Dielectric Behavior of Solutions of Electrolytes in Solvents of Low Dielectric Constant. II. Dielectric Absorption

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second column, corresponds to 25.000°C; V = peak voltage of the field; t = time in sec. for $\Delta h = 3$ mm or 10 mm rise, as indicated; κ_0 = audiofrequency conductance = 5.30×10^{-8} ohm^{-1} cm^{-1}; density = 0.8825 g cm^{-3}; viscosity = 0.00657 poise; dielectric constant (1000 cycles) = 3.60; and index of refraction = 1.5000.

According to Eq. (5), the values of the dipole conductivity and loss factor at 21.1 Mc would be

$$\kappa_\omega = V_0{}^2 t_0 \kappa_0 / V_\omega{}^2 t_\omega = (5.17)(5.30 \times 10^{-8})/0.329$$
$$= 83.4 \times 10^{-8}\ \text{ohm}^{-1}\ \text{cm}^{-1},$$

$$\Delta\kappa' = \kappa_\omega - \kappa_0 - \kappa_{\text{glass}} = (83.4 - 5.30 - 0.3) \times 10^{-8}$$
$$= 78.0 \times 10^{-8}\ \text{ohm}^{-1}\ \text{cm}^{-1},$$

$$\Delta\epsilon'' = \Delta\kappa'(1.80 \times 10^{12})/\nu$$
$$= (78.0 \times 10^{-8})(1.80 \times 10^{12})/21.1 \times 10^6$$
$$= 6.65 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^{-1}/\text{cycle}.$$

Plots of the dipole conductivity *vs.* voltage and frequency for this solution are shown in Figs. 6 and 7. In Fig. 7, the experimental values are represented by the plotted points while the course of the solid curves is determined by calculation based on the Debye theory.

Dielectric Behavior of Solutions of Electrolytes in Solvents of Low Dielectric Constant. II. Dielectric Absorption[1]

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The dielectric losses in solutions of salts in several low dielectric constant solvents are studied as a function of frequency and concentration, using the calorimetric method. The results are interpreted according to the Debye theory, and critical frequencies, molecular radii, and dipole moments are evaluated wherever feasible. Solutions of tri-*iso*amylammonium picrate in benzene and diphenylmethane behave as a monodisperse system having a single well-defined polar structure relatively independent of concentration. Corresponding solutions of tetra-*n*-butylammonium thiocyanate, in contrast, show a marked departure from theoretical behavior for a monodisperse system, having a broad distribution of relaxation times and a high degree of association strongly dependent on concentration. Di-*n*-butyldioctadecylammonium thiocyanate shows monodisperse behavior at low concentrations, with more physically and electrically different polar bodies appearing as the concentration is increased. These results are in good agreement with polarization, conductance, and cryoscopic measurements for these systems.

T HE experimental approach for measuring the dipole or "absorption conductivity" of solutions of electrolytes described in Part I of this series has been used for the study of solutions of tri-*iso*amylammonium picrate, tetra-*n*-butylammonium thiocyanate, di-*n*-butyldioctadecylammonium thiocyanate, di-*n*-butyldioctadecylammonium octadecylsulfate, tetra-*n*-butylammonium bromide, and *n*-butyl alcohol. Benzene and diphenylmethane were selected as solvents

because their dielectric constants are sufficiently low to cause marked ion association and the difference in their viscosities also provides a check against theory. These results are interpreted on the basis of the Debye theory of polar molecules.[3]

EXPERIMENTAL

Commercial, thiophene-free benzene was purified by stirring with successive portions of concentrated sulfuric acid until the acid was no longer colored. The acid was removed by stirring with dilute sodium hydroxide solution, followed

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[1] This paper is based on a portion of a thesis submitted by A. H. Sharbaugh, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Brown University, June, 1943.

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[3] P. Debye, *Polar Molecules* (Chemical Catalog Company, New York, 1929).

by water. After drying over calcium chloride for several days, the benzene was placed in a still and refluxed over sodium-lead alloy for several more days. All solutions were made up from freshly distilled solvent. The specific conductance varied between 10^{-13}–10^{-14} ohm^{-1} cm^{-1}.

Eastman diphenylmethane was distilled, fractionally crystallized two to three times and dried over calcium chloride. M.P., 25°–26°C. Specific conductance, 4×10^{-13} ohm^{-1} cm^{-1}.

Commercial n-butyl alcohol was washed with sodium acid sulfite, boiled with strong sodium hydroxide solution, washed with water, and dried over ignited calcium oxide. It was distilled from fresh calcium oxide, the middle fraction being collected. Immediately before using, this product was refluxed several hours over activated alumina and distilled from it. B.P., 116.8°C. Specific conductance, 5.56×10^{-8} ohm^{-1} cm^{-1}.

Tri-isoamylammonium picrate was prepared by mixing equimolar quantities of tri-isoamylamine and picric acid in hot ethyl alcohol solution. It was purified by recrystallization from ethylene dichloride and petroleum ether. M.P., 126.5°–127.2°C (corrected).

Tetra-n-butylammonium thiocyanate was prepared by the method described by Kraus and Fuoss.[4] This salt was hygroscopic and all solutions were, accordingly, made from freshly vacuum-dried material. M.P., 125.5°–126.5°C (corrected).

Di-n-butyldioctadecylammonium thiocyanate was prepared by Dr. L. E. Strong, of this laboratory.[5] M.P., 84°–85°C (corrected).

Di-n-butyldioctadecylammonium octadecylsulfate was prepared by Dr. W. E. Thompson, of this Laboratory.[6] M.P., 92°–93°C (corrected).

The absorption conductivities were determined with the calorimetric dielectric absorption apparatus as described in Part I of this series.[7]

Audiofrequency measurements of conductance and dielectric constant were made by the substitution method on a special bridge built around the Campbell-Shackleton shielded ratio box for this laboratory by Leeds and Northrup.[5] With this bridge and the available conductance cells,

specific conductances of the order of 10^{-13} ohm could be measured to one or two significant figures. The conductance cells were cleaned with fuming nitric acid, steamed, and baked in an oven at 140°C overnight. They were allowed to cool while a current of dry air was blown through them. In all cases, the conductance cell was placed in an air-bath and allowed to come to equilibrium before measuring. The dielectric constant and conductance measurements were made simultaneously since this bridge contained a three-terminal, quartz-insulated condenser which covered the range from 35–170 $\mu\mu$f. The condenser was calibrated and was linear to better than 0.1 $\mu\mu$f. The dielectric constant of benzene was taken to be 2.276 at 25°C[8] and the cells were calibrated against dry air and constants checked by filling with pure ether. In Table I, are listed the constants for the conductance cells where C_0 is the inherent capacity owing to leads and other strays and C is the capacity of the cell after this correction, C_0, is applied.

Viscosity measurements were made with an Ostwald viscometer which was equipped with stopcocks to prevent evaporation. The viscometer was placed in a battery jar of constant temperature water which was lagged with thermal insulating material. A synchronous motor timer was used to measure time and all the measurements were made relative to benzene.

Refractive index measurements were made with a thermostatically controlled Pulfrich refractometer.

Density measurements were accomplished by means of a Westphal balance.

THEORY

Several mathematical theories have been advanced to account for the variation of dielectric properties with the frequency of an applied

[4] Kraus and Fuoss, J. Am. Chem. Soc. **55**, 21 (1933).
[5] L. E. Strong, Thesis, Brown University (1940).
[6] W. E. Thompson, Thesis, Brown University (1941).
[7] Sharbaugh, Schmelzer, Eckstrom, and Kraus, J. Chem. Phys. **15**, 47 (1947).

TABLE I. Characteristics of conductance cells used in bridge measurements.

	Cell constant	$C(\mu\mu f)$	$C_0(\mu\mu f)$
Cell S No. 1	0.002888	30.75	2.38
Cell S No. 2	0.003048	29.47	0.82
Cell B No. 4	0.01724	5.15	0.79

[8] Smyth, *Dielectric Constant and Molecular Structure* (Chemical Catalog Company, New York, 1931).

alternating voltage. Although such theories may present different physical pictures for the mechanism of the absorption, they all postulate some form of an exponential relaxation function relating the decrease of absorption current with time. Therefore, certain relaxation frequencies where the dielectric loss per cycle reaches a maximum are predicted.

Following Debye,[3] the generalized dielectric constant ϵ may be expressed as the sum of a real and an imaginary part

$$\epsilon = \epsilon' - j\epsilon'', \tag{1}$$

where

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + x^2} \tag{2}$$

and

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)x}{1 + x^2}, \tag{3}$$

$x = \omega\tau(\epsilon_0 + 2)/(\epsilon_\infty + 2)$, ϵ_0 is the audiofrequency value of the dielectric constant, ϵ_∞ is the corresponding value at optical frequencies, $\omega = 2\pi\nu$, where ν is the frequency in cycles per second. Assuming Stokes' hydrodynamics, the relaxation time for the molecules is called τ and for a spherical molecule

$$\tau = 4\pi\eta a^3/kT, \tag{4}$$

where η is the viscosity of the solvent, a is the molecular radius, k is the Boltzmann constant, and T is the absolute temperature.

In order to obtain a relationship between ϵ' and ϵ'' and physically measurable quantities, we may define the complex dielectric constant ϵ of a medium in a condenser as the ratio of the admittance of the filled condenser Y to the admittance of the empty condenser Y_0.[9] It is further assumed that the filled cell may be represented by the equivalent circuit of Fig. 1; where C_0 and C_1 represent the vacuum and solution-filled capacities, respectively, G_0 is the d.c. ionic conductivity, and ΔG is the absorption conductivity. Therefore,

$$\epsilon = \epsilon' - j\epsilon'' = Y/Y_0 = (G_0 + \Delta G + j\omega C_1)/j\omega C_0$$

and, hence,

$$\epsilon' = C_1/C_0 \tag{5}$$
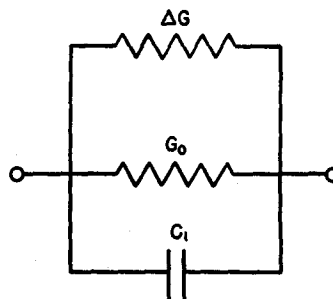
[9] Hubert H. Race, Phys. Rev. **37**, 430 (1931).

Fig. 1.

and

$$\epsilon'' = (\kappa_0 + \Delta\kappa)1.80 \times 10^{12}/\nu = \kappa_\omega 1.80 \times 10^{12}/\nu,$$

where κ_ω, by definition, the specific conductance of a solution at a frequency ω, equals $(G_0 + \Delta G)/9 \times 10^{11} \times 4\pi C_0$. Then, also by definition,

$$\Delta\epsilon'' = \epsilon'' - 1.80 \times 10^{12}\kappa_0/\nu = 1.80 \times 10^{12}\Delta\kappa/\nu. \tag{6}$$

$\Delta\kappa$ is in ohm^{-1} cm^{-1} and ν in cycles sec.$^{-1}$. Therefore, assuming that there is no ionic a.c. loss,[10] $\Delta\kappa$ represents the conductance owing to pure a.c. response and will be called the absorption conductivity. The quantity $\Delta\epsilon''$ is called the loss factor and gives a measure of the energy absorption per cycle. From Eq. (5), it is seen that the real part of the generalized dielectric constant, ϵ', is the quantity commonly known as dielectric constant.

By equating the derivative of Eq. (3) to zero, it may be seen that ϵ'' (which is identical to $\Delta\epsilon''$ of Eq. (6) since Eq. (3) was derived on the basis that $G_0 = 0$) reaches a maximum value when

$$\omega\tau = (\epsilon_\infty + 2)/(\epsilon_0 + 2). \tag{7}$$

Under this condition, then

$$\nu_c = (\epsilon_\infty + 2)/2\pi\tau(\epsilon_0 + 2), \tag{8}$$

where ν_c is called the critical frequency. In terms of ν_c, then Eqs. (2), (3), and (6) become

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \nu^2/\nu_c^2}, \tag{9}$$

$$\Delta\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\nu/\nu_c}{1 + \nu^2/\nu_c^2}, \tag{10}$$

[10] Mead and Fuoss, J. Am. Chem. Soc. **67**, 1566 (1945).

and

$$\Delta\kappa = \frac{(\epsilon_0 - \epsilon_\infty)\nu^2/\nu_c}{(1 + \nu^2/\nu_c^2)1.80 \times 10^{12}}. \qquad (11)$$

From the classical Debye theory, ν_c, as defined above, becomes

$$\nu_c = [kT/8\pi^2\eta a^3][(\epsilon_\infty + 2)/(\epsilon_0 + 2)],$$

and when $\nu^2 \ll \nu_c^2$, Eq. (11) reduces to

$$\Delta\kappa = (\epsilon_0 - \epsilon_\infty)\nu^2/1.80 \times 10^{12}\nu_c. \qquad (12)$$

If a correction for heating of the glass of the cell is applied to $\Delta\kappa$, the corrected quantity will be denoted by $\Delta\kappa'$. These equations will be found useful in interpreting the experimental data.

In a previous paper,[7] it has been shown that the conductance at an angular frequency ω is obtained by measuring the rate of rise $\Delta h/t$ cm sec.$^{-1}$ of the level of the solution in the thermometer cell when a r.m.s. voltage $V_{\text{R.M.S.}}$ is applied to the electrodes of the cell. The relationship thus obtained is as follows:

$$\kappa_\omega = \left\{ \left(\frac{\pi r^2}{0.239}\right)\left(\frac{dc}{\alpha}\right)(z) \right\} \frac{\Delta h}{V_{\text{R.M.S.}}^2 t}, \qquad (13)$$

where $r =$ capillary radius (cm), $z =$ cell constant (cm^{-1}), $d =$ density of solution (g cm^{-3}), $c =$ heat capacity of the solution (cal. g^{-1} degree^{-1}), and $\alpha =$ coefficient of expansion of the solution (degree^{-1}). It was further shown that

$$\kappa_\omega = V_0^2 t_0 \kappa_0 / V_\omega^2 t_\omega \qquad (13a)$$

if the low and high frequency observations are made each time for the same solution in the same cell and for equal temperature rises. When the proportionality constant in Eq. (13) between κ_ω and $\Delta h/V_{\text{R.M.S.}}^2 t$ is evaluated by low frequency data, a value for benzene solutions of $\alpha/dc = 0.00300$ is obtained. This value of α/dc is used in the calculation of κ_ω for those solutions where the correction owing to the conductance of the glass is large in comparison with that for the solution, unless, in using Eq. (13a), the conductance of the glass cell does not dominate the conductance of the solution itself.

In most cases, however, the proportionality constant between κ_ω and $\Delta h/V_{\text{R.M.S.}}^2 t$ was determined for each individual solution by a determination of $\Delta h/V_{\text{R.M.S.}}^2 t$ at 60 cycles or 0.1 Mc

where the conductance was assumed to be that measured at audiofrequencies. Generally, $\Delta h/V_{\text{R.M.S.}}^2 t$ was obtained from the slope of the straight line plot of $(\Delta h/t)^{\frac{1}{2}}$ vs. V. In some cases, it was found that, because of small errors in the voltage measurement, the intercept did not always pass exactly through the origin. Within the limits of experimental error, a straight line plot, indicating no variation of conductance with field strength, was always obtained. All values of absorption conductivity have been corrected for heating of the glass in the cell. These corrections were negligibly small except in the case of the very dilute solutions.

We have calculated the values of the dipole moment by using the following equation, derived by Debye,[11] for dilute solutions (where the loss is proportional to the mole fraction of the solute), where $\omega^2\tau^2 \ll 1$ and $\epsilon'' \ll \epsilon'$:

$$\mu = \{w[3/(\epsilon_0 + 2)]^2[2M_1/\omega^2 d_1] \\ \times [3kT/N\tau][1/N_2 E^2]\}^{\frac{1}{3}}. \qquad (14)$$

Here, $\mu =$ dipole moment (e.s.u.), $w =$ heat generated (ergs cc^{-1} sec.$^{-1}$), $\epsilon_0 =$ static dielectric constant of solvent at low frequencies (e.s.u.), $M_1 =$ molecular weight of solvent, $\omega =$ angular frequency (ra. sec.$^{-1}$), $d_1 =$ density of solvent (g cm^{-3}), $k = 1.37 \times 10^{-16}$ (ergs degree^{-1}), $T =$ absolute temperature, $N_2 =$ mole fraction of solute, $N = 6.06 \times 10^{23}$, $\tau =$ relaxation time (sec.) and $E =$ field strength (peak statvolts cm^{-1}). From considerations of the thermometer cell, it is seen that

$$w = 4.18 \times 10^7 d_1 c \pi r^2 \Delta h / \alpha t A x, \qquad (15)$$

where A, the effective area of the cell electrodes, is calculable from the cell constant, and where x is the separation of the electrodes. When w is expressed in terms of the loss factor $\Delta\epsilon''$ with the help of Eqs. (6) and (13) and substituted in Eq. (14), we have

$$\mu = 1.12 \times 10^{-21}(\Delta\epsilon''/\nu\tau c)^{\frac{1}{2}} \text{ e.s.u.}$$
$$\text{for benzene solutions, and}$$
$$\mu = 1.05 \times 10^{-21}(\Delta\epsilon''/\nu\tau c)^{\frac{1}{2}} \text{ e.s.u.} \qquad (16)$$
$$\text{for diphenylmethane solutions,}$$

where ν is the frequency in megacycles, τ is in seconds and c is molarity. It is understood that the multiplier, $(1 + [2 \times 10^6 \pi\nu\tau]^2)^{\frac{1}{2}}$, must be used

[11] P. Debye, Physik. Zeits. 35, 101 (1934).

in Eq. (14) when $[2\times10^6\pi\nu\tau]^2$ is not very much less than unity.

RESULTS

In Table II are presented the dielectric constants measured for all investigated solutions as a function of concentration and frequency. The number of significant figures listed for each value was determined by the favorability of experimental conditions of frequency, conductance and cell geometry. The last digit of each constant must be considered doubtful. All figures are relative to that of benzene, whose dielectric constant was taken to be 2.276 at 25°C.[8] Some solutions exhibit a large variation with frequency around 1000 cycles and these values must be regarded with caution as they undoubtedly do not represent the true dielectric constant. In these cases, the asymptote values have been taken as ϵ_0. Further investigations must be carried out to explain completely these pseudodispersons.

TABLE II. Audiofrequency dielectric constant data.

Molarity	Frequency (cycles/second)						
	200	500	1000	2000	4000	6000	7500
A. Tetra-n-butylammonium thiocyanate in benzene							
1.51×10^{-4}	2.276	2.275	2.276	2.276	2.275	2.276	2.275
3.66×10^{-3}	2.289	2.287	2.288	2.278	2.288	2.287	2.293
9.36×10^{-3}	2.34	2.322	2.319	2.315	2.315	2.312	2.310
1.72×10^{-2}	2.45	2.425	2.409	2.400	2.389	2.384	2.374
2.66×10^{-2}	4.28	2.78	2.62	2.53	2.56	2.55	2.57
4.28×10^{-2}	14.4	8.8	5.24	3.52	2.95	2.91	2.86
in diphenylmethane containing 17% benzene							
9.73×10^{-3}	2.606	2.605	2.602	2.598	2.597	2.597	2.597
B. Tri-isoamylammonium picrate in benzene							
8.49×10^{-3}	2.41	2.40	2.411	2.409	2.414	2.393	2.412
9.34×10^{-2}	3.86	3.70	3.69	3.67	3.69	3.69	3.71
in diphenylmethane							
1.03×10^{-2}	2.786	2.784	2.783	2.780	2.780	2.781	2.780
6.89×10^{-2}	4.62	3.98	3.77	3.71	3.68	3.64	3.65
C. Dibutyldioctadecylammonium thiocyanate in benzene							
8.99×10^{-4}	2.26	2.279	2.277	2.277	2.276	2.276	2.279
8.41×10^{-3}	2.42	2.37	2.360	2.345	2.335	2.331	2.314
1.12×10^{-2}	2.49	2.437	2.411	2.395	2.386	2.370	2.370
1.37×10^{-2}	2.79	2.617	2.541	2.509	2.495	2.488	2.487
in diphenylmethane containing 30% benzene							
8.34×10^{-3}	2.732	2.700	2.684	2.680	2.674	2.653	2.650
D. Tetra-n-butylammonium bromide in benzene							
3.67×10^{-3}	—	2.282	2.280	2.280	2.280	2.280	2.280
E. Butyl alcohol in benzene							
2.11×10^{-3}	2.271	2.272	2.271	2.273	2.272	2.272	2.272
F. Dibutyldioctadecylammonium octadecylsulfate in benzene							
4.00×10^{-4}	2.27	2.285	2.284	2.284	2.284	2.284	2.284
G. Pure butyl alcohol							
—	18.2	17.8	17.7	17.7	17.7	17.6	17.7

In Table III are summarized all quantities pertinent to the Debye theory. The dielectric constants are taken from Table II for 1000 cycles or the asymptotic limit in cases of dispersion, and benzene was the solvent in all cases except as indicated. Polarizations were calculated on the basis of the Clausius-Mosotti relationship. The symbols used are m, molality; c, molarity; κ_0, specific conductance at 1000 cycles; ϵ_0, dielectric constant (either at 1000 cycles or asymptote value); n, index of refraction; d, density; η, viscosity (poises); P_2, molar polarization of solute (cc) and P_1, molar polarization of the solvent (cc).

DISCUSSION

A. Solvents.—In general, determinations were made with the non-polar solvent benzene. A few observations were made with diphenylmethane as the solvent in order to shift the relaxation frequency to lower frequencies since its viscosity is nearly five times that of benzene. With thermometer cell No. 3 filled with pure benzene, a loss factor $\epsilon''=0.0025$ was measured which was independent of frequency. With the other two thermometer cells, the apparent loss factor was about one-tenth as great and varied somewhat with frequency, approaching a constant value with increasing frequency. Since the trends and amounts of these losses could be reproduced with pure diphenylmethane in the cell, it was concluded that these losses must be caused by the heating of the glass and, possibly, by the leads going to the electrodes. In all cases, a correction has been made for this heating which was negligibly small in all but the most dilute solutions.

B. Pure Butyl Alcohol.—On making the assumption attendant to Eq. (12), viz., that the critical frequency is sufficiently high to make the measuring frequency small by comparison, a straight line plot is to be expected for the absorption conductivity as a function of the square of the frequency. Figure 2 indicates this to be the case here. Applying Eq. (12), a value of 1600 Mc (19 cm) is found for the critical frequency. The values of ν_c found for butyl alcohol by different observers,[12] are not in complete agreement and the underlying reasons need to

[12] C. Schmelzer, Ann. d. Physik 28, 35 (1937).

TABLE III. Constants measured for all investigated solutions and pure solvents at 25°C.**

Salt	m	c	d	η	ϵ_0	κ_0	$\epsilon_\infty = n^2$	P_2 or P_1
Bu$_4$NCNS	1.73×10^{-4}	1.51×10^{-4}	0.8735	0.00607	2.276	2.45×10^{-11}	2.244	5000
Bu$_4$NCNS	4.17×10^{-3}	3.66×10^{-3}	0.8747	0.00606	2.288	1.92×10^{-9}	2.244	740
Bu$_4$NCNS[1]	9.84×10^{-3}	9.73×10^{-3}	0.9890	0.0223	2.597	7.83×10^{-9}	2.451	—
Bu$_4$NCNS	1.07×10^{-2}	9.36×10^{-3}	0.8740	0.00614	2.310	6.91×10^{-9}	2.244	910
Bu$_4$NCNS	1.98×10^{-2}	1.72×10^{-2}	0.8743	0.00623	2.374	4.06×10^{-8}	2.244	1040
Bu$_4$NCNS	3.07×10^{-2}	2.66×10^{-2}	0.8750	0.00635	2.57	1.59×10^{-7}	2.244	1600
Bu$_4$NCNS	4.95×10^{-2}	4.28×10^{-2}	0.8762	0.00668	2.86	6.54×10^{-7}	2.244	2100
i-Am$_3$NHPi	9.72×10^{-3}	8.49×10^{-3}	0.8770	0.00612	2.411	1.15×10^{-11}	2.246	2600
i-Am$_3$NHPi	1.11×10^{-1}	9.34×10^{-2}	0.8825	0.00657	3.69	5.30×10^{-8}	2.250	1610
i-Am$_3$NHPi[2]	1.07×10^{-2}	1.03×10^{-2}	1.0030	0.0290	2.780	3.13×10^{-10}	2.415	2600
i-Am$_3$NHPi[2]	6.94×10^{-2}	6.89×10^{-2}	1.0060	0.0318	3.65	1.19×10^{-7}	2.480	1920
Bu$_2$Oct$_2$NCNS	1.03×10^{-3}	8.99×10^{-4}	0.8735	0.00607	2.277	2.79×10^{-10}	2.242	1200
Bu$_2$Oct$_2$NCNS	9.69×10^{-3}	8.41×10^{-3}	0.8735	0.00624	2.314	2.21×10^{-8}	2.242	1040
Bu$_2$Oct$_2$NCNS[3]	8.67×10^{-3}	8.34×10^{-3}	0.9620	0.0165	2.650	4.46×10^{-8}	2.402	—
Bu$_2$Oct$_2$NCNS	1.30×10^{-2}	1.12×10^{-2}	0.8743	0.00638	2.370	4.55×10^{-8}	2.242	1600
Bu$_2$Oct$_2$NCNS	1.58×10^{-2}	1.37×10^{-2}	0.8750	0.00644	2.487	7.89×10^{-8}	2.242	2120
Bu$_2$Oct$_2$NOctSO$_4$	4.58×10^{-4}	4.00×10^{-4}	0.8735	0.00607	2.284	3.00×10^{-11}	2.243	5300
BuOH	2.41×10^{-3}	2.11×10^{-3}	0.8735	0.00608	2.272	1.22×10^{-12}	2.244	—
Bu$_4$NBr	4.21×10^{-3}	3.67×10^{-3}	0.8735	0.00609	2.280	9.21×10^{-10}	2.242	—
C$_6$H$_6$	Pure solvent		0.8735	0.00605	2.276	10^{-13}–10^{-14}	2.243	(P_1)26.6
BuOH	Pure solvent		0.8082	0.0246	17.7	5.56×10^{-8}	1.954	(P_1)77.6
Ph$_2$CH$_2$	Pure solvent		1.0028	0.0289	2.591	4×10^{-13}	2.484	(P_1)58.1

** The solvent was benzene except as indicated. Bu, butyl; Ph or Φ, phenyl; Oct., octadecyl; Pi, picrate.
[1] Solvent: 83 percent diphenylmethane—17 percent benzene.
[2] Solvent: Diphenylmethane.
[3] Solvent: 69 percent diphenylmethane—31 percent benzene.

be further investigated. In all likelihood, the discrepancies are caused by losses contributed by unknown amounts of unknown electrolyte impurities in the alcohol, depending on the degree of purification.

C. Dibutyldioctadecylammonium Octadecylsulfate.—This salt was investigated to determine the magnitude of the absorption by a salt having a long chain group on both the cation and the anion. Unfortunately, the salt is not very soluble in benzene at 25° and, hence, only a single concentration was within the range of the apparatus. These values are subject to considerable error because of large corrections for heating of the cell. Figure 3 shows the same linearity of absorption conductivity with the square of the frequency as with butyl alcohol. Therefore, this salt at this concentration behaves as a monodisperse system where Debye's equations are valid. The nearly perfect agreement with theory is shown in Fig. 4 where the drawn-in curves, calculated from Eqs. (10) and (11) for $\epsilon_0 = 2.284$, $\epsilon_\infty = 2.243$, and $\nu_c = 1500$ Mc, coincide well with the experimental points. The effective radius $a = 3.8\times10^{-8}$ cm is surprisingly small in comparison with that of other molecules calculated on the same basis.

D. Tri-isoamylammonium Picrate.—This salt

was selected as being representative of a weak electrolyte in a benzene solution. Both its ions are unsymmetrical with respect to shape and charge; the major portion of the positive charge being located on the nitrogen atom of the Am$_3$NH$^+$ ion, and most of the negative charge of the picrate ion being centered on the oxygen atom. Determinations were made at two concentrations of this salt in both benzene and diphenylmethane in order to study the effects of concentration and solvent viscosity. The results are plotted in Fig. 5 on a log-log scale in order to cover the wide range of values. First, it is to be noted that, according to the Debye theory, this type of plot should yield a straight line with a value of $d(\log\Delta\epsilon'')/d\log\nu = 1$, if the measurement frequencies are small in comparison with the critical frequency. Within the limits of experimental error, this is seen to be the case here, there being some small deviation from linearity at the lowest frequencies for the two diphenylmethane solutions. It should be remembered that the probable error for the values of $\Delta\epsilon''$ at low frequencies is greater than at higher frequencies where the amount of absorption is much larger. In Fig. 5, the theoretical straight line was drawn in for comparison with the experimental results, and calculations have been made
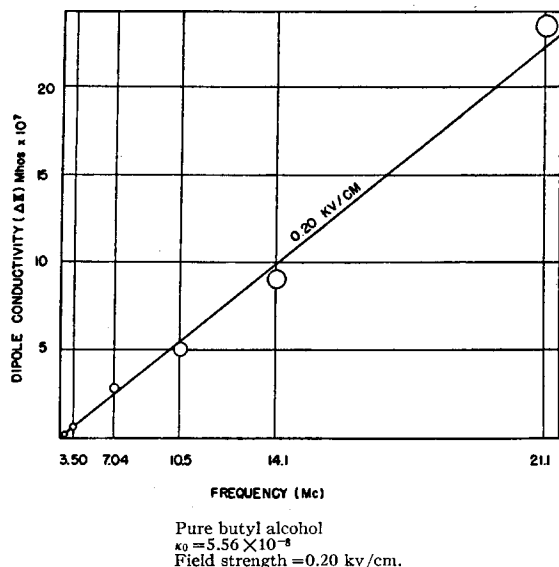
FIG. 2. Dipole conductivity as a function of frequency squared.
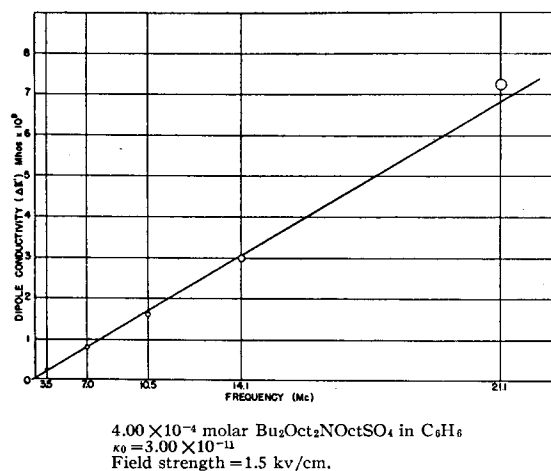
Pure butyl alcohol
$\kappa_0 = 5.56 \times 10^{-8}$
Field strength = 0.20 kv/cm.

4.00 $\times 10^{-4}$ molar $Bu_2Oct_2NOctSO_4$ in C_6H_6
$\kappa_0 = 3.00 \times 10^{-11}$
Field strength = 1.5 kv/cm.

FIG. 3. Dipole conductivity as a function of frequency squared.

4.00 $\times 10^{-4}$ molar $Bu_2Oct_2NOctSO_4$ in C_6H_6
$\kappa_0 = 3.00 \times 10^{-11}$
Field strength = 1.5 kv/cm.

FIG. 4. The dependence of dipole conductivity and loss factor on frequency.
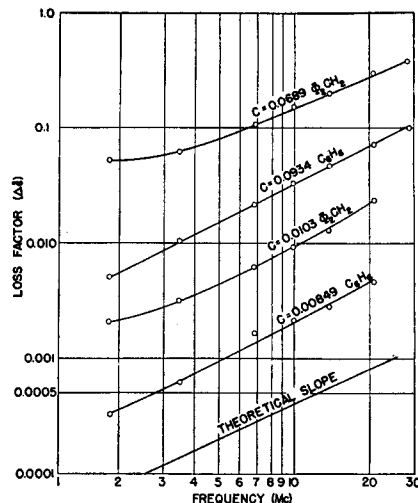
FIG. 5. The dependence of loss factor on frequency for i-Am_3NHPi in C_6H_6 and Φ_2CH_2.

on the basis of the straight line portions of the curves. From Eqs. (12), (8), and (4), values for the critical frequency, relaxation time and molecular radius have been calculated and are listed in Table IV. Unfortunately, the cell corrections for heating of the glass were large in comparison with the absorption heating for the two most dilute solutions, and, therefore, calculated figures for these two solutions can only be regarded as approximate.

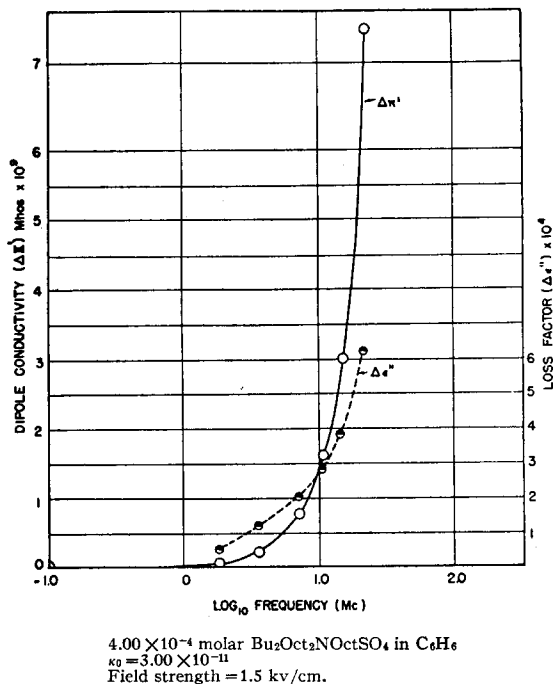The good agreement of the loss factor-frequency curves with theory affords evidence that

this salt at these concentrations forms a monodisperse system and thus indicates the existence of rotating dipolar body of well-defined dimensions. The calculated radii show good agreement and show that the effective spherical radius remains the same in spite of tenfold concentration and fivefold viscosity changes. The excellent
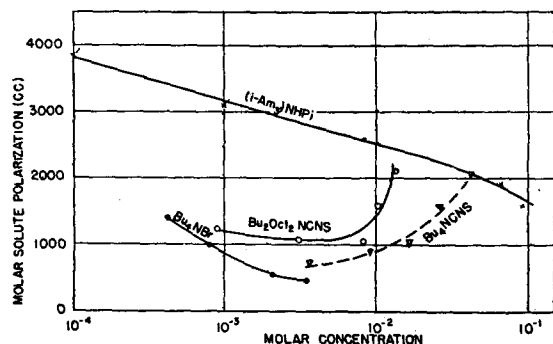
FIG. 6. Dependence of molar solute polarization on concentration (points with tails measured by Strong and by Geddes).

FIG. 7. Equivalent loss factor as a function of concentration and frequency for Bu_2Oct_2NCNS in C_6H_6 and Φ_2CH_2.

agreement with theory is to be noted in the case of the 0.0934 molar benzene and 0.0694 molar diphenylmethane solutions.

Although there are large cell corrections for the two dilute solutions, it is seen that the loss is roughly proportional to the concentration times viscosity at a given frequency. For a precise determination of the dipole moment, it would be necessary to investigate a larger number of concentrations making an extrapolation to infinite dilution, but it is interesting to note the value of $\mu = 12 \times 10^{-18}$ e.s.u. obtained by the use of Eq. (14). This value is in good agreement with the value of 13.3×10^{-18} e.s.u. obtained by dielectric constant (ϵ') measurements.[13]

The molecular radius obtained from the loss measurements on the more concentrated solutions is 5.2×10^{-8} cm. This figure compares favorably with the value of 5.05×10^{-8} cm which was independently obtained from polarization
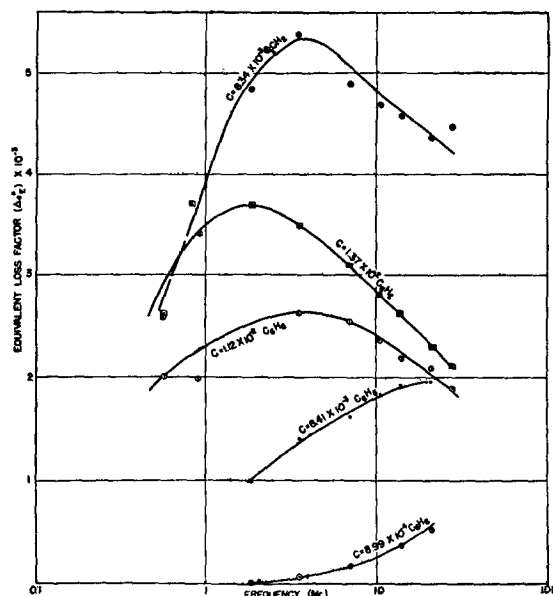
TABLE IV. Constants calculated on the basis of the Debye theory.

Salt	Molar concentrations, c	Critical frequency ν_c(Mc)	Relaxation time τ(sec.)	Molecular radius a(Å)	Dipole moment μ(D)	Solvent
$Bu_2Oct_2NOctSO_4$	4.00×10^{-4}	1500	1.1×10^{-10}	3.8	27.6	C_6H_6
$i\text{-}Am_3NHPi$	8.49×10^{-3}	700	2.2×10^{-10}	4.9	11.8	C_6H_6
$i\text{-}Am_3NHPi$	9.34×10^{-2}	430	2.8×10^{-10}	5.2	12.7	C_6H_6
$i\text{-}Am_3NHPi$	1.03×10^{-2}	380	3.9×10^{-10}	3.5	15.9	Ph_2CH_2
$i\text{-}Am_3NHPi$	6.89×10^{-2}	87	1.5×10^{-9}	5.3	12.5	Ph_2CH_2
Bu_2Oct_2NCNS	8.34×10^{-3}	4.5	3.5×10^{-8}	21	8.7	69% Ph_2CH_2, 31% C_6H_6
Bu_2Oct_2NCNS	8.41×10^{-3}	21	7.5×10^{-9}	16	5.7	C_6H_6
Bu_2Oct_2NCNS	1.12×10^{-2}	3.5	4.4×10^{-8}	28	6.6	C_6H_6
Bu_2Oct_2NCNS	1.37×10^{-2}	1.8	8.7×10^{-8}	35	7.7	C_6H_6
Bu_4NCNS	9.73×10^{-3}	150	1.0×10^{-9}	5.2	11.0	83% Ph_2CH_2, 17% C_6H_6
Bu_4NCNS	9.36×10^{-3}	384	4.1×10^{-10}	6.0	8.0	C_6H_6

[13] C. A. Kraus, J. Frank. Inst. 225, 687 (1938).

measurements. This latter value represents the minor diameter of an ellipsoidal model, where the ratio of major to minor axes is taken as 2:1 and is calculated by an equation developed by Fuoss.[14] These dimensions are also in accord with the value of 5.54×10^{-8} cm calculated from cryoscopic measurements for the ellipsoidal model, using the value of 12.9×10^{-18} e.s.u. for the dipole moment.

Examination of the values of molar solute polarization P_2 (Fig. 6) for this salt shows a relatively slow decrease with increasing concentration. This is interpreted as meaning that the loss factor per mole should be nearly constant (for constant frequency and relaxation time) and association of the dipole ion-pairs into non-polar quadrupoles or other higher order non-polar aggregates is occurring only on a small scale. This interpretation has been further confirmed by cryoscopic measurements for this salt in benzene where it has been found that the polymerization number is only about 1 at 0.01 molar and 1.5 at 0.1 molar.[15] Since our loss measurements show $\Delta\epsilon''$ to be proportional to the (concentration) $\times$ (viscosity) and the molecular radius is constant, we are in complete agree-

[14] R. M. Fuoss, J. Am. Chem. Soc. 56, 1031 (1934).
[15] Copenhafer, Thesis, Brown University (1942).

ment with these other independent determinations.

Audiofrequency conductance values as a function of concentration for tri-*iso*amylammonium picrate[5] are also in accord with the simple dipole picture for this salt with unsymmetrical ions. No inflections are observed beyond the minimum of the equivalent conductance-concentration curve, which increases uniformly up to a value where the viscosity is sufficiently large to cause a decrease in the observed conductance. It is to be observed that the conductance-concentration curve is very steep at concentrations above that corresponding to the minimum in the conductance curve, indicating the presence of ions of higher degree of clustering than triple-ions. However, the very low conductance of this salt in benzene shows that the total ionic concentration is but a minute fraction of the stoichiometric concentration for ternary ammonium salts; hence, most of the salt is present as non-conducting ion-pairs, at any rate, neutral aggregates. The absence of inflections at concentrations above the minimum is in accord with the assumption that association is predominantly dipolar so that a spread of relaxation times would not be expected.

E. Dibutyldioctadecylammonium Thiocyanate. —Structurally speaking, this salt offers a transition between the highly unsymmetrical ions of tri-*iso*amylammonium picrate, previously discussed, and the highly symmetrical ions of tetra-*n*-butylammonium thiocyanate; that is, the dipole of this ion-pair (Bu_2Oct_2NSCN) is composed of an unsymmetrical positive ion and a symmetrical negative ion.

Figure 7 shows the dependence of the equivalent loss factor on frequency, the equivalent loss factor being simply the conventional quantity divided by the number of moles per liter. This type of presentation has been used in order to emphasize the relation between the loss and concentration. Measurements were made at four

different concentrations in benzene and one in diphenylmethane. The values measured at the lowest concentration were nearly out of the range of the apparatus and, hence, must be regarded as giving order of magnitude only. The scattering of points is marked at the low frequencies because of the low losses involved but, if the expected logarithmic symmetry prevails, these points line up with the expected curve within experimental error.

Examination of these curves shows an increasing amount of loss per mole with increasing concentration. This means that the polarity of the complex formed is increasing as indicated by the rising molar polarizations (Fig. 6), calculated from the dielectric constant measurements. From the dispersion theory, we expect the maximum loss to be $(\epsilon_0 - \epsilon_\infty)/2$ for a given dispersion region. In Table V are listed these computed maxima for the dibutyldioctadecylammonium thiocyanate solutions measured, along with the experimental maxima. It is noted that in common with dispersion data in general, the measured loss factor is considerably lower than that predicted by theory. In accordance with the empirical equation suggested by the Coles,[16] the parameter α may be computed from the maximum values of $\Delta\epsilon''$. These are listed in Table V where it is seen that α is of the order of magnitude of one-half. Mathematically, a value of this parameter $\alpha \neq 0$ is consistent with a general spread of the loss factor values about a center relaxation frequency and a simultaneous decrease of the maximum from the value $(\epsilon_0 - \epsilon_\infty)/2$. It is found that all the curves agree qualitatively over the frequency range covered with the values predicted by the Cole equation where $\alpha = 0.5$. The regular increase of α with concentration is to be noted. The value of $\alpha = 0$ for the 8.99×10^{-4} solution was determined by the linear dependence of $\Delta\epsilon''$ upon frequency for this concentration at frequencies much lower than the critical frequency. This means that, at low concentrations, the salt is behaving as a monodisperse system with a single, well-defined polar structure, and that more physically and electrically different polar bodies are appearing with increasing concentration giving rise to the spread of relaxation times.

TABLE V. Theoretical and experimental absorption maxima for dibutyldioctadecylammonium thiocyanate.

Moles/Liter	Solvent	$(\epsilon_0 - \epsilon_\infty)/2$	$\Delta\epsilon_{max}''$(expt.)	α
8.99×10^{-4}	C_6H_6	0.0175	—	0
8.41×10^{-3}	C_6H_6	0.0360	0.017	0.43
1.12×10^{-2}	C_6H_6	0.0640	0.029	0.46
1.37×10^{-2}	C_6H_6	0.122	0.050	0.50
8.34×10^{-3}	Φ_2CH_2	0.124	0.045	0.56

[16] K. S. and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

The shift of critical frequencies to lower values with increasing concentrations would seem to indicate that larger polar aggregates are being formed. The molecular radii computed from the mean relaxation frequencies are listed in Table IV and show that an extremely large aggregate $(a = 35 \times 10^{-8}$ cm) has been formed by the time the concentration has reached 1.37×10^{-2} molar. Since $a = 28 \times 10^{-8}$ at 1.12×10^{-2} molar, the polar cluster is undergoing a very rapid change in size in this concentration range.

Again, to check the validity of the assumed theory, measurements were made at approximately the same concentration in both the solvents—benzene and diphenylmethane. For 8×10^{-3} molar solutions with a $1:2.7$ ratio of viscosities, a shift in critical frequencies of $1:4.7$ was found. The quantitative agreement is not very good but is probably satisfactory in view of the departure from typical Debye behavior which all the more concentrated solutions of the salt show.

With increasing concentration, the benzene solutions of dibutyldioctadecylammonium thiocyanate show a steady increase in dipole moment as listed in Table IV. These moments were calculated from Eq. (16) using values of the loss factor measured at each of the critical frequencies. The values of solute polarization for 8.41×10^{-3}, 1.12×10^{-2}, and 1.37×10^{-2} molar benzene solutions were calculated to be, respectively, 1040, 1600, and 2120 from the measured values of ϵ_0. The ratio of these polarizations is $0.49:0.75:1$ as compared with the ratio of the squares of the dipole moments which is $0.55:0.74:1$. The agreement with theory is, therefore, satisfactory. Here, as with other salts of more symmetrical ions, a minimum in the polarization-concentration curve is found (see Fig. 6) around 0.005 molar. Fuoss[14] has shown that in the limit for dilute solutions, the polarization values should decrease linearly with increasing concentration when there is anti-parallel association of polar dipoles into non-polar quadrupoles. The existence of the minimum would indicate that a competing interaction is taking place which results in forming increasing numbers of polar aggregates of higher complexity.

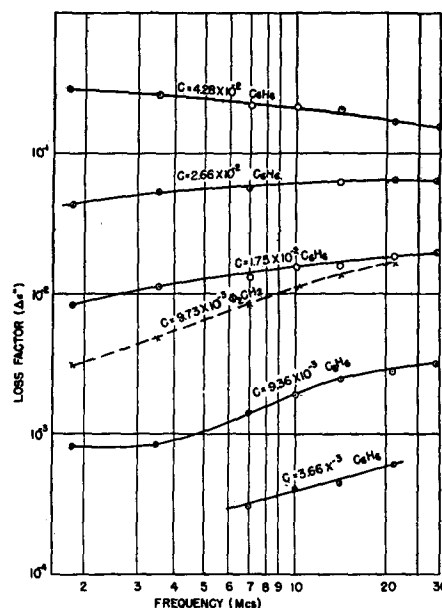In view of the large radii calculated for this salt at these concentrations, the charges must be

FIG. 8. Loss factor as a function of concentration and frequency for Bu_4NCNS in C_6H_6 and Φ_2CH_2.

located with a high degree of symmetry and the charge centroids separated by a distance of the order of molecular dimensions. An idea of the comparatively small separation of unit point charges to give $\mu = 7.7 \times 10^{-18}$ e.s.u. may be found by dividing by the unit charge 4.77×10^{-10}, giving a separation of 1.6×10^{-8} cm.

Conductance data of Strong[5] for solutions of dibutyldioctadecylammonium thiocyanate in benzene show the characteristics of triple-ion formation up to about 0.1 molar where an aggregate of high stability is formed at the expense of other conducting particles. The rapid increase in polarization and molecular radius observed in the loss measurements above 0.01 molar concentration may be interpreted as evidence in support of the formation of a large and stable polar cluster indicated in the conductance measurements.

That an extremely high degree of association for these long chain salts takes place is demonstrated by cryoscopic measurements[15] on n-octadecyltri-n-butylammonium formate which has already reached a polymerization number of 10 at 0.001 molal and 21.5 at 0.00326 molal. These data are qualitatively in accord with the results derived from the loss data for dibutyldioctadecylammonium thiocyanate.

F. Tetra-n-butylammonium Thiocyanate.—This salt, in contrast to the ternary picrate and quaternary thiocyanate previously 'discussed, consists of two ions which may be considered to be relatively symmetrical with respect to both shape and charge. For such symmetrical salts in solvents of low dielectric constant, all the evidence from dielectric constant, cryoscopic and conductance measurements points to a highly associated molecule accompanied by a complex behavior. The dielectric loss measurements here are no exception.

In Fig. 8 are shown the loss factor *versus* frequency results for 3.66×10^{-3}, 9.36×10^{-3}, 1.75×10^{-2}, 2.66×10^{-2}, and 4.28×10^{-2} molar solutions in benzene. It is seen that within this range of concentrations, the absorption peak is gradually shifted to lower frequencies with increasing concentration until, with the most concentrated solution, the portion of the curve has been reached when the loss factor is decreasing with increasing frequency. Table III shows that the viscosity change with concentration could not be very effective in changing the relaxation times for the benzene solutions of tetra-*n*-butylammonium thiocyanate; hence, the increase of relaxation times must be ascribed chiefly to an increase in the size of the polar aggregate. The flatness of the curves suggests that with this salt we have a large spread of relaxation times about some mean value.

With the 2.66×10^{-2} molar solution, we are close to the absorption maximum at 30 Mc, reaching a value of $\Delta \epsilon'' = 0.065$. For this concentration, $\epsilon_0 = 2.62$ and $\epsilon_\infty = 2.244$; hence, the predicted maximum is $(\epsilon_0 - \epsilon_\infty)/2 = 0.188$, which is three times as large as the experimentally measured loss. From the relation between ϵ_0, ϵ_∞, and $\Delta \epsilon_{max}''$, we may compute $\alpha = 0.58$ and, using this value of α, the solid curve drawn in Fig. 8 was computed for this concentration ($2.66 \times 10^{-2}M$) from the modified Debye equation.[16] The lineup, with the experimental points as indicated by the circles, is excellent.

If we may assume that the points for the 3.66×10^{-3} molar solution lie on a straight line and, therefore, that the measurement frequencies are very much lower than the critical frequency, we see that $\Delta \epsilon''$ is increasing with the 0.75 power of the frequency. Accordingly, $\alpha = 0.25$ for this concentration, indicating less spread of relaxation times than for the more concentrated solutions.

From Table III, it is seen that the ratio of viscosities for 9.7×10^{-3} and 9.4×10^{-3} molar solutions in diphenylmethane-benzene mixture and in benzene, respectively, is 3.7:1, while the ratio of the relaxation times computed from Eqs. (12) and (8), using the average slopes of the $\Delta \epsilon''$-frequency curves, is 2.4:1. It is to be noted that here the relaxation times are more nearly proportional to η/V_m (where V_m is the molecular volume) than they are to η.

The gradual increase of the loss factor per mole with increasing concentration is consistent with the molar polarization-concentration curve for this salt (see Fig. 6). Of course, a part of this increase is due to the shifting of the relaxation frequency to lower values with increasing concentration. With a nominal frequency coverage of only one decade, it is impossible to separate these two effects.

The existence of a large number of aggregates of different sizes with overlapping dispersion regions is concordant with cryoscopic measurements on this salt. The freezing point measurements show that the polymerization number increases from 2.7 to 12.3 in the range from 0.004 to 0.049 molal.[15]

Conductance measurements[5] for this salt as a function of concentration yield a very complex curve having a minimum followed by some five inflections which indicate equilibria between a variety of neutral and charged ionic species of higher order.