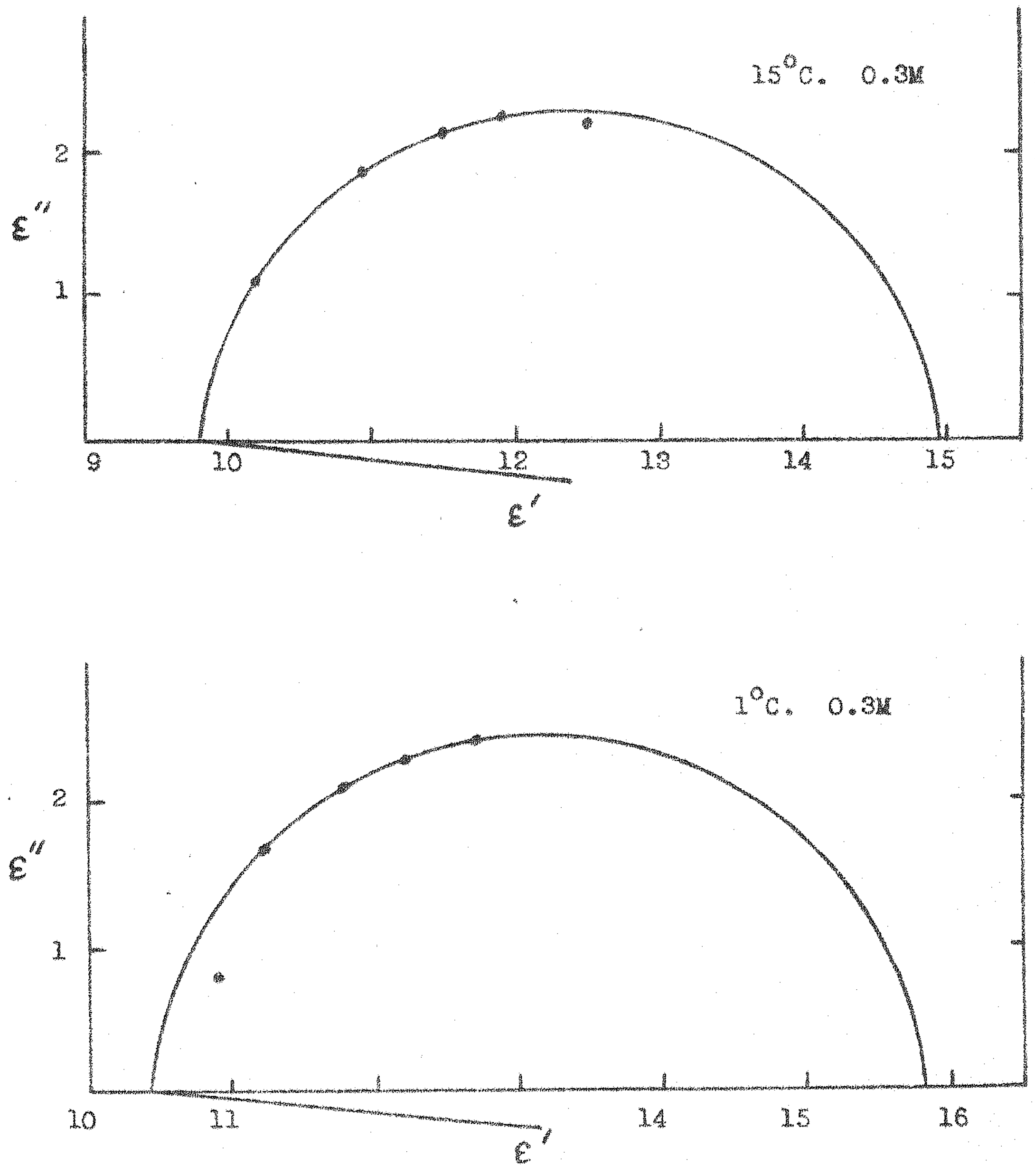


Fig. 4.29 Bu_4NBr in 1,2-dichloroethane. (at 1° and 15°C.)

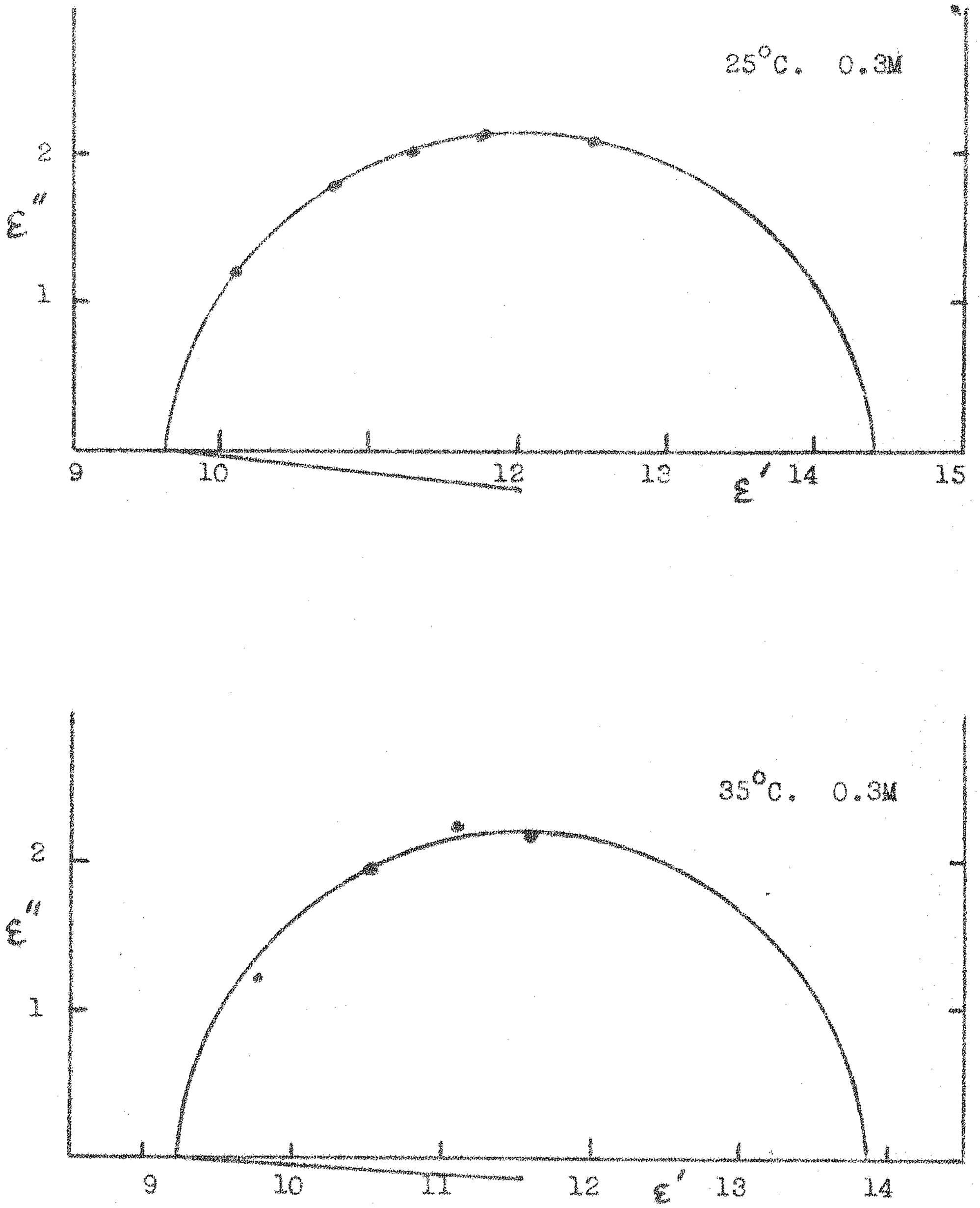


Fig. 4.29 Bu_4NBr in 1,2-dichloroethane (at 25° and 35°C.)

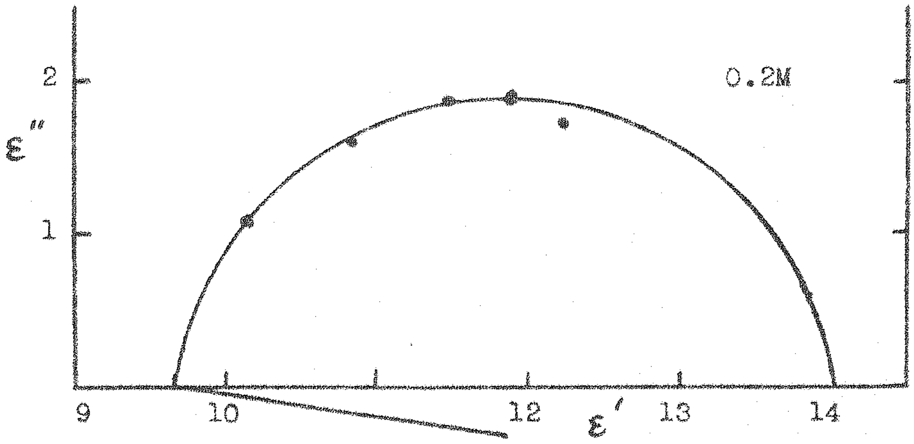


Fig. 4.30 Bu_4NNO_3 in 1,2-dichloroethane.

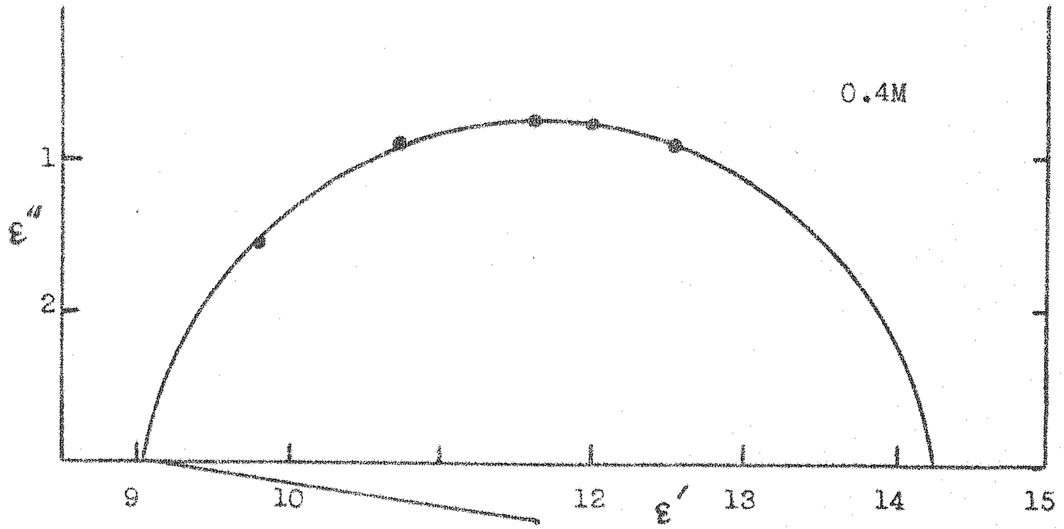


Fig. 4.31 Bu_4NClO_4 in 1,2-dichloroethane.

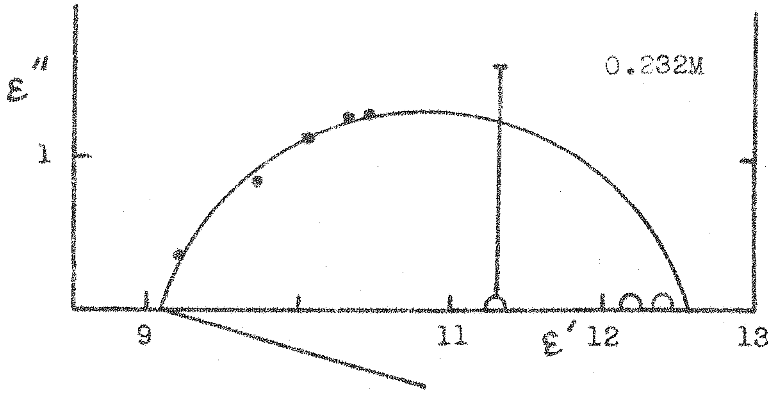


Fig. 4.33 Bu_4NBPh_4 in 1,2-dichloroethane.

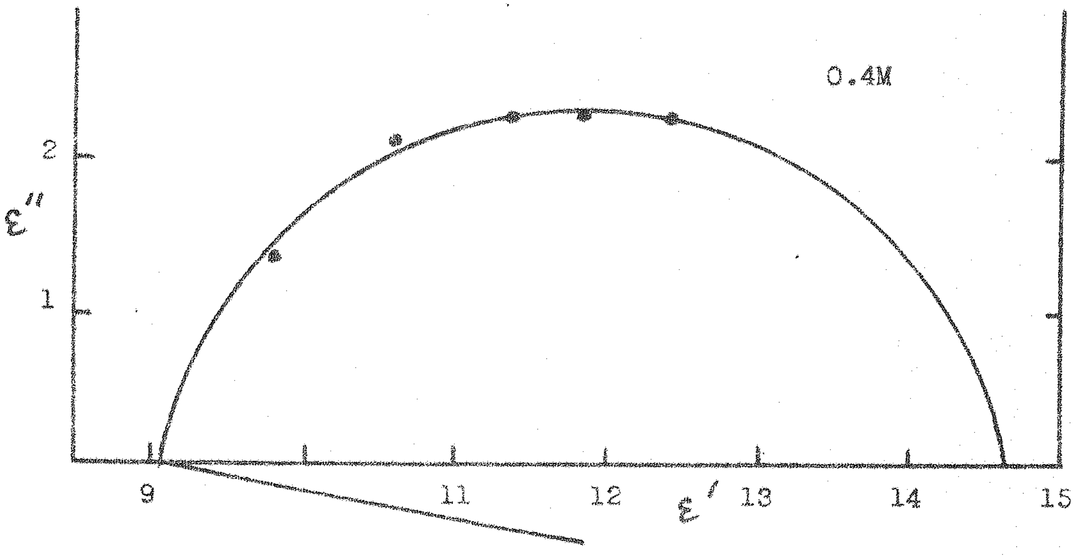


Fig. 4.32 Bu_4NI in 1,2-dichloroethane.

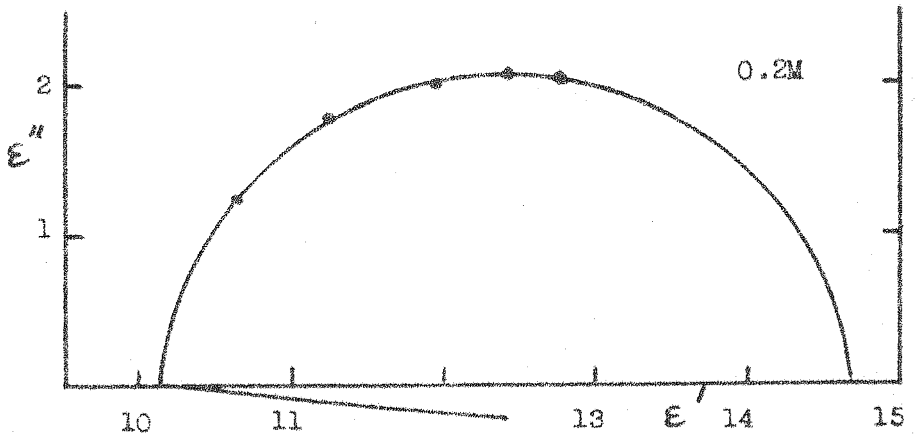


Fig. 4.34 Pr_4NBr in 1,2-dichloroethane.

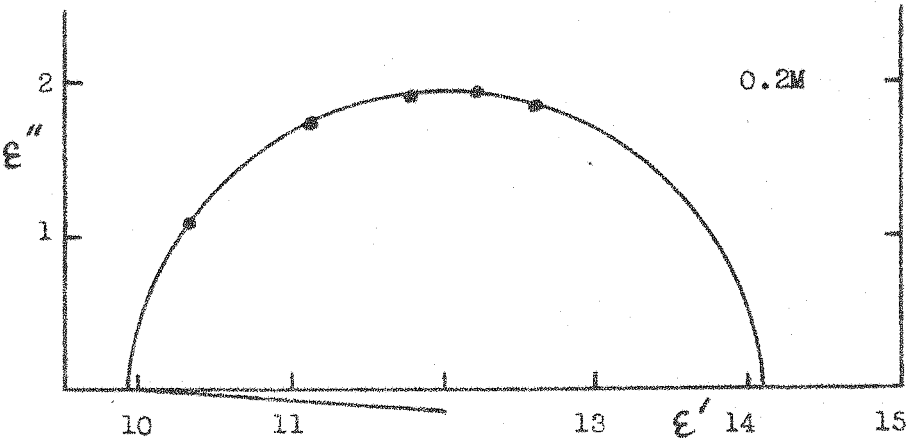


Fig. 4.35 Pr_4NI in 1,2-dichloroethane.

The best fitting arc of a circle was drawn through the corrected data plotted on a Cole diagram. The distribution parameter (α) was obtained from this plot, and τ_o evaluated by means of equation 4.12.

$$\left(\frac{V}{u}\right) = (\omega\tau_o)^{1-\alpha} \qquad 4.12$$

If the data are adequately represented by Cole and Cole's (43) equation, then a plot of log. (V/u) against log. f, should be a straight line of slope ($1-\alpha$). In nearly all the systems described so far, values of α found from the slopes of such plots, which are subject to considerable experimental error, are less than those found directly from Cole diagrams. Matsumoto (120) has pointed out that often data are not exactly represented by the Cole-Cole equation.

In the case of solutions of electrolytes in 1,1 and 1,2-dichloroethane, however, it is possible by a reiterative procedure to get reasonable agreement between values of α obtained by the two methods.

A comparative study of solutions in 1,1 and 1,2-dichloroethane was undertaken, because although these solvents have similar densities, permittivities and relaxation times, their viscosities are somewhat different. Another important difference between them, concerns the hindered rotation about the carbon-carbon bond existing in the 1,2-dichloroethane molecule. Mizushima et al (121) estimated that the ratio of the number of molecules of 1,2-dichloroethane in the gauche form (i.e. having an angle of 60° between the C-Cl bonds when the molecule is viewed from the direction of the C-C bond) to the number in the trans form to be 1.3:1 at 25°C., in the liquid state.

Dissociation constants of electrolytes in 1,2-dichloroethane are often larger than those in 1,1-dichloroethane (123). Denison and Ramsey (122), Inami, Bodenseh and Ramsay (94), and Lydy, Mode and Kay (124) have all attributed this to preferential ionic solvation by the gauche (polar) form of 1,2-dichloroethane. Inami et al have found that the "effective" permittivity for solutions of tetrabutylammonium perchlorate is 12.4, and for the picrate 11.2. From a study of infra red spectra of solutions of tetrabutylammonium perchlorate, Inami and Ramsay (125) have concluded that the ratio of trans to gauche isomers is increased by the presence of the salt. Other evidence cited by Inami et al, for the effect of ions on 1,2-dichloroethane, is that its static permittivity increases with increasing field strength (126).

The dielectric properties of 1,2-dichloroethane, may therefore be reasonably expected to be modified in the presence of electrolyte. The reduction in static permittivity of the solvent $[\varepsilon'_o(\text{solvent}) - \varepsilon'_\infty(\text{solution})]$ in the presence of electrolyte, is caused both by the replacement of solvent by the electrolyte, and by electrostriction due to ions and other charged species within the solution. If for equimolar solutions of a given electrolyte, the number of ions in the two solvents were nearly the same, then the preferential formation of gauche isomers would probably make values of $[\varepsilon'_0(\text{solvent}) - \varepsilon'_\infty(\text{solution})]$ smaller for solutions in 1,2-dichloroethane than for those in 1,1-dichloroethane. Examination of results contained in tables 4.5 and 4.8, shows that values of $[\varepsilon'_0(\text{solvent}) - \varepsilon'_\infty(\text{solution})]$ for equimolar solutions are about the same for the two solvents, but because conductances are higher in 1,2-dichloroethane (see Appendix 2), the comparison is inconclusive. For a solution of tetrabutylammonium bromide in 1,2-dichloroethane, with a concentration of 0.005 M., $\varepsilon'_\infty = 10.45$, yet the static permittivity of the pure solvent is 10.36. Probably, a comparitive study of dilute solutions in both solvents is needed to decide whether the value of ε'_∞ of 10.45, is caused by an increased number of gauche isomers.

Corrected permittivity and loss data, in most cases, satisfactorily define the absorption maxima. For a single relaxation time of about 200 psec., permittivity calculated for 100 MHz., is within about 1% of ε'_0. Inspection of figures 4.28 shows that values of permittivity measured with the admittance bridge at 60 and 100 MHz., lie satisfactorily on the Cole-Cole plots. Thus, unless a further dispersion region exists at frequencies below 60 MHz., ε'_0 is the static permittivity of the solutions. For the more dilute solutions studied, the Cole distribution parameter is given an average value of 0.06. Even in the most dilute solution of tetrabutylammonium bromide in 1,2-dichloroethane investigated (0.005 M.), a small, but poorly defined dispersion is detectable.

With the exception of the single (nearly saturated) solution of tetrabutylammonium tetraphenylboride, all the quaternary ammonium salt solutions studied in both solvents, exhibit similar dielectric behaviours. This probably indicates that equimolar solutions in both solvents contain approximately the same concentration of ion pairs, although the different conductances suggest that the concentrations of charged species are different. In comparison, equimolar solutions of tributylammonium iodide in these solvents have different dielectric behaviours, and possible reasons for this have already been described.

In detail, however, the various solutions do behave slightly differently. The Cole distribution parameters for solutions of tetrabutylammonium nitrate, perchlorate and iodide are slightly greater than those of the bromide in 1,2-dichloroethane. Within experimental error, distribution parameters are the same for solutions of the same electrolyte in both solvents. Relaxation times of solutions of quaternary salts in 1,1-dichloroethane, are about 10% less than those in 1,2-dichloroethane (see table 4.8). Within the errors involved, similar differences also obtain for solutions of tertiary ammonium salts in these solvents (see table 4.5).

Relaxation times for electrolytes in 1,2-dichloroethane decrease in the following order:

$Bu_4NBPh_4 > Bu_4NBr > Bu_4NI > Bu_4NNO_3 > Bu_4NClO_4$,
(337) (220) (210) (193) (179)

and $Pr_4NBr > Pr_4NI$
(195) (186)

The numbers given in brackets below the salts, are the average values of τ_o (in psec.), for the electrolytes in the concentration range 0.2 to 0.4 M., taken from table 4.8.

The manner of the variation of values of τ_o, can be rationalised by comparing them with limiting ionic conductances, given in table 4.9. Hence, salts of ions having the highest mobility, have the smallest relaxation times, and vice versa.

There are, however, several reasons for regarding relaxation times, corresponding to maximum loss, as not being entirely determined by the ion pair rotational process. These are summarised below:

1. The above argument, concerning limiting ionic conductances, cannot be applied to solutions of tributylammonium picrate and iodide.

Table 4.9. Limiting Ionic Conductances in 1,2-dichloroethane at 25°C.

Ion	λ_o	ref.
Bu_4N	26.2	127
Pr_4N	31.5	128
ClO_4	39.2	129
NO_3	40.1	129
Pi	31.2	129
BPh_4	(26)	estimated
Br	33.8	129
I	(33)	estimated

This is because the small difference in limiting ionic conductances of picrate and iodide ions, cannot account for the considerable difference in relaxation time of the appropriate ion pairs.

2. As predicted by Debye-Stokes' theory, the relaxation times of tributylammonium iodide and picrate are approximately proportional to the molar volumes of these electrolytes (see tables 4.3 and 4.7). It seems reasonable to infer, therefore, that tetrabutylammonium bromide, nitrate, iodide and perchlorate should have somewhat similar rotational relaxation times, and that these should all be significantly larger than those for the analagous tetrapopylammonium

salts. This is not the case, so far as values of τ_o or τ_P are concerned, as can be seen by comparing values of rotational relaxation time estimated from molar volume, given in table 4.11 (p.140) as values of $(1/2k_3)$, with values of τ_P.

3. Fröhlich's two position model, leads to equation 4.13.

$$\tau = \frac{\pi}{\omega_o} e^{E/kT} \quad , \qquad 4.13.$$

The pre-exponential factor in this equation is determined by the angular frequency of oscillation about an equilibrium position. The magnitude of this frequency should be dependent on the moment of inertia of the molecule, so that its relaxation time should also depend on moment of inertia. Approximate estimates of the moments of inertia of various ion pairs have been made, and values obtained for tetrabutylammonium perchlorate, iodide and tetraphenylboride ion pairs are greater than those estimated for tetrabutylammonium bromide and tetrapropylammonium bromide. Provided therefore, the energy barriers to rotation for different ion pairs are similar in magnitude, the relaxation times of ion pairs would be expected to parallel their moments of inertia.

4. The interaction of ion pairs with their surroundings, would be expected to increase as the dipole moment of the ion-pair increases. Thus, the dipole moment of tetrabutylammonium perchlorate is larger than that of the bromide (see table 1.2), so that a corresponding

difference in relaxation time might also be expected. However with values of τ_0, the converse is in fact found to be true.

5. The variation in the values of the Cole distribution parameters with chemical character, requires some explanation. It is possible that different structures obtaining in different electrolyte solutions, can cause a variation in the factors governing the departure from the conditions assumed in the derivation of the Debye-Pellat equation. Alternatively, the distribution parameter may be regarded as resulting from a superposition of variable numbers of discrete processes, each of which is describable by a Debye type dispersion.

According to Cole (61), curves of the types shown in figures 4.26 to 4.35, can always be formally reproduced by a superposition of independent relaxation processes, each of which is governed by an exponential law, with its own relaxation time. For solutions of electrolytes in solvents of low polarity, a multiplicity of relaxation processes is possible. In the case of solutions of tributylammonium iodide in non polar solvents, Davies and Williams (19) have suggested that the absorption observed there may possibly consist of a superposition of only a very limited number of components. If only a single broad absorption peak is observed, then the resolution of experimental data is generally restricted to two superposed dispersions.

For the reasons outlined above, values of relaxation time for which loss is a maximum do not seem to correspond to those expected to be associated with orientational displacements of contact ion pairs, although they are of the expected order of magnitude. It has therefore been assumed that the observed behaviour results from a superposition of two processes, each characterised by the Debye-Pellat equation, with relaxation times τ_1 and τ_2. The resultant values of permittivity and loss are then given by equation 4.14.

$$\varepsilon' - j\varepsilon'' = \varepsilon'_\infty + (\varepsilon'_o - \varepsilon'_\infty)\left[\frac{C_1}{1+j\omega\tau_1} + \frac{C_1}{1+j\omega\tau_2}\right] . \qquad 4.14.$$

For ε'_o and ε'_∞, values obtained from Cole-Cole plots, and given in table 4.8, were used. This cannot be regarded as completely satisfactory, but as these cannot be directly measured in every case, it seems the best procedure to adopt at present. Also, the assumption that the observed dispersion consists principally of a superposition of two exponential processes, can only be justified on the grounds that it is the simplest possible assumption. These assumptions seem most reasonable for small values of the Cole distribution parameter α. Whether an analysis of this kind is physically meaningful, can probably be best judged by seeing whether, or not, values of the principal relaxation times conform more closely than τ_o to expected values.

Values of τ_1, τ_2 and C_1, given in table 4.10, are those for which the sum of the squared difference between values of permittivity and loss, calculated by means of equation 4.14, and the experimental values of permittivity and loss, is a minimum. They were found by using a computer (the program used is given in Appendix 5) to calculate successive sums of the deviations squared, for a series of trial values of τ_1, τ_2 and C_1. The set of values of τ_1, τ_2 and C_1 chosen, was that set for which the sum of the squared deviations is a minimum. In table 4.10, δ is the average value of:

$$\tfrac{1}{2}\left|\varepsilon'_{\text{calc.}} - \varepsilon'_{\text{expt.}}\right| + \tfrac{1}{2}\left|\varepsilon''_{\text{calc.}} - \varepsilon''_{\text{expt.}}\right| , \qquad 4.15$$

calculated for permittivities and losses for each of the five frequencies of measurement. Thus δ is in permittivity units. Since values of δ are of the same magnitude as experimental error, data are satisfactorily represented, in a purely numerical sense, by a superposition of two Debye relaxation processes.

Values of τ_1 and τ_2 obtained by the computational procedure employed here, are usually considered to be accurate to about ±20%, while the values of C_1 are probably not better than ±0.1. Values of τ_1, given in table 4.10, increase in a manner which roughly parallels the increase in dipole moments and moments of inertia of the ion pairs concerned. On the basis of dipole moment, τ_1 values are consistent with values of relaxation time of tributylammonium picrate and iodide. Values of τ_1 increase in the same manner as do

Table 4.10. Values of τ_1, τ_2 and C_1 required for equation 4.14, and δ, for some solutions of univalent electrolytes in 1,2-dichloroethane. Temperature is 25°C.

Electrolyte	Conc. (M)	τ_1(psec)	τ_2(psec)	C_1	δ
Pr_4NBr	0.2 0.4	280 250	100 80	0.67 0.74	0.05 0.11
Pr_4NI	0.2	220	80	0.80	0.06
Bu_4NBr	0.2 0.3 0.4	295 285 280	75 85 100	0.80 0.76 0.70	0.03 0.05 0.05
Bu_4NI	0.2 0.4	400 460	100 90	0.56 0.63	0.06 0.10
Bu_4NNO_3	0.2 0.4	400 450	120 100	0.45 0.42	0.05 0.06
Bu_4NClO_4	0.2 0.4	400 350	100 100	0.50 0.44	0.05 0.06
Bu_4NBPh_4	0.232	700	150	0.50	0.13

molar volumes of the electrolytes concerned, but the magnitude of the change is greater than the corresponding change in molar volume.

In the case of the nitrate, however, its dipole moment, and thus its charge separation, apparently is not known. Its moment of inertia can be estimated from a consideration of the two ionic radii concerned, but then its relaxation time τ_1 is larger than that which would be estimated on this basis. It is worth noting that the increase in viscosity produced by a given concentration of tetrabutylammonium nitrate, is slightly larger than that produced by the same concentration of any of the other electrolytes studied, except the tetraphenylboride. The peculiar characteristic of the nitrate ion is its disc-like structure (see Appendix 4), and it may be this feature, which is responsible for these anomalies and also its high limiting conductance (see table 4.9).

If τ_1 is identified with the orientational displacement of contact ion pairs, then it seems that the shorter time (τ_2) may refer to a dispersion mechanism of a different type, rather than to the orientational motion of another class of ion pair. The variation of τ_2 with the character of the electrolyte is less marked than the corresponding variation of τ_1. In general, any net displacement of charge resulting from the application of the field, which produces an additional component of electric moment in the direction of the field, will make a characteristic contribution to the dielectric properties of the system. One can speculate that the process characterised by the relaxation time τ_2, is associated with a damped resonance vibration of ions constituting an ion pair, about their equilibrium positions. Such vibrations will not necessarily be restricted to contact ion pairs, but may also occur with other ionic aggregates. In either case, some reorganisation of the alkylammonium chains and/or the solvent cage surrounding the electrolyte could be involved. Trialkylammonium salts would be expected to behave differently, because of their much smaller interionic distances (see Appendix 4), and also, because of the directional characteristics of hydrogen bonds. The zero Cole distribution parameters found for solutions of tetrabutylammonium bromide in acetone (31) and dichloroethane, may simply be the consequence of an insufficient damping of the ionic vibrations in these solvents. In this case, a sharper resonance absorption at a frequency closer to the natural vibration frequency of the ion pair might be expected. If this interpretation of τ_2 is correct, then one would expect the magnitude of τ_2 to be determined more by the characteristics of the solvent environment, rather than by the nature of the ions involved.

In view of the complexities of electrolytic solutions in solvents of low permittivity, a more positive identification of the mechanism involved may not be possible until systematic measurements have been made with a variety of ions and over a wider range of temperatures (particularly at lower temperatures). On the other hand, the possibility should not be overlooked that τ_2 arises from the limitations of the computational procedure used to analyse the experimental data, rather than from any single dispersion process.

Because the method used here to find ε'_0 and ε'_∞ assumes a symmetrical Cole-Cole plot, C_1 tends to a half as the Cole distribution parameter increases. Never the less, the present author prefers to take the view that because of the inadequacy of the methods available for analysing data, this tendency may be misleading. The dielectric dispersion seems mainly to arise as the result of the orientational motion of ion pairs.

It should also be pointed out that in the case of solutions for which C_1 does not approximate to 0.5, the values of τ_1, τ_2 and C_1, given in table 4.10, do not represent a unique analysis of the experimental data. For example, with a 0.4 M. solution of tetrabutylammonium bromide, an equally satisfactory set of values is $\tau_1 = 550$ psec., $\tau_2 = 160$ psec. and $C_1 = 0.26$. The values given in table 4.10, are more consistent with those for which C_1 approximates to 0.5.

Some solutions of tetrabutylammonium bromide were studied at temperatures of 1°, 15°, 25° and 35°C. The energy of activation, calculated from the average value of the experimental relaxation times (τ_o) at each temperature, by means of an Arrhenius plot, is 2.3 ± 0.2 kcal.Mole^{-1}. For the dielectric dispersion of solutions of dipolar molecules in non polar solvents, energies of activation of between 1 and 2 kcal.mole^{-1} are commonly found (130, 131). Hence the value of 2.3 kcal.mole^{-1} is not inconsistent with the conclusion that the dispersion is principally due to the orientational motion of ion pairs.

An alternative interpretation for values of τ_o being somewhat smaller than expected, is that the limited life time of an ion pair can reduce the value of τ_o. Nederbragt and Pelle (132), Price (133), Davies and Sobczyk (134), Anderson and Smyth (135) and Brownsell and Price (136) have all investigated the dielectric relaxations of charge transfer complexes. Such charge transfer complexes are transient species, and in this respect resemble ion pairs. Anderson and Smyth have given an expression which relates the dielectric relaxation time (τ_μ) of such transient species to their rate of dissociation (k_1) and their rate of orientational relaxation (k_3).

$$\tau_\mu = 1/(k_1 + 2k_3) \qquad 4.16.$$

If k_1 is negligible, then $\tau_\mu = 1/2k_3$.

Estimated values of intrinsic orientational relaxation times ($1/2k_3$) for various ion pairs, calculated from the average experimental value of τ_p for tributylammonium iodide in 1,2-dichloroethane, on the assumption that relaxation times are proportional to molar volume, are given in table 4.11. Thus it is assumed that for tributylammonium iodide in 1,2-dichloroethane, k_1 is negligible compared with k_3. Average experimental values of intrinsic relaxation time (τ_p) for various electrolytes in 1,2-dichloroethane are also given in table 4.11. Values of k_1, calculated by means of equation 4.16, are given in table 4.11. They are probably larger in magnitude than those expected for rates of ion pair dissociation, but

Table 4.11.

Salt	Intrinsic Relaxation Times τ_p		$k_1 \times 10^{-9}$ (sec^{-1}.)
	Average of Observed values of τ_p (psec)	Estimated from molar volumes $\left(\frac{1}{2k_3}\right)$	
Bu_3NHI	189	189	-
Bu_3NHPi	314	261	-
Pr_4NBr	172	164	negative
Pr_4NI	168	177	0.3
Bu_4NBr	196	218	0.5
Bu_4NI	186	230	1
Bu_4NNO_3	170	229	1.5
Bu_4NClO_4	159	233	2
Bu_4NBPh_4	290	400	9.5

they do vary in the manner expected from a consideration of the association constants, and estimated distances of closest approach of the electrolytes concerned.

Petrucci and Atkinson (11) investigated ultrasonically the kinetics of association and dissociation in solutions of tetrabutylammonium bromide with a solvent permittivity of sixteen. The precise values of rates of dissociation and association obtained in this investigation may be open to objection, because the variation of association constant with permittivity was ignored in the calculations. In a carbon tetrachloride-nitrobenzene mixture, Petrucci and Atkinson (11) reported k_1 as 0.8×10^8 sec^{-1}. for tetrabutylammonium bromide. This value is smaller than the values of k_1, given in table 4.11, by approximately a factor of ten. The values of k_1 themselves (given in table 4.11) are subject to considerable error, since they depend on the difference between experimental relaxation times, and those estimated for ion pair orientation. Even so, it does seem that for solutions in dichloroethane, the experimental relaxation time is likely to be only slightly reduced by ion pair dissociation. In solvents of lower permittivity, k_1 would be expected to be smaller, and dissociation could therefore hardly account for the reductions in relaxation time, which have been observed in the present investigation. Moreover, this interpretation provides no explanation for the occurrence and variability of the Cole distribution parameter, since the treatment of Anderson and Smyth (135) leads to Debye-Pellat behaviour. However, as the permittivity of the solvent is increased, k_1 would be expected to increase also, so its effect is then likely to become more pronounced.

i. Solutions of Tetrabutylammonium Bromide in Diethyl ketone.

Cole diagrams for 0.3 M. solutions of tetrabutylammonium bromide in diethyl ketone are illustrated in figure 4.36. Because of the

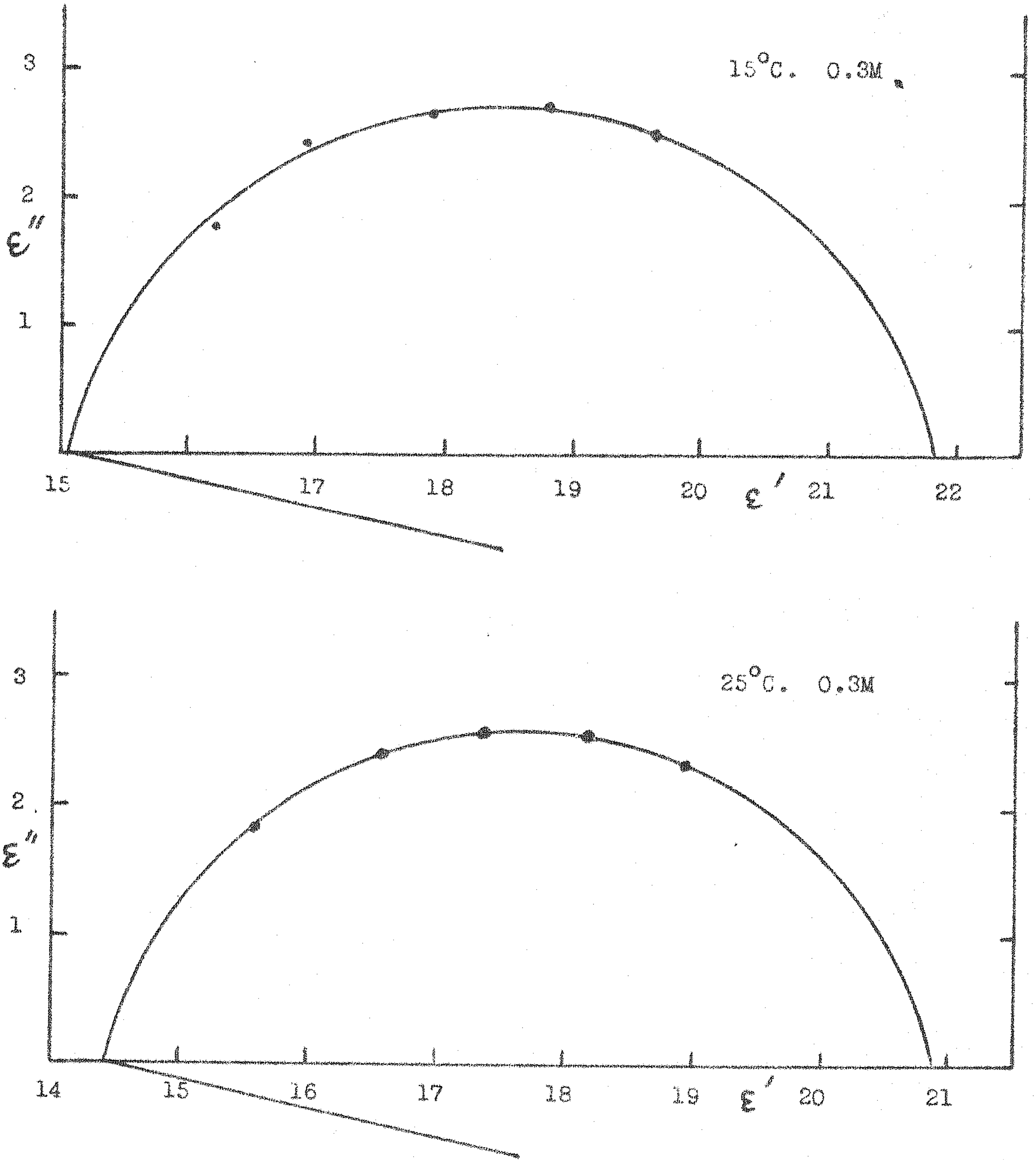


Fig. 4.36 Bu_4NBr in Diethyl ketone (at 15° and 25°C.).

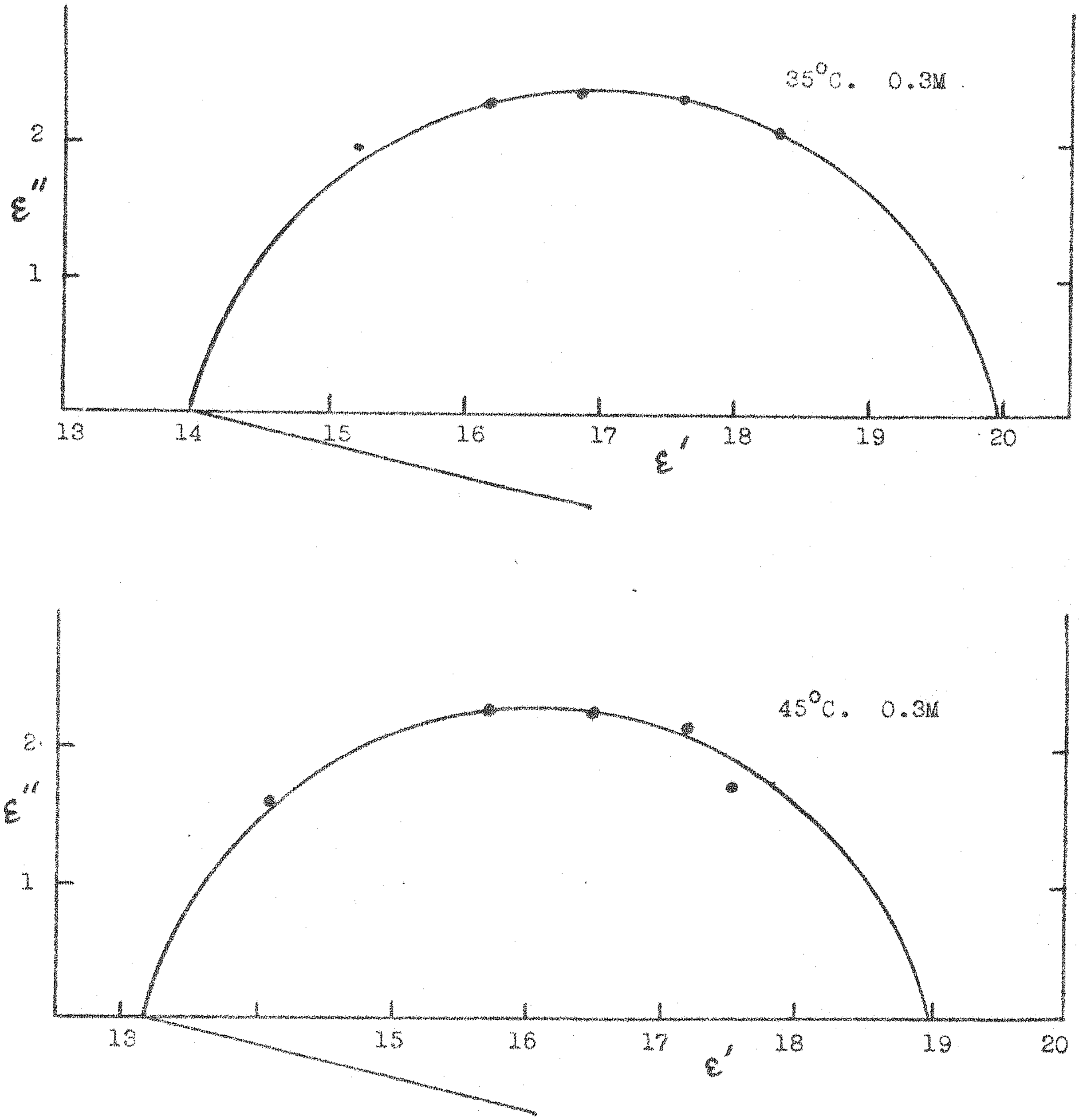


Fig. 4.36 Bu_4NBr in Diethyl ketone (at 35° and 45°C.)

larger correction for solvent loss required, relaxation times and Cole distribution parameters are probably less accurate than those for some other systems, although the experimental data do define the absorption maximum quite well.

Values of the distribution parameter (α), given in table 4.8, are larger than those found for solutions of this electrolyte in most other solvents. This is an important observation, because it demonstrates that broadening of the dispersion is not necessarily restricted to solvents of low permittivity.

Solutions of tetrabutylammonium bromide in diethyl ketone were investigated in the temperature range 15° to 45°C. Measurements were not made at lower temperatures because of the limited solubility of the salt. In fact, the 0.3 and 0.4 M. solutions are slightly supersaturated at 15° and 25°C. respectively. The results are not sufficiently precise to detect any temperature dependence of the Cole distribution parameter. By using average values of τ_o for each temperature, an energy of activation of 1.8 ± 0.3 kcal. mole^{-1}, was obtained by means of an Arrhenius plot. Within experimental error, this value is identical with that found for the same electrolyte in 1,2-dichloroethane.

For a 0.2 M. solution of tributylammonium iodide, τ_p is 149 psec., whilst for 0.2 to 0.4 M. solutions of tetrabutylammonium bromide, values of τ_p lie in the range 149 to 159 psec. This again indicates that the relaxation time is a little lower than that of 180 to 250 psec. expected for ion pair orientational displacements.

The experimental data ~~has~~ have been analysed into two relaxation times by means of the graphs given in Appendix 6. Approximate values found in this way are 340 psec. for τ_1, and 85 psec. for τ_2, with $C_1 = 0.5$. The value of τ_1 is larger than that expected for ion pair orientation. Apart from the errors involved in the use of the graphs given in Appendix 6, this is probably also due to the inadequacy of representing the dispersion by only two processes, both described by the Debye-Pellat equation, and to the uncertain method of obtaining the high and low frequency limiting values of permittivity.

4.14. Application of the theory of Onsager, Böttcher and Scholte.

According to Böttcher (140), the relationship between the static permittivity (ε'_o) of a mixture, containing n_k molecules per cm^3., which have a vapour phase molecular moment of μ_k, and a polarisability of α_k, is given by equation 4.17, in which f_k is equal to

$$\frac{1}{a_k^3}\ \frac{2\varepsilon'_o - 2}{2\varepsilon'_o + 2}\ .$$

$$\frac{\varepsilon'_o - 1}{4\pi} = \frac{3\varepsilon'_o}{2\varepsilon'_o + 1} \sum_k \frac{n_k}{1-f_k\alpha_k}\left[\alpha_k + \frac{\mu_k^2}{3kT(1-f_k\alpha_k)}\right] . \qquad 4.17$$

Equation 4.17 was developed from the model proposed by Onsager, in which each molecule of type k is represented as a point dipole, situated at the centre of a spherical cavity of radius a_k. The polarisability of a dipolar molecule (α_k) is assumed to be uniformly spread throughout its spherical cavity. Outside the cavity, the medium is treated as a continuum, with a permittivity ε'_o.

Equations similar to equation 4.17, have been applied to mixtures of polar molecules by Gäumann (137), Gilkerson and Srivastava (138), Aaron and Grant (139), and Pottel (34). Gilkerson and Srivastava have concluded that, apart from association effects, determination of dipole moments of polar solutes in polar solvents is just as feasible as the calculation of dipole moments from pure liquids, as suggested by Böttcher (140). Equation 4.17 should therefore in principle be applicable to the electrolyte solutions studied here, particularly since the size of an ion pair is larger than that of the surrounding solvent molecules.

The total polarisation (P_T) of an electrolyte solution produced by the application of a field E is given by:

$$P_T = \frac{\varepsilon'_c - 1}{4\pi} E \quad . \qquad 4.18$$

If P_R is defined as:

$$P_R = \frac{\varepsilon'_\infty - 1}{4\pi} E \quad , \qquad 4.19$$

then P_R represents the contributions to the total polarisation arising from orientation of polar solvent molecules, and from the electronic and atomic polarisations of both solvent and solute molecules. The polarisation arising from the orientation of solute dipoles is therefore given by:

$$P_T - P_R = \frac{\varepsilon'_o - \varepsilon'_\infty}{4\pi} \quad E \quad . \tag{4.20}$$

Equation 4.17 can be rearranged to include both P_T and P_R:

$$P_T \;=\; P_R + \frac{3\varepsilon'_o}{2\varepsilon'_o + 1} \, \frac{n\mu^2}{(1 - f\alpha)^2} \, \frac{E}{3kT} \; . \tag{4.21}$$

$$\text{i.e.} \quad \frac{P_T - P_R}{E} \;=\; \frac{\varepsilon'_o - \varepsilon'_\infty}{4\pi} \;=\; \frac{3\varepsilon'_o}{2\varepsilon'_o + 1} \, \frac{n\mu^2}{(1 - f\alpha)^2 . 3kT} \; . \tag{4.22}$$

Equation 4.22 has been used to calculate values of $(\varepsilon'_o - \varepsilon'_\infty)$ for representative solutions of tributylammonium iodide and picrate, by the following procedure. The radius of the cavity (<u>a</u>) of the ion pair was calculated from the molar volume (V) of the electrolyte (given in table 4.3), by means of equation 4.23, because this method gives good results for pure liquids.

$$4/3\pi a^3 = \; V/N \quad . \tag{4.23}$$

In equation 4.23, N is the Avagadro number. The polarisability (α) of ions was estimated by summing bond refractions. The latter have been tabulated by Smith (142), Smyth (141) and Vogel et al (143). For the tributylammonium ion, a value of 23.84×10^{-24} has been found for α, whilst for the picrate ion, a value of 17.78×10^{-24} has been obtained. For the iodide ion (141), α is 7.33×10^{-24}. Average values of μ (see table 1.2) of 7.9 D and 12.1 D for tributylammonium iodide and picrate respectively, were employed in the present calculations. Values of $(\varepsilon_o' - \varepsilon_\infty')$ were calculated by substituting appropriate experimental values of ε_o' into the right hand side of equation 4.22. Plots of the values of $(\varepsilon_o' - \varepsilon_\infty)$ so obtained, against concentration (M.) of electrolyte are shown in figures 4.37 and 4.38. The upper plot in figure 4.37 refers to solutions of tributylammonium picrate in 1,2-dichloroethane, and the lower one to solutions of the same salt in trichloroethylene. For a given electrolyte concentration, the dispersion amplitude is smaller in trichloroethylene solution than it is in 1,2-dichloroethane solution. This is because, according to the theory of Onsager and Böttcher, the solution dipole moment of the ion pair concerned, is smaller in the lower permittivity solution. A similar effect causes the slight curvature upwards in the plots shown in both figures 4.37 and 4.38.

The experimental values of $(\varepsilon_o' - \varepsilon_\infty')$ for solutions of tributylammonium picrate in 1,2-dichloroethane, are shown in figure 4.37 by means of small open circles (O), while those for solutions in

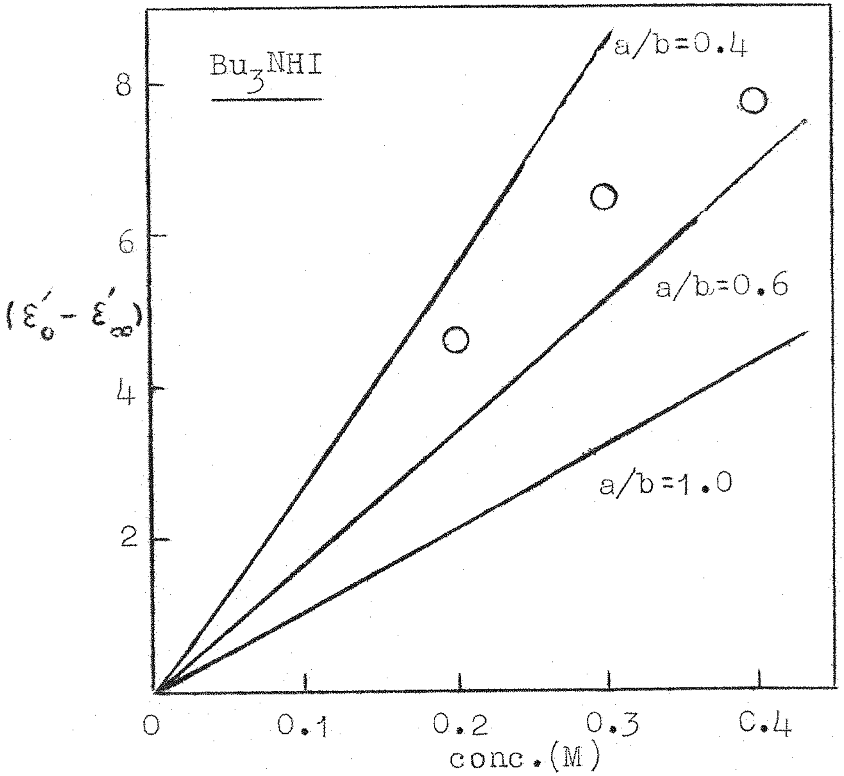


Fig. 4.38

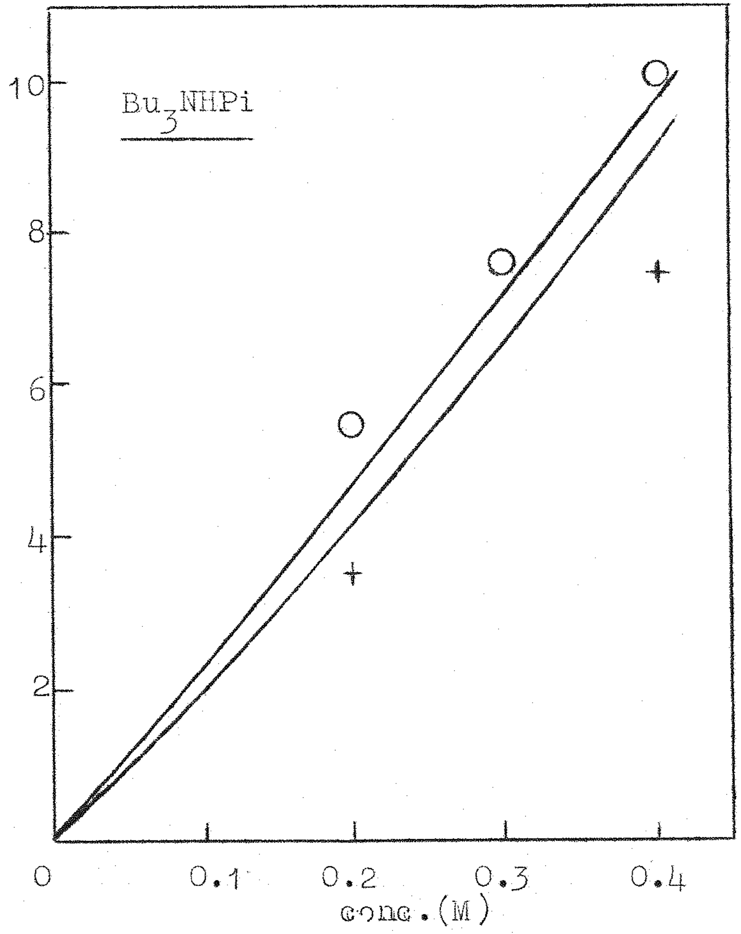


Fig. 4.37

trichloroethylene are represented by crosses (+). For solutions in 1,2-dichloroethane, experimental values of $(\varepsilon'_0 - \varepsilon'_\infty)$ agree satisfactorily with those calculated by means of equation 4.22, and shown as a line in figure 4.37. However the agreement is less satisfactory for trichloroethylene solutions. Instead of being due to the inadequacies of the theory, this lack of agreement, may be due to the formation of non polar aggregates such as quadrupole ions. In support of this conclusion (as is illustrated in figure 4.16) values of $(\varepsilon'_0 - \varepsilon'_\infty)$ observed for equimolar solutions of tributylammonium picrate are very similar in magnitude for all the solvents investigated, except for trichloroethane and trichloroethylene. The similar magnitudes are expected from the theory, if all the electrolyte is in the form of ion pairs, and the smaller dispersion amplitudes observed in trichloroethylene and trichloroethane could, as noted above, be due to association past the ion pair stage.

In comparison with both plots for tributylammonium picrate solutions, that for tributylammonium iodide in 1,2-dichloroethane (which is the plot with the smallest dispersion amplitude shown in figure 4.38), is much less satisfactory. An explanation for this apparent anomaly may be that while a spherical cavity is a reasonable approximation for a tributylammonium picrate ion pair, an ellipsoidal cavity may be required for tributylammonium iodide.

In the case of an ellipsoidal cavity, equation 4.22 becomes:

$$\frac{\varepsilon'_o - \varepsilon'_\infty}{4\pi} = \frac{\varepsilon'_o}{\varepsilon'_o + A(1-\varepsilon'_o)} \frac{n\mu^2}{(1-f\alpha)^2 . 3kT} , \qquad 4.24$$

where now, $f = \frac{3}{abc} \cdot \frac{A(1-A)(\varepsilon'_o - 1)}{\varepsilon'_o + (1-\varepsilon'_o)A}$.

The constant A is calculated from the semiaxes (a,b,c) of the ellipsoid, with the a axis taken to lie in the direction of the dipole. Böttcher (144) has given some values of A for various values of the axial ratios a/b, assuming b and c are equal. The polarisability of the dipole is again assumed to be uniformly distributed throughout the cavity.

The plots of $(\varepsilon'_o - \varepsilon'_\infty)$ against electrolyte concentration, illustrated in figure 4.38, with a/b = 0.4 and 0.6, and a.b.c taken to be equal to a^3, were obtained from equation 4.24. With a/b = 0.5, the calculated dispersion amplitudes would appear to be close to the experimental values. A model of a tributylammonium iodide ion pair, with semi axes a = 3Å and b = c = 6Å is considered to be not unreasonable.

The Onsager-Böttcher-Scholte theory predicts that dispersion amplitude should be approximately proportional to ion pair concentration. This is observed experimentally in those cases where it is thought that the electrolyte is predominantly in the form of ion pairs. It seems that estimates of ion pair concentrations, calculated from this theory, can be seriously in error unless the correct shape of cavity is employed.

4.15. Estimation of Ion Pair Concentrations.

In section 4.14, it is shown that according to the theory of Onsager, Böttcher and Scholte, the dispersion amplitude $(\varepsilon'_0 - \varepsilon'_\infty)$ is nearly proportional to the concentration of ion pair dipoles. Such linearity is apparently most nearly realised experimentally with those solutions of tributylammonium picrate in which there is evidence that the electrolyte is predominantly in the form of ion pairs.

In figures 4.39, plots of $(\varepsilon'_0 - \varepsilon'_\infty)$ against concentration are illustrated for solutions of tetrabutylammonium bromide in chloroform, 1,2-dichloroethane and diethylketone. The dotted lines are the slopes of the plots as the concentration tends to zero (actually in the limit as concentration tends to zero, of course, this slope would also be zero, as ion association would be absent). To obtain estimates of the fraction (x) of the electrolyte in the form of ion pairs at a given concentration, the ratio of the measured dispersion amplitude to that obtained from the limiting slope has been used. This avoids the difficulty of having to select appropriate ion pair cavity dimensions. Values of x, as a function of electrolyte concentration, are illustrated in figure 4.40. They must be regarded

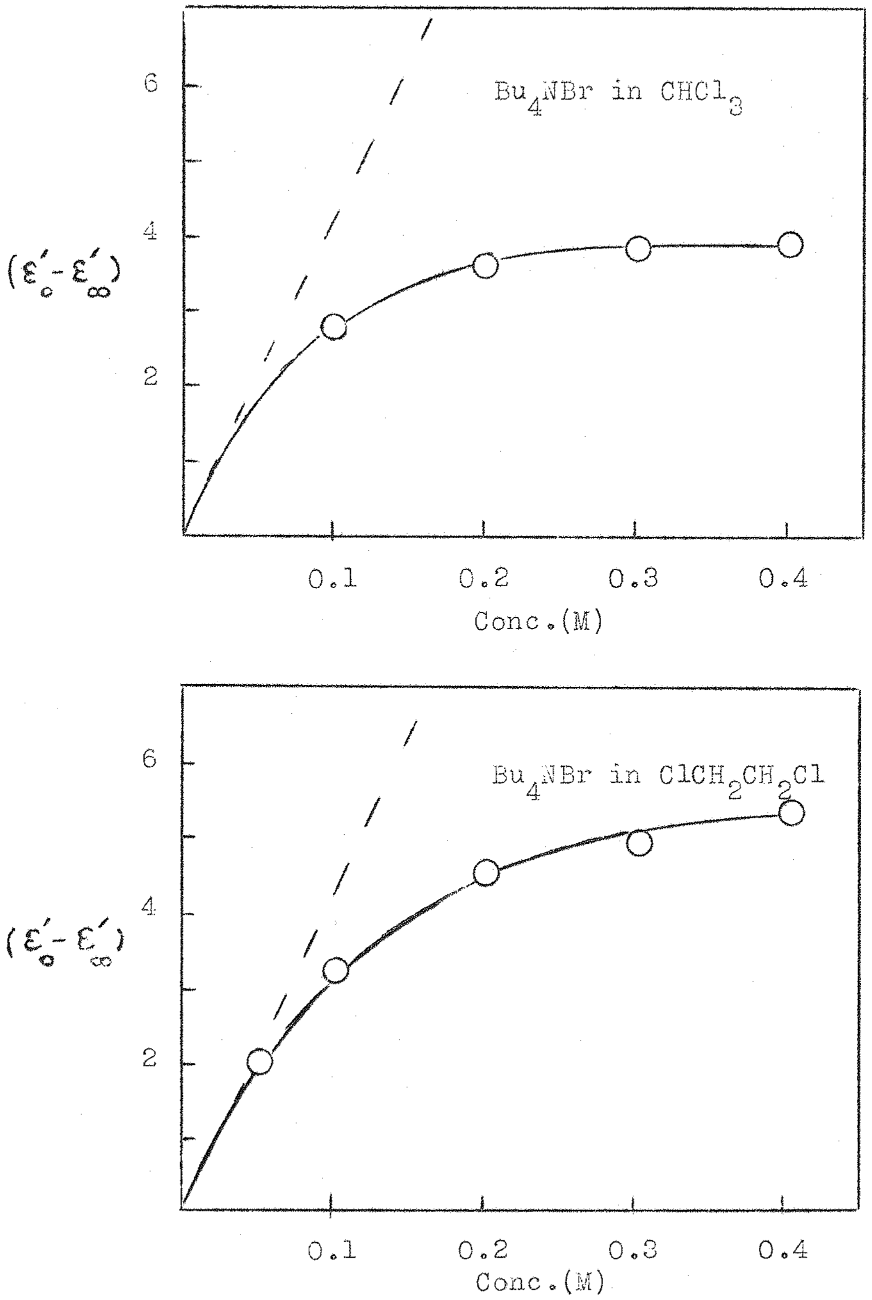


Fig. 4.39 Dispersion amplitude against electrolyte concentration.

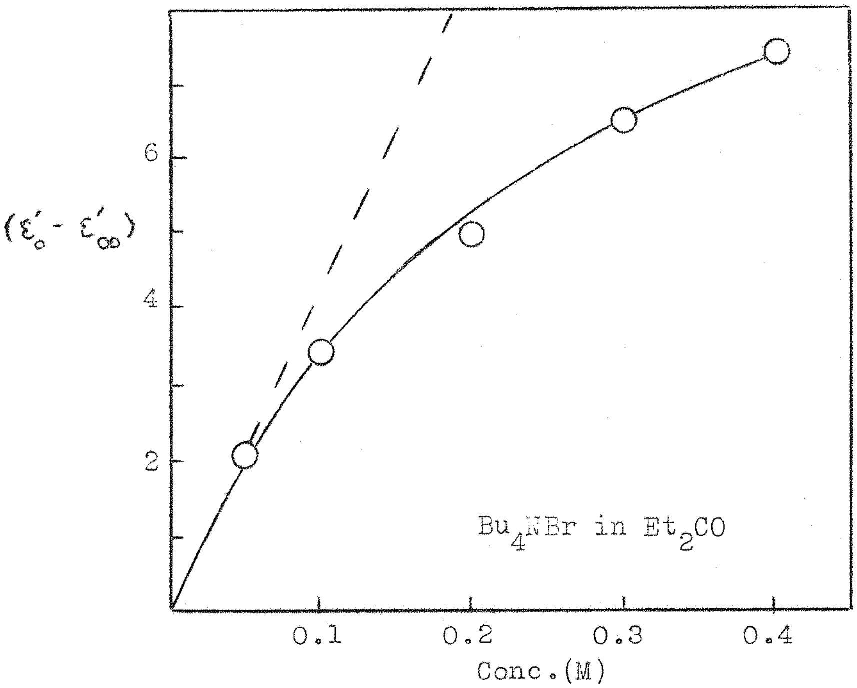


Fig. 4.39 Dispersion amplitude against electrolyte concentration.

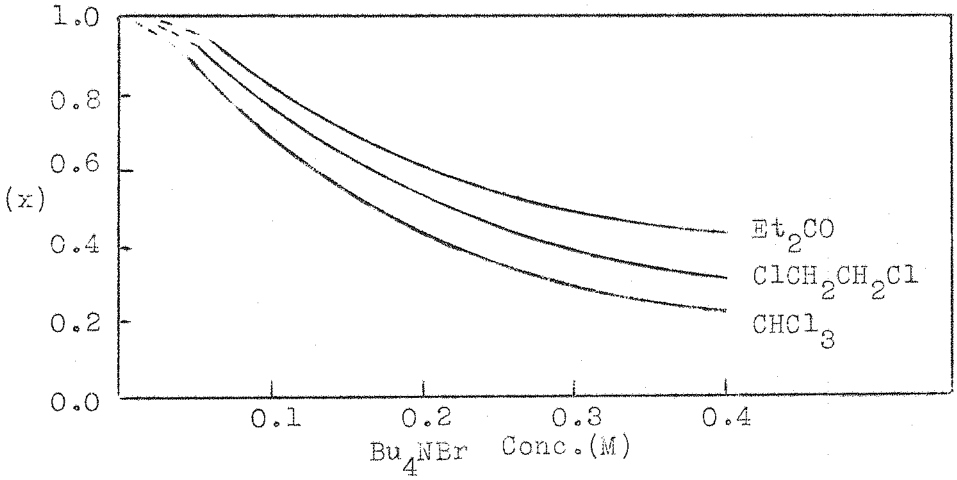


Fig. 4.40 Fraction (x) of electrolyte in the form of ion pairs against electrolyte concentration.

as being only approximate. The plots do show, however, that in these solutions, that the fraction of the electrolyte in the form of ion pairs decreases appreciably at concentrations above about 0.05 M.

4.16. Generalisations regarding the dispersion amplitudes of quaternary ammonium salt solutions.

Dispersion amplitudes ($\varepsilon'_0 - \varepsilon'_\infty$) of equimolar solutions of tetrabutylammonium bromide in different solvents, illustrated in figure 4.41, increase as the permittivity of the solvent increases, until this has a value of about 17 (diethyl ketone), although the maximum could be concentration dependent. If it is assumed that ($\varepsilon'_0 - \varepsilon'_\infty$) is approximately proportional to the concentration of ion pair dipoles, then a simple interpretation of these observations is that as the solvent permittivity is increased, association past the ion pair stage becomes less significant, with a proportionate increase in the ion pair concentration. In addition, an increase in permittivity also favours increased dissociation into free ions. For any given electrolyte concentration, there will be a permittivity at which the two effects combine to give a maximal ion pair concentration. Thereafter in higher permittivity solvents, the ion pair concentration diminishes.

It is obvious from both figures 4.39 and 4.41 that proportionate increases in ($\varepsilon'_0 - \varepsilon'_\infty$) become less as the electrolyte concentration

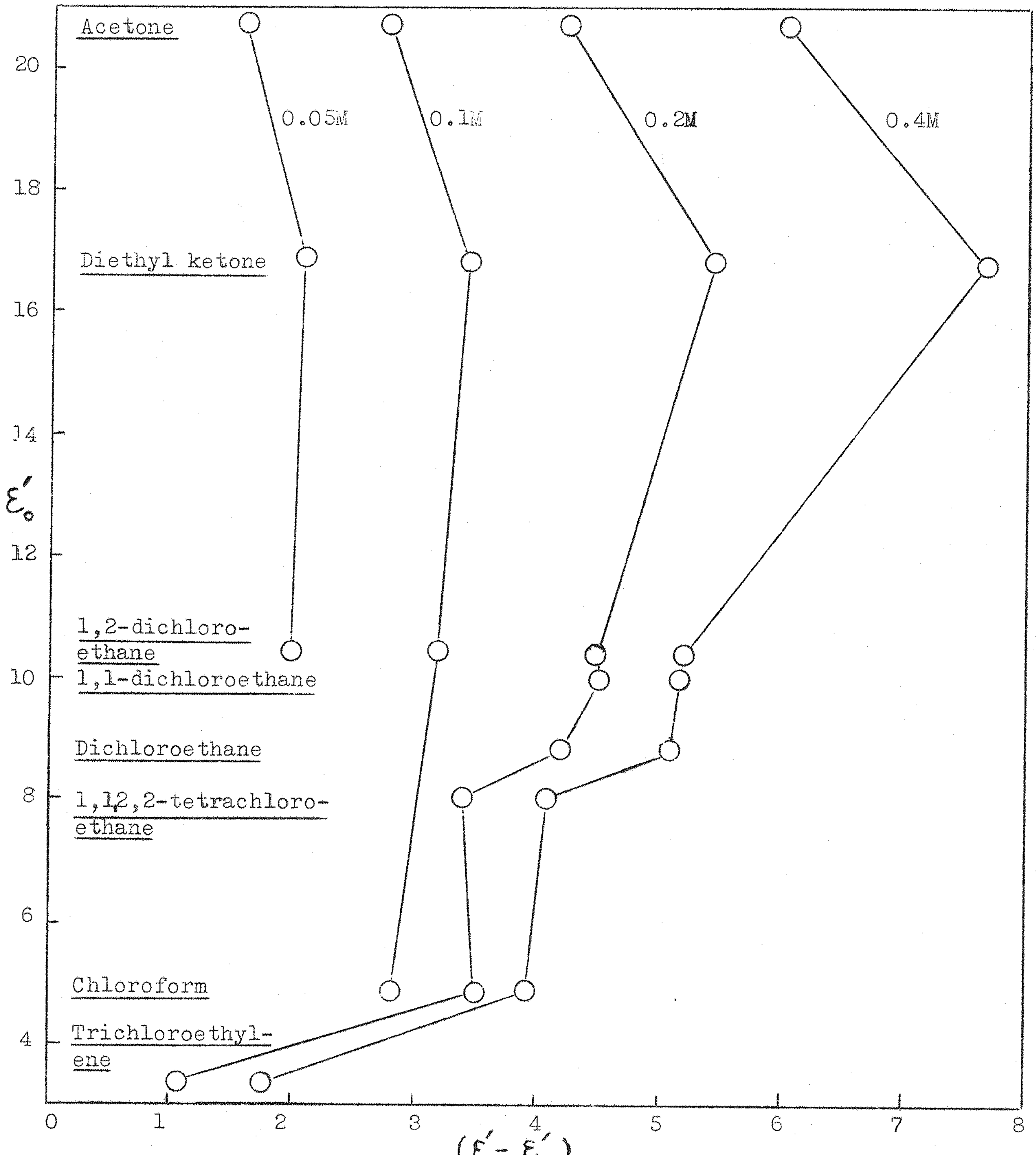


Fig. 4.41 Effect of solvent permittivity on dispersion amplitudes of tetrabutylammonium bromide solutions (at 25°C.). (Data for acetone solutions from Cavell, ref. 31).

is increased. Thus, for a given solvent, the concentration of ion pairs may well approach a maximum value. As this limit is approached, increasing association to larger aggregates would be expected to offset the increase in total electrolyte concentration. The higher the permittivity of the solvent, the higher in principle should the maximum possible concentration of ion pairs become.

4.17. Effect of Electrolytes on the "Static Permittivity" of Solvents.

The "static permittivity" of solvents in the presence of electrolytes is given by ε'_∞. The overall effect of electrolytes on the value of ε'_∞ represents the net result of a number of distinguishable contributions, which may be summarised as follows:

a. The introduction of electrolyte replaces polar solvent molecules by molecular species having atomic and electronic polarisability only, since the dipolar contribution of the electrolyte is contained in the dispersion amplitude $(\varepsilon'_0 - \varepsilon'_\infty)$.

b. The electric field near ions, and other ionic aggregates within the solution, inhibits surrounding solvent molecules from making their contribution to dipolar polarisation, thereby reducing ε'_∞.

c. Electrolytes may alter the structure of solvents, as for example they do in aqueous solutions, and in solutions in 1,2-dichloroethane.

The principal effect in all systems studied here, seems to be that which derives from the replacement of solvent molecules by

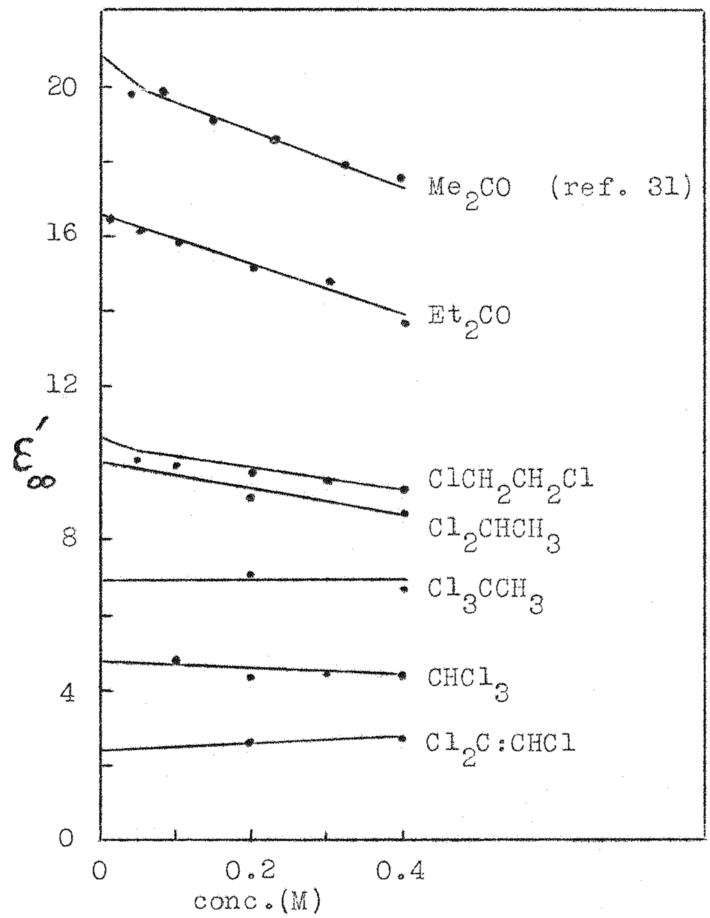


Fig. 4.42 Variation of (ε'_∞) of various solvents in tetrabutylammonium bromide solutions with concentration at 25°C.

electrolyte, i.e. species which contribute only an atomic and an electronic polarisation term to ε'_∞.

In solutions of tetrabutylammonium bromide and tributylammonium picrate in trichloroethylene, ε'_∞ is larger than the static permittivity of the pure solvent. This is probably because, in a given electric

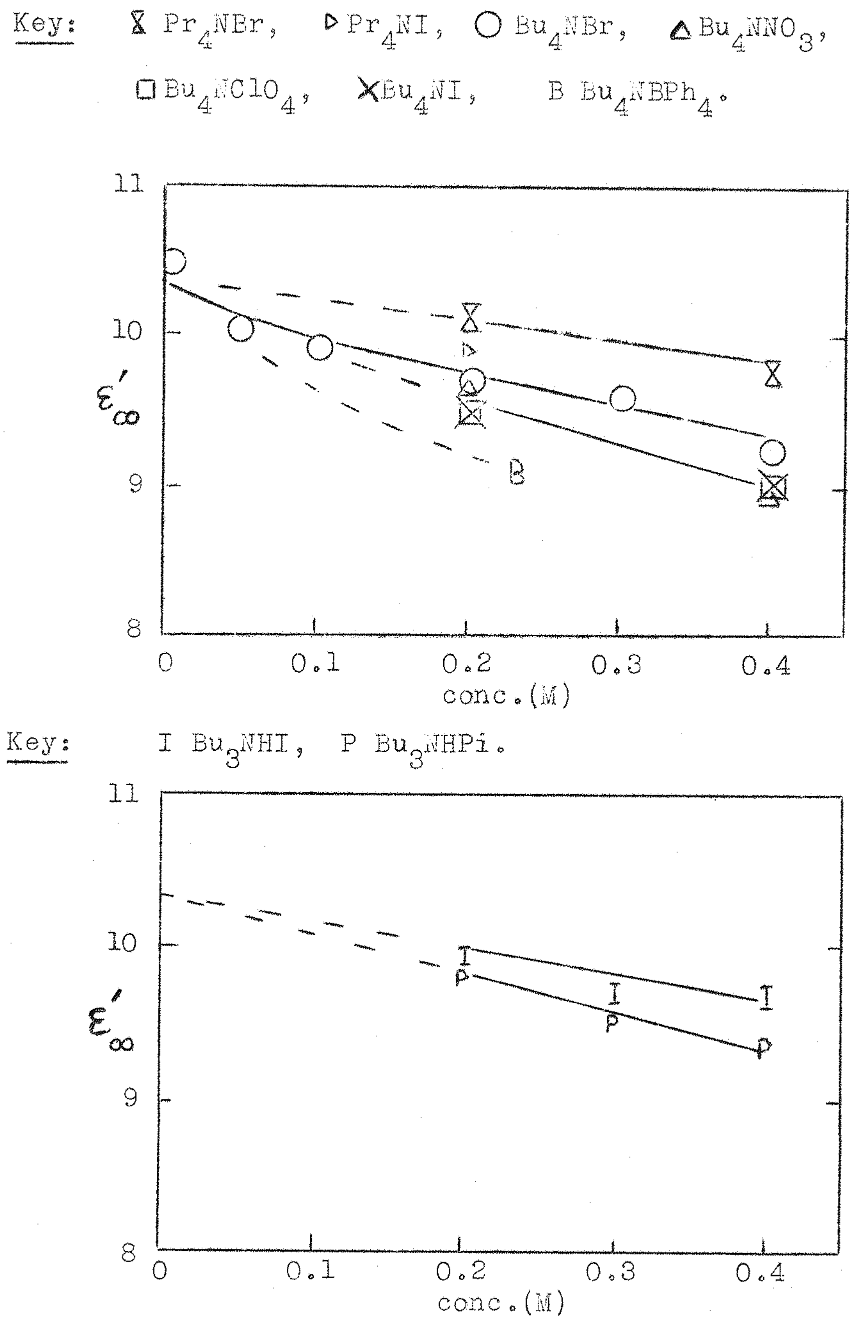


Fig. 4.43 Variation of the static permittivity of 1,2-dichlorethane in electrolyte solutions with concentration, at 25°C.

field, the sum of the atomic and electronic polarisations of the electrolyte, is larger than the sum of the atomic, electronic and dipolar polarisations of the solvent which it replaces.

In other systems, ε'_∞ decreases with increasing electrolyte concentration, and this is illustrated in figures 4.42 and 4.43. Solutions of tributylammonium iodide and picrate, generally probably contain very few free ions, so that for this reason, the decrease in ε'_∞ with increasing electrolyte concentration is linear, and proportional to the molar volume of the electrolyte. When allowance for the different molar volumes has been made, the reduction in ε'_∞ for corresponding solutions is slightly greater in the case of quaternary ammonium salts. Solutions of tetrabutylammonium nitrate, perchlorate and iodide in 1,2-dichloroethane have somewhat lower values of ε'_∞ than equivalent solutions of the bromide. The conductance ratios (Δ_c/Δ_o) indicate that in the former solutions, dissociation into ions is greater than in the latter. At present, there seems to be no certain method of estimating concentrations of free ions in such highly associated solutions, although Inami and Ramsay (125) have given some justification for the use of the expression: $(\Delta_c\eta_c)_{solution}/\Delta_o\eta_o$, to determine the fraction of the total electrolyte in the form of free ions.

APPENDICES

APPENDIX 1.

Permittivities (ε'_m) and Losses (ε''_d) of Electrolyte Solutions

All temperatures are 25°C., unless otherwise stated.

A.1.1. Tri-n-butylammonium Iodide in Acetone.

conc (M).	0.4		0.3		0.2	
freq. (GHz)	ε'	ε''	ε'	ε''	ε'	ε''
3.0	20.5	5.08	20.3	4.46	21.1	3.39
1.5	22.66	4.82	22.47	3.89	22.10	2.86
1.0	24.10	4.30	23.69	3.29	22.75	2.39
0.7	25.17	3.48	24.48	2.97	23.30	1.97
0.5	25.89	3.07	24.99	1.76	23.56	1.33

A.1.2. Tri-n-butylammonium Iodide in Diethyl Ketone.

conc. (M)	0.2	
freq. (GHz)	ε'	ε''
3.0	16.4	3.63
1.5	17.19	3.46
1.0	18.02	3.22
0.8	18.48	3.08
0.6	18.99	2.4

A.1.3. Tri-n-butylammonium Iodide in 1,2-dichloroethane.

conc.(M)	0.4		0.3		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''	ε'	ε''
3.0	10.2	2.95	10.0	2.76	10.3	2.24
1.5	11.18	3.69	11.00	3.23	10.94	2.55
1.0	12.22	4.02	11.99	3.41	11.72	2.69
0.8	12.99	4.21	12.59	3.61	12.13	2.69
0.6	13.57	3.93	13.21	3.44	12.56	2.3
0.1	17.0	1.7	-	-	14.1	0.85
0.06	17.7	0	-	-	14.3	0

A.1.4. Tri-n-butylammonium Picrate in 1,2-dichloroethane.

conc.(M)	0.4		0.3		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''	ε'	ε''
3.0	9.3	2.49	9.5	2.17	9.8	1.96
1.5	10.03	3.10	10.08	2.63	10.29	2.20
1.0	10.79	3.76	10.69	3.22	10.84	2.52
0.8	11.39	4.28	11.24	3.52	11.26	2.73
0.6	12.15	4.72	12.00	3.72	11.67	2.79
0.1	18.8	2.4	-	-	14.9	1.8
0.06	19.1	1.2	-	-	15.2	0.7

A1.5. Tri-n-butylammonium Iodide in 1,1-dichloroethane.

conc.(M).	0.4		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''
3.0	9.7	2.52	9.8	2.20
1.5	10.64	3.09	10.64	2.20
1.0	11.60	3.23	11.29	2.06
0.8	12.16	3.49	11.62	2.0
0.6	12.54	3.5	11.97	2.0

A1.6. Tri-n-butylammonium Picrate in 1,1-dichloroethane.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''
3.0	9.2	2.60	9.6	1.92
1.5	9.95	3.56	10.15	2.34
1.0	11.01	4.27	10.90	2.71
0.8	11.81	4.80	11.42	2.84
0.6	12.67	5.26	-	-

A1.7. Tri-n-butylammonium Picrate in Dichloromethane.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''
3.0	8.45	2.75	8.8	1.62
1.5	9.54	4.00	9.43	2.30
1.0	10.97	4.66	10.34	2.60
0.8	11.97	5.23	10.97	2.76
0.6	13.12	5.49	11.52	2.78

A1.8. Tri-n-butylammonium Picrate in Tetrahydrofuran.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''
3.0	7.4	2.15	7.6	1.45
1.5	8.14	3.42	8.03	2.21
1.0	9.23	4.19	8.83	2.60
0.8	10.07	4.71	9.33	2.77
0.6	11.18	5.16	-	-

A1.9 Tri-n-butylammonium Picrate in 1,1,1-trichloroethane.

conc.(M)	0.4		0.2	
freq(GHz)	ε'	ε''	ε'	ε''
3.0	7.5	1.69	7.6	1.29
1.5	7.95	2.29	7.85	1.37
1.0	8.48	2.98	8.23	1.72
0.8	8.84	3.31	8.43	1.79
0.5	10.2	3.97	-	-

A1.10 Tri-n-butylammonium Iodide in Chloroform.

conc.(M)	0.4		0.2	
freq(GHz)	ε'	ε''	ε'	ε''
3.0	5.11	1.75	4.95	1.33
1.5	5.72	2.50	5.54	1.82
1.0	6.42	2.97	6.12	2.08
0.8	6.90	3.36	6.45	2.27
0.5	8.05	3.69	7.36	2.08

A1.11. Tri-n-butylammonium Picrate in Chloroform.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''
3.0	4.93	1.67	5.00	1.10
1.5	5.38	2.66	5.23	1.68
1.0	6.08	3.48	5.77	2.17
0.8	6.98	4.24	6.21	2.39

A1.12 Tri-n-butylammonium Picrate in Trichloroethylene.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''
3.0	3.88	1.12	3.58	0.78
1.5	4.12	1.80	3.90	1.11
1.0	4.49	2.37	4.23	1.49
0.7	5.13	2.90	4.76	1.62

A1.13 Tetra-n-butylammonium Bromide in Diethyl Ketone.

conc.(M)	0.4		0.3		0.2		
freq.(GHz)	ε'	ε''	ε'	ε''	ε'	ε''	
3.0	13.8	3.38	14.1	2.98	15.1	2.72	45°
1.5	15.49	3.15	15.71	2.96	15.88	2.60	
1.0	16.35	3.03	16.48	2.70	16.43	2.35	
0.7	17.17	2.82	17.18	2.52	17.03	1.98	
0.5	17.69	2.22	17.50	2.02	17.41	1.78	

conc.(M)	0.4		0.3		0.2		
freq.(GHz)	ε'	ε''	ε'	ε''	ε'	ε''	
3.0	14.9	3.07	15.1	3.47	-	-	35°
1.5	15.90	3.35	16.17	3.13	-	-	
1.0	16.79	3.22	16.83	2.90	-	-	
0.7	17.62	3.13	17.62	2.76	-	-	
0.5	18.22	2.4	18.30	2.35	-	-	
3.0	14.95	4.00	15.6	3.52	16.2	3.27	25°
1.5	16.05	3.55	16.55	3.43	16.96	2.97	
1.0	17.02	3.36	17.36	3.25	17.58	2.84	
0.7	18.02	3.27	18.17	3.09	18.23	2.41	
0.5	18.85	2.86	18.82	2.66	18.75	2.23	
	<u>at 0.1M:</u>		<u>at 0.05M:</u>		<u>at 0.01M:</u>		
3.0	15.9	2.36	16.0	1.76	16.4	1.89	
1.5	16.84	2.24	16.67	1.72	-	-	
1.0	17.33	2.07	17.14	1.42	16.71	0.84	
0.7	17.81	1.70	17.53	1.33	-	-	
0.5	18.20	1.72	17.60	0.84	-	-	
3.0	-	-	16.2	3.87	16.2	3.31	15°
1.5	-	-	16.91	3.54	17.29	3.02	
1.0	-	-	17.87	3.43	17.95	3.07	
0.7	-	-	18.78	3.31	18.62	2.63	
0.5	-	-	19.61	2.92	19.34	2.2	

A1.14 Tetra-n-butylammonium Bromide in 1,2-dichloroethane.

conc.(M)	0.4		0.3		0.2		
freq.(GHz)	ε'	ε''	ε'	ε''	ε'	ε''	
3.0	9.2	2.34	9.75	2.19	9.3	1.98	35°
1.5	10.21	2.58	10.49	2.44	10.53	2.13	
1.0	11.06	2.69	11.10	2.55	11.07	2.20	
0.8	11.60	2.66	11.57	2.41	11.40	2.14	
0.6	12.30	2.4	12.16	2.0	11.90	1.8	
3.0	9.6	2.38	9.95	2.35	10.0	2.09	25°
1.5	10.53	2.60	10.74	2.38	10.65	2.13	
1.0	11.22	2.67	11.28	2.40	11.23	2.27	
0.8	11.77	2.65	11.75	2.44	11.60	2.27	
0.6	12.38	2.39	12.50	2.33	12.18	2.22	
0.1	-	-	-	-	14.0	-	
0.06	-	-	-	-	14.1	-	
	at 0.1M:		at 0.05M:		at 0.00493M:		
3.0	10.0	1.93	10.0	1.48	10.37	1.20	
1.5	10.67	1.64	-	-	10.46	0.70	
1.0	11.04	1.73	10.75	1.21	10.49	0.40	
0.8	11.28	1.8	-	-	-	-	
0.7	-	-	-	-	10.47	0.46	
0.5	-	-	-	-	10.53	0.35	
0.1	13.2	-	12.0	-	-	-	
0.06	13.2	-	12.1	-	-	-	

3.0	9.65	2.52	10.0	2.45	10.5	2.31	15°
1.5	10.95	2.68	10.93	2.52	11.19	2.25	
1.0	11.50	2.84	11.49	2.58	11.76	2.36	
0.8	12.07	2.87	11.89	2.63	12.18	2.24	
0.6	12.72	2.76	12.47	2.47	12.65	2.0	
3.0	10.0	2.76	10.6	2.66	-	-	1°
1.5	11.00	2.65	11.21	2.58	-	-	
1.0	11.64	2.79	11.76	2.73	-	-	
0.8	12.04	3.02	12.20	2.75	-	-	
0.6	12.62	3.01	12.74	2.79	-	-	

A1.15 Tetra-n-butylammonium Nitrate in 1,2-dichloroethane.

ocnc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''
3.0	9.7	2.76	9.95	2.24
1.5	10.80	2.72	10.84	2.16
1.0	11.55	2.68	11.46	2.25
0.8	12.05	2.66	11.87	2.20
0.6	12.56	2.3	12.21	1.9

A1.16. Tetra-n-butylammonium Perchlorate in 1,2-dichloroethane.

conc. (M)	0.4		0.2	
freq.(GHz)	ε'	ε"	ε'	ε"
3.0	9.7	2.60	10.1	2.29
1.5	10.71	2.69	10.83	2.16
1.0	11.58	2.66	11.40	2.19
0.8	11.96	2.52	11.82	2.11
0.6	12.51	2.30	12.17	1.92

A1.17 Tetra-n-butylammonium Iodide in 1,2-dichloroethane.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε"	ε'	ε"
3.0	9.7	2.51	10.1	2.16
1.5	10.58	2.68	10.67	2.14
1.0	11.37	2.68	11.26	2.13
0.8	11.83	2.67	11.66	2.12
0.6	12.42	2.5	11.97	2.0

A1.18. Tetra-n-butylammonium Tetraphenylboride in 1,2-dichloroethane.

conc.(M)	0.232	
freq.(GHz)	ε'	ε"
3.0	9.1	1.52
1.5	9.72	1.42
1.0	10.06	1.52
0.8	10.31	1.58
0.6	10.44	1.4
0.1	11.3	-
0.08	12.2	-
0.06	12.4	-

A1.19. Tetra-n-propylammonium Bromide and Iodide in 1,2-dichloroethane.

	Pr_4NBr				Pr_4NI	
conc. (M)	0.4		0.2		0.2	
freq. (GHz)	ε'	ε"	ε'	ε"	ε'	ε"
3.0	10.5	2.73	10.5	2.40	10.2	2.12
1.5	11.34	3.08	11.22	2.43	11.11	2.28
1.0	12.18	3.04	11.96	2.37	11.79	2.29
0.8	12.74	2.98	12.40	2.38	12.21	2.25
0.6	13.36	2.6	12.75	2.3	12.59	2.1

A1.20. Tetra-n-butylammonium Bromide in 1,1-dichloroethane.

conc. (M)	0.4		0.2	
freq. (GHz)	ε'	ε"	ε'	ε"
3.0	9.3	2.12	9.6	1.94
1.5	10.13	2.41	10.31	2.11
1.0	10.85	2.57	10.91	2.08
0.8	11.30	2.51	11.31	2.16
0.6	11.67	2.3	11.5	2.1

A1.21. Tetra-n-butylammonium Nitrate in 1,1-dichloroethane.

conc. (M)	0.4		0.2	
freq. (GHz)	ε'	ε"	ε'	ε"
3.0	9.45	2.25	9.85	2.00
1.5	10.50	2.39	10.54	2.08
1.0	11.25	2.37	11.16	1.97
0.8	11.77	2.30	11.49	2.1
0.6	12.05	2.1	11.75	1.9

A1.22. Tetra-n-butylammonium Bromide in Dichloromethane.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''
3.0	9.0	2.16	9.0	1.83
1.5	9.98	2.62	9.91	2.15
1.0	10.80	2.63	10.68	2.22
0.8	11.35	2.55	11.18	2.09
0.6	11.86	2.34	11.55	1.88

A1.23. Tetra-n-butylammonium Bromide in 1,1,2,2-tetrachloroethane.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''
3.0	5.6	2.06	6.2	2.41
1.5	6.47	1.90	7.01	1.98
1.0	6.86	1.83	7.43	1.~~19~~91
0.8	7.10	1.89	7.61	2.0
0.5	7.4	2.0	8.0	1.85

A1.24. Tetra-n-butylammonium Nitrate in Tetrahydrofuran.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''
3.0	7.77	1.35	7.70	1.03
1.5	8.28	1.47	8.09	1.08
1.0	8.70	1.56	8.38	1.25
0.7	9.07	1.43	8.76	1.1
0.5	9.50	1.37	8.98	1.25

A1.25. Tetra-n-butylammonium Bromide in 1,1,1-trichloroethane.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε''	ε'	ε''
3.0	7.05	1.08	7.35	0.88
1.5	7.35	1.09	7.49	0.88
1.0	7.62	1.14	7.67	0.90
0.7	7.95	1.1	7.87	0.94
0.5	8.29	1.1	8.03	0.98
0.25	9.0	1.2	8.4	1.08
0.1	9.6	1.1±.2	9.2	1.0±.2
0.06	9.6	1.1±.3	9.6	0.9±.3
0.03	10.2	0	10.2	0

A1.26. Tetra-n-butylammonium Bromide in Chlorobenzene.

conc.(M)	0.33	
freq.(GHz)	ε'	ε''
3.0	5.76	1.09
1.5	6.05	0.96
1.0	6.27	0.9
0.7	6.5	0.8
0.5	6.7	0.9
0.25	6.95	0.9
0.1	7.1	0.8±.2
0.06	7.1	0.7±.3
0.03	7.7	~~0.5±.6~~

A1.27. Tetra-n-butylammonium Bromide in Chloroform.

conc.(M)	0.4	
freq.(GHz)	ε	ε
3.0	5.00	1.29
1.5	5.57	1.55
1.0	6.01	1.73
0.8	6.31	1.76
0.5	6.9	1.59

conc.(M)	0.3		0.2		0.1	
3.0	5.06	1.16	4.98	1.32	4.99	0.92
1.5	5.48	1.50	5.36	1.38	5.32	1.24
1.0	5.95	1.62	5.79	1.52	5.66	1.45
0.7	6.42	1.59	6.24	1.47	6.11	1.3

A1.28. Tetra-n-butylammonium Nitrate in Chloroform.

conc.(M)	0.4		0.3	
freq.(GHz)	ε'	ε"	ε'	ε"
3.0	5.56	1.40	5.30	1.21
1.5	6.40	1.55	6.03	1.44
1.0	7.08	1.60	6.60	1.45
0.7	7.38	1.58	6.99	1.54
0.5	8.44	1.20	7.85	1.22
freq.(GHz)	0.2		0.1	
3.0	5.40	1.17	4.98	0.84
1.5	5.83	1.34	5.28	0.93
1.0	6.30	1.45	5.63	1.15
0.8	6.67	1.52	5.86	1.18

A1.29. Tetra-n-butylammonium Bromide in Trichloroethylene.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε"	ε'	ε"
3.0	3.90	0.54	3.65	0.34
1.5	4.02	0.62	3.75	0.41
1.0	4.3	0.67	3.85	0.40
0.7	4.6	0.62	3.95	0.48
0.5	4.8	0.6	4.0	0.6
0.35	4.9	0.7	4.14	0.43
0.1	5.0	0.8±.2	4.5	0.1±.2
0.06	5.2	-	4.6	-
0.03	5.3	-	-	-

A1.30. Tetra-n-butylammonium Bromide in Benzene.

conc.(M)	0.4		0.2	
freq.(GHz)	ε'	ε"	ε'	ε"
3.0	2.80	0.23	2.51	0.11
1.5	2.90	0.20	2.56	0.10
1.0	2.90	0.20	2.59	0.10
0.7	2.98	0.21	2.62	0.10
0.4	3.00	0.19	2.64	0.09
0.1	3.2	0.4	2.6	0.4
0.06	3.0	0.3	2.6	0.3
0.03	3.1	0.2	2.6	0.3
0.01	2.9	-	2.6	-
0.005	3.0	-	2.9	-

APPENDIX 2

Conductances κ of the electrolyte solutions investigated (at 25°C unless otherwise stated).

Solvent	Electrolyte	κ x 10^3 ohms^{-1} cms^{-1}			°C
		0.4M	0.3M	0.2M	
acetone	Bu_3NHI	2.41	2.01	1.48	
diethyl ketone	Bu_3NHI	0.740	-	0.571	
	Bu_4NBr	2.88	2.52	2.02	45
	Bu_4NBr	2.64	2.38	1.88	35
	Bu_4NBr	2.48	2.15	1.77	
	Bu_4NBr	1.19(0.1M)	0.81(0.05M)	0.287(0.01M)	
	Bu_4NBr	-	1.94	1.62	15
1,2-dichloroethane	Bu_3NHI	0.455	0.309	0.193	
	Bu_3NHPi	0.0766	0.0502	0.0233	
	Bu_4NBr	3.11	2.51	1.75	35
	Bu_4NBr	2.77	2.27	1.62	
	Bu_4NBr	0.8~~65~~52(0.1M)	0.453(0.05M)	0.074(0.0049M)	
	Bu_4NBr	2.45	2.03	1.51	15
	Bu_4NBr	2.06	1.68	-	1
	Bu_4NNO_3	3.27	-	1.88	
	Bu_4NClO_4	3.43	-	2.02	
	Bu_4NI	3.15	-	1.84	
	Bu_4NBPh_4	-	2.17(0.232M)	-	
	Pr_4NBr	3.21	-	1.80	
	Pr_4NI	-	-	1.94	

APPENDIX 2 (cont.)

1,1-dichloroethane	Bu_3NHI	0.642	-	0.304
	Bu_3NHPi	0.0843	-	0.0364
	Bu_4NBr	1.69	-	0.954
	Bu_4NNO_3	1.92	-	1.07
dichloromethane	Bu_3NHPi	0.144	-	0.0604
	Bu_4NBr	4.29	-	2.24
1,1,2,2-tetrachloroethane	Bu_4NBr	1.25	-	0.788
tetrahydrofuran	Bu_3NHPi	0.334	-	0.118
	Bu_4NNO_3	0.691	-	0.313
1,1,1-trichloroethane	Bu_3NHPi	0.0555	-	0.0177
	Bu_4NBr	0.194	-	0.130
chlorobenzene	Bu_4NBr	-	0.0232(0.33M)	-
chloroform	Bu_3NHI	0.307	-	0.0785
	Bu_3NHPi	0.0438	-	0.00955
	Bu_4NBr	1.42	1.06	0.620
	Bu_4NBr	-	-	0.450(0.1M)
	Bu_4NNO_3	1.36	0.995	0.577
	Bu_4NNO_3	-	-	0.205(0.1M)

APPENDIX 2 (cont.)

trichloroethylene	Bu_3NHPi	0.0315	-	0.00697
	Bu_4NBr	0.187	-	0.0793
benzene	Bu_4NBr	0.033	-	0.011

APPENDIX 3

Permittivity and Loss data of the Solvents employed.

All temperatures are 25°C., unless stated otherwise.

A.3.1. Diethyl Ketone.

Temp. °C.	15		25		35		45	
freq.(GHz)	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
3.0	17.4	2.11	16.6	1.68	15.9	1.51	15.2	1.38
2.0	17.3	1.43	16.6	1.24	15.8	1.08	15.1	0.93
1.5	17.51	1.12	16.72	1.00	16.05	0.87	15.3	0.71
1.0	17.56	0.75	16.73	0.66	15.95	0.57	15.15	0.48
0.7	17.58	0.54	16.72	0.50	15.99	0.47	15.20	0.37
0.5	17.56	0.41	16.73	0.33	16.04	0.30	15.16	0.29

A.3.2. 1,2-dichloroethane.

Temp. °C.	1		15		25		35	
freq. GHz	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
3.0	11.5	1.86	10.7	1.42	10.2	1.16	9.8	0.97
2.0	11.64	1.23	10.84	0.99	10.36	0.84	9.85	0.70
1.5	-	-	-	-	10.36	0.62	9.85	0.52
1.0	11.81	0.64	10.88	0.50	10.36	0.43	9.82	0.35

A.3.3. 1,1-dichloroethane

freq. GHz	ε'	ε''
3.0	10.0	0.84
2.0	9.97	0.57
1.0	9.98	0.29

A.3.4. Dichloromethane

3.0GHz	$\varepsilon' = 8.75$	$\varepsilon'' = 0.31$

A.3.5. 1,1,2,2-tetrachloroethane

freq. GHz	ε'	ε''
3.0	6.69	2.41
1.5	7.73	1.57
1.0	7.94	1.09
0.5	8.14	0.58

$\varepsilon'_0 = 8.20$, $\varepsilon'_\infty = 2.85$, $\tau = 33$psec.

A.3.6. Trichloroethylene.

freq. GHz	ε'	ε''
3.0	3.38	0.15
1.0	3.37	0.05

A.3.7. Data calculated by interpolation where necessary from data in the literature.

Acetone (31).

$\varepsilon'_o = 20.70$	3.0GHz $\varepsilon' = 20.6$ $\varepsilon'' = 1.06$

Tetrahydrofuran (96) (said to possibly contain 1% water).

$\varepsilon'_o = 8.04$	3.0GHz $\varepsilon' = 8.02$ $\varepsilon'' = 0.31$

1,1,1-trichloroethane (97).

$\varepsilon'_o = 7.04$	3.0GHz $\varepsilon' = 6.99$ $\varepsilon'' = 0.48$

Chlorobenzene (93).

$\varepsilon'_o = 5.63$	3.0GHz $\varepsilon' = 5.50$ $\varepsilon'' = 0.64$

Chloroform (98).

	3.0GHz $\varepsilon' = 4.8$ $\varepsilon'' = 0.36$

APPENDIX 4

SIZES OF IONS AND ION PAIRS

A4.1. Quasi Crystal Radii from Molecular Models.

a. From bond lengths and angles and from van der Waals radii.

Pauling obtained ionic radii from internuclear distances in crystals, by making assumptions about the relative sizes of isoelectronic anions and cations. Alternatively, ionic radii may be found from internuclear distances by the use of an electron density map to find the sizes of sodium and chloride ions (145). If the latter method is used, isoelectronic anions and cations are more nearly equal in size. For molecular ions, ionic radii can be estimated from bond lengths and the appropriate van der Waals atomic radii, and are given in table A4.1. However, the van der Waals radius of an oxygen atom possessing a fractional electronic charge seems uncertain, and hence the sizes of nitrate and perchlorate are necessarily uncertain. The volume of a disc-shaped model of the nitrate ion of radius 2.31 Å and thickness 2.2 Å is 24.8 $Å^3$, which is the same as that of a chloride ion on Pauling's scale (146).

Since the hydrocarbon chains in alkylammonium ions can have many configurations, it is consequently difficult to estimate the size of these ions. Radii obtained from Courtald models may be regarded as maximum values, since in actual molecules some contraction

Table A4.1. Estimated Crystal Radii (in Å) of some anions.

F	1.36 (Pauling)	1.16 ref. (145)
Cl	1.81 "	1.64 "
Br	1.95 "	1.80 "
I	2.16 "	2.05 "
NO_3	2.3-2.5 disc shaped, thickness 2.2-2.6.	
ClO_4	2.75-3.0 approximately spherical	
BPh_4	6.2 tetrahedral, contains tetrahedral 'holes'	
Pi	4.5-5.1 asymmetric disc shaped, thickness ∿ 3.7	

and mixing of orbitals might be expected. From an X-ray diffraction study of tetrapropylammonium bromide, the N-Br distance was found (147) to be 4.94 Å in the crystal.

b. Estimation of the minimum radii of quaternary ammonium ions from atomic contributions to molecular volumes.

Edward (148) has compiled atomic contributions to the van der Waals radii of molecules, by using molecular models. The volume V (in Å^3) actually occupied by the molecular ion can be found by summing the atomic volumes. Then its radius can be calculated, if the ion is regarded as spherical and as containing no "free" or "empty volume". The radii obtained in this way, should be minimum radii, and are listed in table A.4.2.

Table A4.2. Estimated van der Waals radii (in Å) of alkylammonium cations.

Ion	Minimum radius (A4.1b)	Maximum radius from ref.(123)	Robinson and Stokes' radius
Me_4N	2.8	3.2	3.47
Et_4N	3.3	4.3	4.00
Pr_4N	3.8	4.9	4.52
Bu_4N	4.1	5.5	4.94
Am_4N	4.4	5.9	5.29
Bu_3NH	Possibly similar to Pr_4N, van der Waals radius in N-H direction is 2.2.		

c. Robinson and Stokes' estimation of the sizes of quaternary ammonium cations (149).

Essentially, Robinson and Stokes found that the empirical expression:

$$r \approx 0.72\, \bar{v}^{\frac{1}{3}}$$

relates the ionic radii (in Å) found from atomic models of tetramethyl and tetraethylammonium ions to the molar volumes ($\bar{v}$) (in cm^3/mole) of the paraffins $C(Me)_4$ and $C(Et)_4$. Values of r for the higher members, found by means of this formula, assuming a value of 0.75 for their density, are given in table A4.2.

A.4.2. Quasi Crystal Radii of Quaternary Ammonium Ions from Partial Molal Volumes.

Conway et al (42) have determined the partial molal volumes of quaternary ammonium halides in aqueous solution at infinite dilution, and by an empirical extrapolation procedure have separated the ionic constituents ($\bar{v}_i$). Crystal radii (in Å), which contain the effects of "hydrophobic hydration", were obtained by correcting for the "dead space" surrounding the ions in aqueous solution by means of :

$$\bar{v}_i = 2.51\ r^3 + 3.15\ r^2.$$

Radii obtained from the above relation are given in table A4.3.

Molar volumes of alkylammonium electrolytes have also been measured by Gilkerson and Stewart (100) as well as in the present investigation. The electrolytes are considered to be in the forms of spherical ion pairs, and radii found on this basis are given in table A.4.4.

Table A.4.3. Cationic radii (in Å) in aqueous solution from ref.(42).

Me_4N	2.85
Et_4N	3.48
Pr_4N	3.98
Bu_4N	4.37

Table A4.4. Radii of ion pairs, assuming them to be spherical (calculated from the molar volumes given in table 4.3).

Pr_4NBr	4.47
Bu_3NHI	4.67
Bu_4NBr	4.92
Bu_4NClO_4	5.02
Bu_4NBPh_4	6.02

Table A4.5. Intercharge separations ('a') (in Å) reported by various authors.

Salt	Dipole moment used (D)	'a'		ref.
		from eqn 2	from eqns 3 & 4	
Bu_4NBr	12.2	4.44	4.69	21
	11.9	-	4.25	20
	11.6	4.4	-	19
Bu_4NI	12.7	4.56	4.86	21
Bu_4NClO_4	17.2	5.08	5.21	21
Bu_4NPi	15.3	5.39	5.94	21
	15.7	-	5.50	20
	15.1	5.0	-	19
Bu_4NBPh_4	17.3	-	6.70	20
Bu_3NHI	7.7	3.9	-	19
Bu_3NHPi	11.4	4.6	-	19

A.4.3. Intercharge Separations from Polar measurements.

a. Notes on table 1.2 (page 9).

All moments given in table 1.2 are "vapour phase" moments, except those of Richardson and Stern, and Gilkerson and Srivastava, which are solution moments obtained by means of the relation of Onsager and Böttcher (140). Richardson and Stern used a spherical cavity, and values of vapour phase moments calculated by the authors are given in parentheses. Gilkerson and Srivastava suggested the use of an ellipsoidal cavity with an axial ratio of two. In this latter case, the vapour phase moment is greater than the solution moment by about 5 to 10%.

b. Determination of Intercharge Separations.

The relationship:

$$\mu = e\,a \quad , \qquad \text{A.1}$$

where e is the electronic charge and 'a' the intercharge separation, is inapplicable owing to the mutual polarisation of the ions. This effect was allowed for by Davies and Williams (19) by means of:

$$\mu = e\,a - \frac{e}{a^2}(\alpha_1 + \alpha_2) - (\mu_1 + \mu_2) \quad , \qquad \text{A.2}$$

where α_1 and α_2 are the polarisabilities of the ions, and μ_1 and μ_2 are the dipole moments of the ions in the direction opposite to that of the resultant dipole. It seems possible that the treatment of Rittner (150), which Bauge and Smith (21) have extended to include the case of ions having permanent dipoles, is an improvement on equation A2., because it includes the mutual polarisation of each of the ions by the dipoles induced in each other. One then has:

$$\mu = e\ a - (\mu_1 + \mu_2) - (\mu_1' + \mu_2') \ , \qquad \text{A.3}$$

where the induced dipole moments are given by:

$$\mu_1' = \alpha_1/a^2\ \left[e + \frac{2}{a}\,(\mu_2 + \mu_2')\right] \ , \qquad \text{A.4}$$

with a similar expression for μ_2'.

Bauge and Smith have solved equations A3 and A4 graphically for 'a'.

In table A4.5, intercharge separations reported by Davies and Williams (19), Gilkerson and Srivastava (20) and Bauge and Smith (21) are compared. Gilkerson and Srivastava have used the treatment of Rittner, i.e. equations A3 and A4 with $\mu_1 = \mu_2 = 0$, and have also estimated the polarisabilities of ions in a way which differs from that of Davies and Williams and Bauge and Smith.

For salts of quaternary ammonium cations, values of 'a' are less than the sums of the appropriate ionic radii. In such cases, it seems reasonable to suppose that the anions penetrate, or distort cations, by "brushing aside" the paraffin chains.

A.4.4. Determination of Ion Size Parameters from Conductance Data.

According to Accascina and Fuoss (151) the conductance equation:

$$\Delta = \Delta_o - Sc^{\frac{1}{2}}\gamma^{\frac{1}{2}} + Ec\gamma\log.c\gamma + Jc\gamma - K_A c\gamma f^2\Delta \ ,$$

is valid provided that $\kappa'a'$ does not exceed 2, and also provided that triple and higher aggregation does not occur. For aqueous solutions of 1:1 electrolytes, this corresponds to a maximum concentration of 0.016 M., and for solutions in acetone to a maximum concentration of 0.004 M (151). Here, κ and the other symbols in the conductance equation, have their conventional (151) meaning. The conductance equation contains three constants: Δ_o, J and K_A, which in optimum cases, provide three independent methods of finding the intercharge distance 'a' of two ions in contact. Firstly, if K_A is finite, 'a' can be obtained from (151):

$$K_A = \frac{4\pi Na^3}{3000} e^{e^2/a\varepsilon kT} .$$

If K_A is known as a function of solvent permittivity, a plot of log. K_A against $1/\varepsilon$ can be used.

Secondly, J is a function of 'a', so that 'a' can be obtained from it. Thirdly, hydrodynamic radii $\underline{r}$ of ions, can be obtained from Stokes' formula:

$$r^{\pm} = \frac{0.8194\times 10^{-8}}{\lambda_o^{\pm}\,\eta} ,$$

in which case, it is necessary to know the limiting ionic conductances $\lambda_o^{\pm}$. For a given ion, $\underline{r}$ often increases in size with decreasing solvent permittivity, which may be due to the electrostatic drag experienced by an ion moving through a relaxing dielectric.

Fuoss (152) has used the equation:

$$r^{\pm} = r^{\pm}_{\varepsilon'_o = \infty} + s/\varepsilon'_o \quad ,$$

to allow for this, and (s) has subsequently been given a quantitative meaning (80). The value of $\left(r^{\pm}_{\varepsilon'_o = \infty}\right)$ can be found by extrapolating values found for $\underline{r}^{\pm}$ to infinite permittivity.

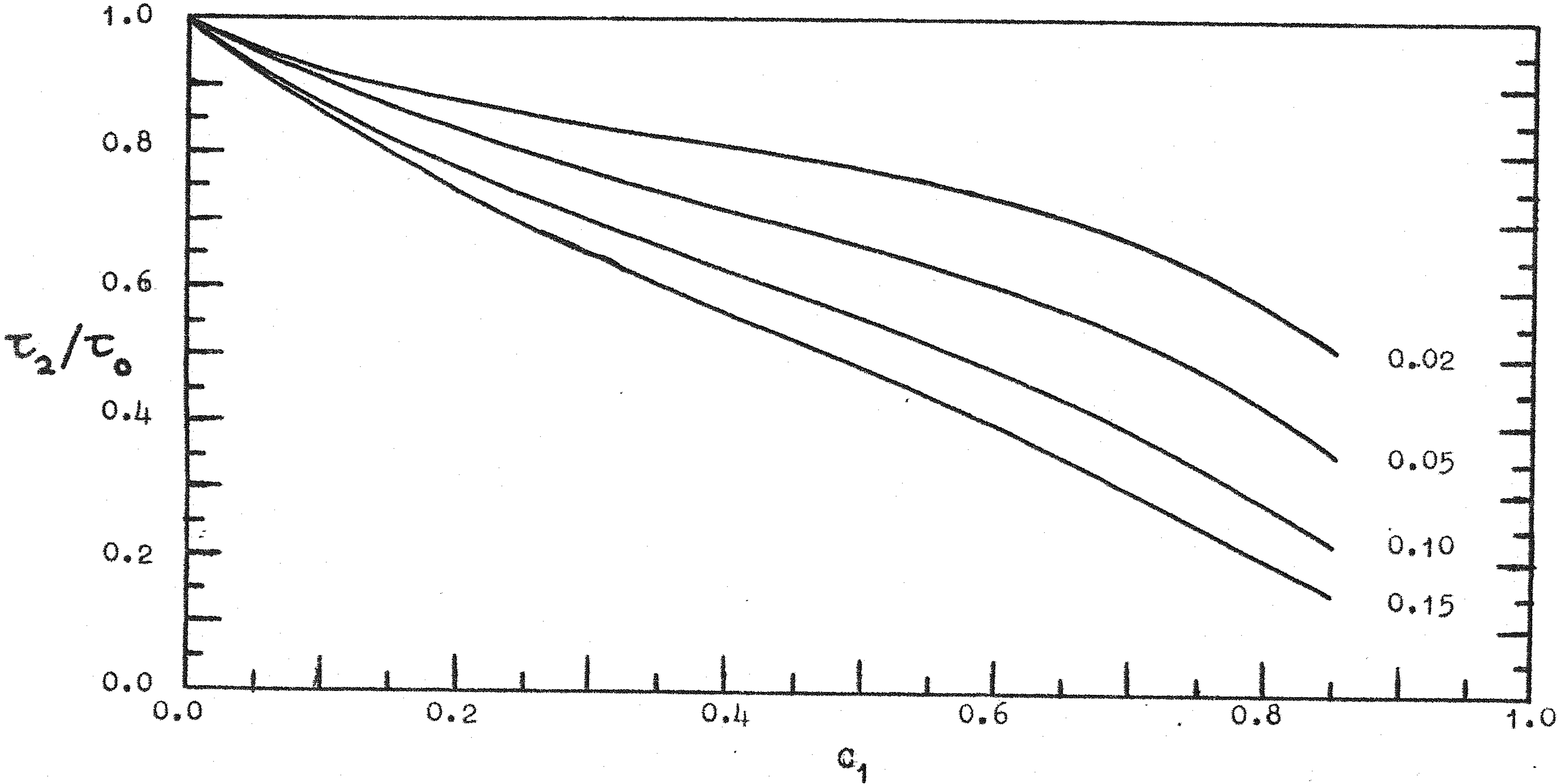
For solutions of tetrabutylammonium tetraphenylboride in mixed solvents investigated by Fuoss and Hirsch (153), values of 'a' derived from J or K_A agree approximately with those calculated from the corrected Stokes' law equation i.e. $\left(r^{+}_{\varepsilon'_o = \infty} + r^{-}_{\varepsilon'_o = \infty}\right)$. The authors reported a value for 'a' of 7.1 Å, which is in agreement with the value given in table A4.5.

However, according to Fuoss (154), for alkali halides in dioxane-water mixtures, 'a' from Stokes' law is too small in water rich mixtures, 'a' calculated from J increases with decreasing permittivity, and 'a' estimated from K_A is unreasonably large.

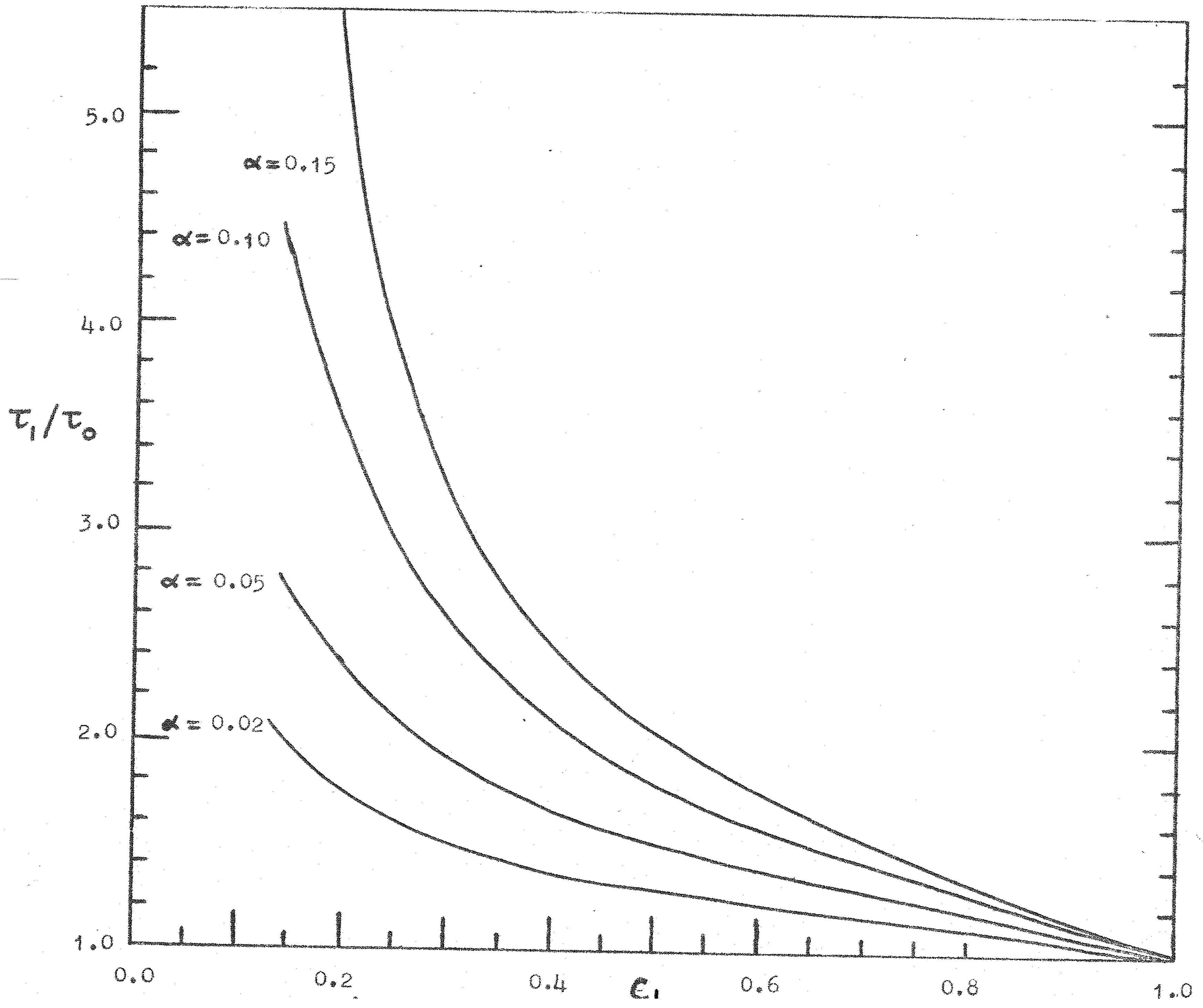
APPENDIX 5

```
'BEGIN'

'REAL' L,P,P10,AMP,C,W,W1,W2,W3,W4,W5,T1,T2,SC,MC,DC,STI,MT1,DT1,ST2,MT2,DT2,DEV;

'INTEGER' J;

'ARRAY' EP,EL[1:5];

SELECT INPUT (0);

P10: = READ; AMP: = READ;

SC: = READ; MC: = READ;DC: = READ;

ST1: = READ;MT1: = READ;DT1: = READ;

ST2: = READ;MT2: = READ;DT2: = READ;

W1: = READ;W2: = READ;W3: = READ;W4: = READ;W5: = READ;

WRITE TEXT ('('BQOIB#')');

'FOR' J: = 1,2,3,4,5'DO'

'BEGIN'

EP[J]: = READ;EL[J]: = READ;

'END';

'FOR'C: = SC,C+DC'WHILE'C<MC'DO'

'FOR'T1: = ST1,T1+DT1'WHILE'T1<MT1'DO'

'FOR'T2: = ST2,T2+DT2'WHILE'T2<MT2'DO'

'BEGIN'

DEV: = 0; J: = 0;

'FOR' W: = W1,W2,W3,W4,W5 'DO'

'BEGIN'

P: = P10+AMP*(C/(1+(W*T1)↑2)+(1-C)/(1+(W*T2)↑2));

L: = AMP*(C*W*T1/(1+(W*T1)↑2)+(1-C)*W*T2/(1+(W*T2)↑2));

J: = J+1;

'BEGIN'
```

```
DEV: = DEV+(EP[J]-P)↑2+(EL[J]-L)↑2;

'END';

NEWLINE(1);PRINT(T1,0,3);PRINT(T2,0,3);PRINT(C,1,2);PRINT(W,0,2);PRINT(P,2,2);

PRINT(L,2,2);

PRINT(DEV,0,4);

'END';

'END';

PAPER THROW;

'END';
```



APPENDIX 6. Graphs showing the relationship between values of τ_1, τ_2, C_1 in equation 2.28 and τ_0 and α in equation 2.25.


5.0
4.0
3.0
2.0
1.0
τ_1/τ_0
$\alpha = 0.15$
$\alpha = 0.10$
$\alpha = 0.05$
$\alpha = 0.02$
0.0
0.2
0.4
ϵ_1
0.6
0.8
1.0

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