A Dielectric Study of Benzene Solutions of Triisoamylammonium Picrate

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The dielectric constant and loss of triisoamylammonium picrate in benzene was measured over the dispersion region, 120 kc/s—8500 Mc/s. The dipole moment, relaxation times, and conductivities are calculated and discussed in terms of the overall state of the solute.

Particularly in non-hydroxylic media there is much of interest in the dielectric study of electrolyte solutions. Varied evidence shows that the major part of the solute is often present in a non-conducting association of ions, *i.e.*, ion-pairs, quadrupoles, *etc.* The great majority of such studies have been confined to the low-frequency range and correspond to determinations of the effective dipole moments and (sometime simultaneously) of the ionic conductances. Kraus and collaborators [1-3] extended measurements to the frequency range where dispersion of the dielectric polarization appears and these results have been summarized by Cole and Strobel.[4] In most of this earlier work the frequency did not exceed 70 Mc/s ($\lambda = 4$ metres) and so rarely, if ever, defined more than the initial phase of the dipolar absorption.

The present study was undertaken to provide a more adequate survey of the behaviour of a typical hydrocarbon salt solution. The frequencies available (120 kc/s — 8500 Mc/s) ensured an adequate display of the dielectric factors. Accordingly, over a range of concentrations there have been measured: (i) the ionic conductance of the solution; (ii) the mean dipole moment of the solute; (iii) the effective dielectric relaxation time; (iv) the distribution factor for this relaxation time which reflects the departure of the solute from the condition of a simple ion-pair; (v) the viscosity of the solution.

Two dielectric factors have been measured, the real dielectric constant (ε') and the absorption or loss factor (ε'') often expressed as tan $\delta = \varepsilon''/\varepsilon'$. Where absorption occurs the complex dielectric constant is:

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

Here ε_0' and ε_∞' are the low and high frequency limits of ε'; the angular frequency $\omega = 2\pi f$ (c/s); τ is an effective relaxation time and the extent by which n falls short of unity is a measure of deviation from a single relaxation time. Conducting media make two contributions to the total absorption,

$$\tan\delta \text{ (total)} = \tan\delta \text{ (ionic)} + \tan\delta \text{ (dielectric)}$$

$$= 1.13 \times 10^{13}\, \varkappa/\omega\varepsilon' + \frac{(\varepsilon_0' - \varepsilon_\infty')}{\varepsilon'} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2} \qquad (2)$$

In (2), $\varkappa$ = specific conductance (ohm^{-1} cm^{-1}) and it is assumed that $n = 1$. At frequencies not too near the critical value ($\omega_c\tau = 1$), $\tan\delta$ (dielectric) is simply proportional to ω, so that the two contributions are readily resolved by their different frequency dependence.

EXPERIMENTAL

Measurements have been made on triamylammonium picrate in benzene solution at $19 \pm 0.3°C$ over a wide frequency range using different methods.

From 120 kc/s to 9 Mc/s impedance measurements were made on a twin-T-bridge (Wayne Kerr, Mod. 66A) which provided direct readings of capacitance and resistance to an accuracy of 0.5 % for the capacitance and 0.5 % for small resistances. For higher resistances the uncertainty rapidly increased. The cell used was of rhodium flashed stainless steel having a quartz spacer and large electrode areas (Marconi Instrument Co.).

The bridge is intended for use up to 5 Mc/s. Calibration with noninductive resistors and capacitors shows that the capacitance readings became erroneous at about 4 Mc/s. The resistance measured was independent of frequency up to 15 Mc/s.

The system described by Williams [5] was used in the frequency region 250—900 Mc/s. Part of a coaxial transmission line was filled with solution and the node positions and widths were determined by a General Radio Co. standing wave indicator. The calculations followed the procedure described by Williams using the chart from Roberts and von Hippel [6,7] in evaluating the equations

$$\frac{\tanh\gamma_2 d}{\gamma_2 d} = \frac{(E_{min}/E_{max}) - j\tan\beta_1 x_0}{j\beta_1 d\,[1 - j(E_{min}/E_{max})\tan\beta_1 x_0]} = C \times \exp(j\xi)$$

$$\gamma_2 d = T \times \exp(jt)$$

$$\varepsilon' = \frac{T^2\sin^2 t}{(\beta_1 d)^2}(1 - \cot^2 t); \qquad \varepsilon'' = \frac{2T^2\sin^2 t}{(\beta_1 d)^2}\cot t$$

where $\beta_1 = 2\pi/\lambda_1$

γ_2 is the propagation constant of the liquid,

$\dfrac{E_{min}}{E_{max}}$ is the inverse standing-wave ratio;

d is the liquid depth;
x_0 is the distance of the first node from the liquid surface;
λ_1 is the wave length in the air portion of the line;
C, ξ are computed and then T and t are found from the charts.

In the frequency range 1000 Mc — 8500 Mc the v.h.f. dielectrometer (Model 3) from the Central Research Laboratories, Minnesota, was used for standing-wave measurements. The procedure followed was described above. The dielectric constants and losses given in the tables are generally mean values from measurements at two or three liquid depths.

Material. Triisoamylammonium picrate was prepared by mixing equimolecular amounts of triisoamylamine and picric acid in benzene solution. Recrystallised several times from benzene washed with petroleum ether, dried in a vacuum desiccator, it had m.p.corr $126.3 - 127.0°C$. Analar benzene (B.D.H.) was used without further purification.

RESULTS

The data on the Wayne—Kerr bridge provide a significant measure of the ionic conductance and of the low-frequency tan δ values. A typical set of values is shown in Table 1. Benzene was used as a standard in determining

Table 1. 0.1659 M solution of triisoamylammonium picrate in benzene.

Freq. Mc/s	Capacitance pF	Resistance ohm	1/RC 10^{-7}	Δ(dielectric)/f^2 10^6
0.12	279	4840	7.40	
0.20	279	4860	7.38	
0.40	279	4850	7.39	
0.80	279	4720	7.59	
1.20	278	4620	7.76	
1.80	279	4430	8.08	2.22
3.00	283	3790	9.29	2.11
4.00	286	3380	10.39	1.88
5.00		2902	11.72	1.74
6.5		2120	15.41	1.90
7.0		1942	16.56	1.89
9.0		1220	24.40	2.10

the effective cell capacitance. The dielectric constant of the solution investigated can be found after subtracting the dead-space capacity from the measured value. The constancy of the factor ($\varepsilon'' \times f$) at the lower frequencies (evaluated as 1/RC) provided a measure of the ionic conductance. The mean value of this factor at the three lowest frequencies could be regarded as entirely due to ionic conductance. This value, $\Delta_{(\text{ionic})}$, was substracted from the loss measured at higher frequencies, giving $\Delta_{(\text{dielectric})}$. For a simple relaxation process, $\Delta_{(\text{dielectric})}/f^2$ should be a constant in this frequency range. The mean value of Δ/f^2 equals $2\pi \tan\delta/f$.[4]

In this way the dielectric constants, ε', (Table 2), dielectric losses, ε'', (Table 3) and the equivalent ionic conductances, Λ (Table 4) are determined for a series of concentrations. The values of the ionic conductances are compared with those of Kraus.[3,8,9]

Table 2. Dielectric constants (ε').

Conc.	0.5394	0.2697	0.1659	0.0830	0.0498	0.0299	0.0179
Freq. Mc/s							
1	14.8	7.66	5.34	3.78	3.26	2.78	2.57
269	6.28	5.02		3.53		2.81	
524	4.47	3.79		3.21		2.63	
883	4.23	3.34	.	2.95		2.63	
1000		3.43		2.81		2.45	
3000		2.89		2.44		2.37	
8500		2.42		2.29			

Table 3. Dielectric losses (ε'').

Conc. 0.5394		0.2697	0.1659	0.0830	0.0498	0.0299	0.0179
Freq.							
Mc/s							
10	1.92	0.443	0.155	0.056	0.024	0.013	0.009
269	5.76	2.58		0.627		0.184	
524	3.57	2.09		0.772		0.250	
883	2.36	1.66		0.625		0.250	
1000		1.40		0.557		0.223	
3000		0.741		0.252		0.108	
8500		0.258		0.108			

Table 4. Conductances ohm^{-1} cm^{-1} mole^{-1}.

Conc.	Found (19°C)	Kraus and Fouss (25°C)
0.5394	2.57×10^{-2}	2.95×10^{-2}
0.2697	7.16×10^{-3}	8.30×10^{-3}
0.1659	2.11×10^{-3}	1.70×10^{-3}
0.0830	2.68×10^{-4}	3.85×10^{-4}
0.0498	5.06×10^{-5}	5.66×10^{-5}
0.0299		1.40×10^{-5}
0.0179		4.50×10^{-6}

Table 5. Viscosities of triamylammonium picrate in benzene at 20.0°C.

Conc. mole/l	d g/cm^3	t_{mean} sec	viscosity cP	lit. cP	$10^{12}\,\tau_0$ calc.
0.5394	0.931	33.1	1.32		760
0.2697	0.903	22.2	0.86		500
0.0299	0.879	17.5	0.66		380
Benzene	0.877	17.2		0.647	
CCl$_4$	1.596	15.5	1.03	1.01	

Viscosities were measured in an Ostwald viscometer at 20.0°C in a thermo-stat. The viscometer was calibrated with benzene and carbon tetrachloride. Densities were plotted from the work of Strong and Kraus [3] and values for actual concentrations were interpolated. The results are shown in Table 5.

DISCUSSION

The results are summarized in Tables 1—6.

(i) *The dipole moment.* A plot of the low frequency dielectric constant against molarity is given in Fig. 1. The linearity of the plot for the lower concentration gives an effective dipole moment (following Guggenheim [10]) of 12.1 ± 0.2 D compared with Copenhafer's value of 13.3 D. This is a value typical of such an ion-pair in this medium, *cf. inter alia* Davies and Williams [11] who report

11.5—15.1 D for other tri- and tetra-alkyl ammonium salts. If one envisages localized ionic charges (e = electronic charge) at a separation r_i in the triisoamyl ammonium picrate, they will contribute to the dipole moment:

$$\mu_i = er_i \left(1 - \alpha_{eff}/r_i^3\right)$$

where a_{eff} is the effective polarizability of the ion pair.

$\mu_{obs} = 12.1 = (\mu_i - 1.5)$ where 1.5 D is the net estimated contribution to the total moment from the (C—N), (N—H), and (C—O) bonds. In this way [11], $r_i \simeq 4.7$ Å.

An atomic model (Courtauld's) allows the N and O atoms, presumably carrying the charges in this ammonium picrate, to approach to 3.7 Å. The larger value deduced from μ_{obs} could result from at least partial delocalization of the charges — more particularly in the picrate ion.

In Fig. 1, the straight line does not include the points at the two highest concentrations. Thus a more adequate functional representation is:

$$\varepsilon_0' \text{ (solution)} = \alpha_0 + \beta_0 c + \gamma_0 c^2$$

At least two interpretations of the non-linearity can be offered. The linear Debye—Guggenheim relation is one limited to dilute solutions and it is a measure of the simplicity of the present solute that departures from it are not appreciable below 0.2 M. (90 g solute per litre). In addition to deviations from ideal dilute solutions, the $(\gamma_0 c^2)$ term could arise from aggregation of the ion pairs to quadrupoles. If simple electrostatic factors governed such interaction, it would be expected that a reduction in the mean effective moment would occur. The positive value of the $(\gamma_0 c^2)$ term means that if quadrupole formation is responsible for it, then this must be of a geometrical form leading to an increased moment, e.g., head-to-tail association.
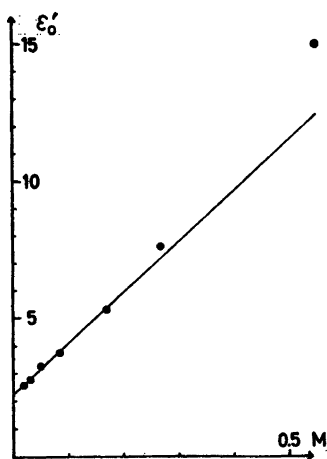

Fig. 1. Plot of ε_0' against molarity for triisoamylammonium picrate in benzene solution at 19°C.
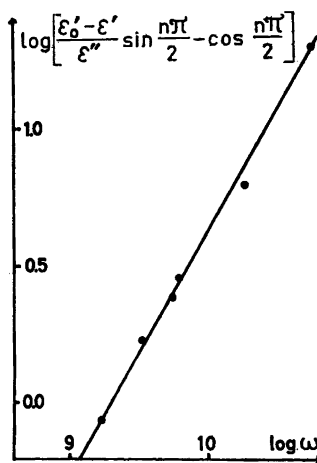
Fig. 2. Evaluation of the distribution factor n for 0.2697 M solution of triisoamylammonium picrate in benzene.

(ii) *The relaxation time.* A variety of methods can be used to evaluate the relaxation time. As Table 3 shows, the data cover the critical frequency region, so a careful assessment can be made. For the two lowest concentrations (0.0299 M and 0.0830 M) the data conform to a single relaxation time whose value can be deduced, *e.g.* from one of the various plots proposed by Cole.[12] For the higher concentrations a number of criteria, including the circular arc plot[13] indicated that a single relaxation time did not provide a precise representation. Accordingly, Williams's procedure, based on the relation

$$(\omega\tau)^n = \left[\left(\frac{\varepsilon_0{}' - \varepsilon'}{\varepsilon''}\right)\sin\frac{n\pi}{2} - \cos\frac{n\pi}{2}\right] \tag{3}$$

was used. This involves a log-plot (Fig. 2) in which the value of n, the distribution factor, is varied in the r.h.s. of eqn. (3) so as to provide a linear plot. In this way the values of Table 6 are obtained. The values of $n = 1.00$ and the constancy of (τ/η) again conform to a simple state of the solute up to 0.1

Table 6. Measured relaxation times.

Conc.	0.0299	0.0830	0.2697	0.5394
$\tau \times 10^{12}$	230[a]	243	503	888
n	1.00	1.00	0.90	0.95
η	0.66	(0.69)	0.86	1.32
$10^{12}\tau/\eta$	350	350	585	672

a. For the smallest concentrations the uncertainty is considerable because the $\varepsilon_0{}'$ and the ε' are of the same magnitude.

M. At higher concentrations the same criteria agree in showing an increasing complexity of the solute. The increase in the (τ/η) value which in the Debye approximation, is proportional to the molecular volume of the dipole particle, suggests that at 0.5 M the mean volume of the solute aggregates approaches twice that in dilute solutions. The slope of the plot in Fig. 1 at this concentration also indicates a mean effective moment about twice that in dilute solutions: the equality of these two factors is of no physical significance beyond their qualitative confirmation of aggregation.

The relaxation time may be estimated from the relation

$$\tau_0 = 4\pi\, abc\eta/kT \tag{4}$$

The molecular dimensions are taken from Catalin molecular models; $a = 7.5$, $b = 5.5$ and $c = 4.5$ Å. The calculated relaxation times and the measured viscosities may be found in Table 5. The measured relaxation times in Table 6 vary over a greater range than the calculated relaxation time. The simple model used in the calculations obviously cannot account for the complex behaviour of the molecules. In the calculations the macroscopic viscosity was used. A 'molecular' viscosity can be deduced to provide agreement between

τ(obs) and the molecular volume, $4\pi abc$, which would be $243/380 = 0.64$ times the macroscopic value.

The acceptance of η(molecular) $= 0.64 \times \eta$(macroscopic) would thus provide quantitative agreement between τ(obs) and τ_0(calc.) from the Debye-Perrin equation, eqn. (4). The factor 0.64 is larger than that (0.36) found by Fischer[14] for small polar molecules in benzene. The reason for this is made explicit by Hase[15] who has shown that the ratio η(molecular)/η(macroscopic) is a function of the relative molecular volumes for the solute and solvent. When the former is very much the larger, the molecule approaches a macroscopic particle (i.e. Stokes's condition) and the ratio is close to 1.0. For small solute molecules appreciable rotation can occur without much displacement of the solvent molecules whose effective viscosity is much reduced. The triisoamyl ammonium picrate ion-pair is clearly much larger than Fischer's molecules (nitrobenzene, etc.). This accounts for the factor being as large as 0.64.

When conclusions are drawn from measurements of relaxation times it should be borne in mind that the question of the correct expression for the internal field is of considerable importance. The suggestion arises that the variations in τ may be a function of the changing permittivity of the solutions. Davies and Williams[11] calculated reduced relaxation times, τ^*, defined as

$$\tau^* = \tau \varepsilon'(\text{solvent})/\varepsilon'(\text{solution})$$

Table 7 shows that the empirical τ^* is independent of concentration. The deviation of the τ^* for the lowest concentration may be insignificant because of the uncertainty in the relaxation time. The correlation between τ and ε' must, however, be regarded as a purely empirical one.

Table 7. Reduced relaxation times.

Conc.	$\tau_0 \times 10^{13}$	$\tau^* \times 10^{12}$
0.5394	888	137
0.2697	503	150
0.0830	243	147
0.0299	230	189

(iii) *Conductivities.* The equivalent conductances measured at 19°C are compared in Table 4 with those interpolated from Fuoss and Kraus[16] and the data of Strong and Kraus[3] (at 25°) are included for comparison in Fig. 3. Kraus has emphasized the great increase in conductivity between the minimum value $\lambda = 2.7 \times 10^{-4}$ at 10^{-3} M and a maximum value $= 4.8 \times 10^{-2}$ at 1.08 M; over our concentration range of 0.05 M to 0.5 M it increases at thousand-fold, and the log-plot shows that an approximate representation from 0.05 M to 0.25 M is:

$$\lambda c = 0.355\, c^{3.97}$$

This form of conductance equation is relevant in terms of Rutgers and de Smet's model. They have shown[18] that for a salt consisting of ionpairs (AB), and other
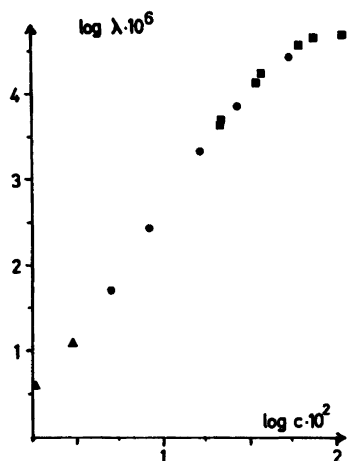
Fig. 3. Plot of log (equivalent conductance) against log (concentration) for triisoamyl ammoniumpicrate in benzene solution at 19°C over the higher concentration range. Data of: ▲ Kraus and Fuoss, ■ Strong and Kraus, ● Davies and Johansson.

aggregates $(AB)_m$, $(AB)_n$, *etc.* each species dissociating only slightly into free ions,

$$\lambda c = A_1 c^{1/2} + A_m c^{m/2} + A_n c^{n/2} + \dots \tag{5}$$

Thus, more detailed calculation[11] shows that the extensive conductivity data for triisoamylammonium picrate up to 0.1 M at 25° are adequately fitted by the expression:

$$\lambda c = 5.0 \times 10^{-9} c^{1/2} + 4.0 \times 10^{-6} c^{1/2} + 1.08 \times 10^{-2} c^{1/2} + 25\, c^{11/2}$$

This representation serves to emphasize the complexity of the ionization equilibria in a solution where the overwhelming proportion of the solute is present as a simple ion-pair. The absence of any demonstrable correlation between the conductivities and the over-all state of the solute results from the fact that a fraction of only about 10^{-4} is in the form of ions: this follows from the equivalent conductances observed and the sums of the expected ionic mobilities, which is of the order of 100.

The fraction ionized is clearly highest at the higher concentrations. The reason for this condition, which is very different from that in hydroxylic or high dielectric solvents is as follows: the small amounts of complex ion-aggregates, $(A^+B^-)_n$, formed at the highest concentrations, dissociate to ions such as $(A_m B_{m-1})^+$ and $(A_p B_{p+1})^-$ where $(m + p) = n$, far more readily than the simple ion-pair $(AB)_1$ dissociates. Alternatively expressed, the B^- ion has far greater stability in the very low permittivity solvent benzene when it is solvated by p (A^+B^-) ion pairs.

CONCLUSIONS

It is well known from the measurements of conductivity [3,16] that solutions of triisoamylammonium picrate are complex, with a conductance minimum at 3×10^{-2} molar and a conductance maximum at 1.08 molar. These dielectric

measurements show that the solute exhibits a slight distribution of relaxation times in the dispersion region. In the low frequency part of the dispersion region, measurements suggest a subsidiary relaxation process which is more marked at the two highest concentrations. Such a behaviour might be explained by the role of a small concentration of larger aggregates than the simple ion-pair which is the piincipal form of the solute. More data are necessary, however, to assess quantitatively the proportions of the various molecular species. As has been emphasized by other studies (*e.g.* Ref.[11]) the equivalent conductance is a very poor criterion for studying the solute complexity in such solutions. The dielectric data (and the conductivities) show that in the present instance nearly all the solute is probably present as undissociated ion-pairs.

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