816. *The Dipole Moments of Some Quaternary Ammonium Salts.*

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The dielectric constants of benzene solutions of some quaternary ammonium salts have been measured at 25°. The results indicate that, for some of these salts, association of the ion-pairs to form larger aggregates occurs even at very low concentrations. A method for deducing the dipole moments of the free ion-pairs in such systems is suggested. The charge separations in the ion-pairs, as calculated from their dipole moments, show a reasonable variation with the sizes of the ions involved, but are less than the interionic distances derived from conductance measurements.

SEVERAL series [1-5] of measurements of the dipole moments of quaternary ammonium salts, and of other salts which form ion-pairs in solvents of low dielectric constant, have been reported, but the results show considerable discrepancies. These arise, no doubt, through the sparing solubilities of these salts in non-dipolar solvents and the circumstance, observed by Geddes and Kraus,[2] that for some salts the decrease of the effective molar polarisation with concentration is non-linear and thus renders extrapolation of the results to zero concentration difficult. This anomalous behaviour is attributable to association of the ion-pairs to more-complex units even at low concentrations in the solution.

In view of the interest attached to a knowledge of the dipole moments of the ion-pairs, a method has been devised for interpreting the variation of the dielectric constant with concentration when association between ion-pairs occurs. This is similar to the method used by Pohl, Hobbs, and Gross [6] in interpreting the concentration-dependence of the apparent molar polarisation of acids in solution, but is simpler, since the experimental values of the dielectric-constant increments can be used directly.

It is assumed that, at low concentrations, the ion-pairs associate to form dimers only, and that in these circumstances each solute species produces an increment in the dielectric

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[1] Hooper and Kraus, *J. Amer. Chem. Soc.*, 1934, **56**, 2265.
[2] Geddes and Kraus, *Trans. Faraday Soc.*, 1936, **32**, 585.
[3] Richardson and Stern, *J. Amer. Chem. Soc.*, 1960, **82**, 1296.
[4] Davies and Williams, *Trans. Faraday Soc.*, 1960, **56**, 1619.
[5] Gilkerson and Srivastava, *J. Phys. Chem.*, 1961, **65**, 272.
[6] Pohl, Hobbs, and Gross, *J. Chem. Phys.*, 1941, **9**, 408.

constant which is proportional to its weight fraction in the solution. Thus, for monomeric and dimeric forms, one can write

$$\Delta\varepsilon_{\mathrm{M}} = \alpha_{\mathrm{M}} w_{\mathrm{M}}, \text{ and } \Delta\varepsilon_{\mathrm{D}} = \alpha_{\mathrm{D}} w_{\mathrm{D}},$$

where w_{M} and w_{D} are the weight fractions of monomer and dimer respectively. Further, if the dielectric constant increments are additive, then

$$\Delta\varepsilon = \Delta\varepsilon_{\mathrm{M}} + \Delta\varepsilon_{\mathrm{D}} = \alpha_{\mathrm{M}} w_{\mathrm{M}} + \alpha_{\mathrm{D}} w_{\mathrm{D}}.$$

If the active masses of the monomer and dimer can be represented by their concentrations, c, in mole/c.c., then the association constant, K, is given by

$$K = \frac{c_{\mathrm{D}}}{c_{\mathrm{M}}^2} = \left(\frac{w_{\mathrm{D}} d}{2M_{\mathrm{M}}}\right) \Big/ \left(\frac{w_{\mathrm{M}} d}{M_{\mathrm{M}}}\right)^2 = \frac{w_{\mathrm{D}}}{w_{\mathrm{M}}^2} \cdot \frac{M_{\mathrm{M}}}{2d},$$

where M_{M} is the molecular weight of the monomer and d is the density of the solution. However, $w_{\mathrm{M}} + w_{\mathrm{D}} = w$, the total weight fraction of solute, which is known for each solution studied, and if for any particular solution, $\Delta\varepsilon/w = \alpha$, then

$$\Delta\varepsilon = \alpha(w_{\mathrm{M}} + w_{\mathrm{D}}) = \alpha_{\mathrm{M}} w_{\mathrm{M}} + \alpha_{\mathrm{D}} w_{\mathrm{D}}.$$

Hence,

$$w_{\mathrm{M}}/w_{\mathrm{D}} = (\alpha - \alpha_{\mathrm{D}})/(\alpha_{\mathrm{M}} - \alpha).$$

Further,

$$\alpha w = \alpha_{\mathrm{M}} w_{\mathrm{M}} + \alpha_{\mathrm{D}}(w - w_{\mathrm{M}}),$$

and hence,

$$w_{\mathrm{M}} = w(\alpha - \alpha_{\mathrm{D}})/(\alpha_{\mathrm{M}} - \alpha_{\mathrm{D}}).$$

Thus,

$$K = \frac{(\alpha_{\mathrm{M}} - \alpha)(\alpha_{\mathrm{M}} - \alpha_{\mathrm{D}})}{(\alpha - \alpha_{\mathrm{D}})^2} \cdot \frac{M_{\mathrm{M}}}{2dw}. \qquad (1)$$

For any particular system, $(\alpha_{\mathrm{M}} - \alpha_{\mathrm{D}})$ and M_{M} are constant; thus by putting

$$2K/(\alpha_{\mathrm{M}} - \alpha_{\mathrm{D}})M_{\mathrm{M}} = K',$$

it follows that

$$K' = \frac{\alpha_{\mathrm{M}} - \alpha}{(\alpha - \alpha_{\mathrm{D}})^2} \cdot \frac{1}{dw}$$

and

$$\alpha = \alpha_{\mathrm{M}} - (\alpha - \alpha_{\mathrm{D}})^2 dwK'. \qquad (2)$$

If, therefore, α is plotted against $(\alpha - \alpha_{\mathrm{D}})^2 dw$, a straight line should result, with intercept α_{M} and slope $-K'[= -2K/(\alpha_{\mathrm{M}} - \alpha_{\mathrm{D}})M_{\mathrm{M}}]$. By successive approximations, the value of α_{D} giving the best linearity of plot can be ascertained, and hence the values of α_{M} and K deduced. The dipole moments of the monomeric and dimeric species can then be calculated from α_{M} and α_{D}, respectively.

The dielectric constants of benzene solutions of a few quaternary ammonium salts, selected for variety of type coupled with reasonable solubility, have been measured. The results are shown in Table 1, where $\Delta\varepsilon$ and Δv denote the differences between the dielectric constants and specific volumes, respectively, of the solutions and those of benzene.

For tetra-n-butylammonium picrate and cetylpyridinium benzoate, the dielectric constant varies almost linearly with the concentration over the range studied, so that the limiting value of $(\partial\varepsilon/\partial w) = \alpha$ can be deduced directly. For the remaining salts, however, there is a rapid decrease in $\Delta\varepsilon/w$ with increase in concentration, corresponding to a decrease in the molar polarisation of the solute. Application of eqn. 2 leads to the inference that, for tetra-n-butylammonium iodide, the data for the lower concentrations can be interpreted satisfactorily on the basis of association to give non-polar dimers. At the highest concentrations, where the solutions are almost saturated, however, association to give larger aggregates seems to occur. The results for tetra-n-butylammonium chloroacetate and benzoate, however, suggest that the dimers of these compounds have significant apparent dipole moments. This would be expected if they tend to assume flexible structures such as (I), which would lead to high atom polarisations. Such an explanation was suggested by Pohl, Hobbs, and Gross[6] to account for the apparent moments of the dimeric forms of carboxylic acids. The dimer of the chloroacetate would be expected to have a true dipole moment, since the C–Cl bonds are not co-linear with the C–C bonds, but this should not have a mean value greater than about 1·5 D.

TABLE 1.

Polarisation data for benzene solutions.

Tetra-n-butylammonium iodide.

10^4w	0·539	1·105	1·867	3·687	4·831	
$10^4\Delta\varepsilon$	19·65	32·53	49·93	67·92	70·29	
$\Delta\varepsilon/w$	36·4	32·0	26·7	18·9	14·6	

Tetra-n-butylammonium chloroacetate.

10^4w	0·2313	0·4317	0·7304	1·446	2·049	2·130
$10^4\Delta\varepsilon$	13·24	22·01	33·15	48·29	53·86	55·12
$\Delta\varepsilon/w$	57·2	51·0	45·4	33·4	26·3	25·9

Tetra-n-butylammonium benzoate.

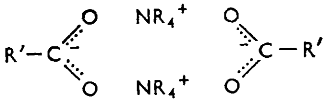
10^4w	1·867	3·774	6·945	12·72	24·31	47·83
$10^4\Delta\varepsilon$	53·4	93·1	153·7	246·0	410·6	721·1
$-10^4\Delta v$	0·3	0·6	1·3	2·0	3·9	7·6
$\Delta\varepsilon/w$	28·6	24·7	22·1	19·3	16·9	15·1
P_2 (c.c.)	2058	1789	1613	1421	1249	1119

Tetra-n-butylammonium picrate.

10^4w	1·247	2·531	3·464	4·699	6·828	10·130
$10^4\Delta\varepsilon$	67·10	136·01	186·56	252·98	367·34	540·22
$\Delta\varepsilon/w$	53·8	53·7	53·9	53·8	53·8	53·3

Cetylpyridinium benzoate.

10^4w	1·040	2·005	3·543			
$10^4\Delta\varepsilon$	14·81	29·03	50·44			
$\Delta\varepsilon/w$	14·24	14·48	14·23			



(I)

The monomeric ion-pairs, too, may have appreciable atom polarisations arising from the compressibilities of the ions, but such an effect is unlikely to be of sufficient magnitude to alter the observed moments appreciably. The atom polarisation would need to have the improbably high value of about 50 c.c. to alter the calculated values of the moments by 0·1 D. The fact that the results for all the salts, other than those of the two carboxylic acids, can be explained satisfactorily on the basis of a zero apparent moment for their dimers, which presumably form planar quadrupoles, supports the view that the atom polarisation in the monomers is not very large, as otherwise it would also appear in the dimers.

Using the experimental data of Geddes and Kraus,[2] similar calculations have been made for tetra-n-butylammonium bromide and perchlorate and tetraisopentylammonium thiocyanate.

For many of the compounds, the specific volumes of the solutions varied very little over the concentration ranges studied and the refractive indices were indistinguishable from that of the pure solvent. Hence the dielectric constants only of these solutions were measured, and the orientation polarisations $_{\mu}P$ of the solutes were calculated by application of the relationship $_{\mu}P = 3\alpha v_1 M_2/(\varepsilon_1 + 2)^2$, where α is the limiting value of $(\partial\varepsilon/\partial w)$ at zero concentration, v_1 is the specific volume of the solute, and ε_1 is its dielectric constant. This is identical with an expression suggested previously,[7] except that here we neglect the equivalent refractive index term which for these compounds is very small.

TABLE 2.

	α_M	$_{\mu}P_M$ (c.c.)	μ_M (D)	α_D	$_{\mu}P_D$ (c.c.)	μ_D (D)	$10^{-6}K$ (cm.^{3} mole^{-1})
Tetra-n-butylammonium iodide	47·8	3319	12·7	0	0	0	1·56
,, ,, chloroacetate	70·5	4465	14·8	5·0	633	5·6	2·66
,, ,, benzoate	43·5	2969	12·06	10·0	1354	8·2	1·51
,, ,, picrate	53·9	4770	15·3 *	—	—	—	—
Cetylpyridinium benzoate	14·3	1148	7·59	—	—	—	—
Tetra-n-butylammonium bromide	50·8	3051	12·2 †	0	0	0	2·96
,, ,, perchlorate ...	94·9	6047	17·2 ‡	0	0	0	7·76
Tetraisopentylammonium thiocyanate	73·0	4866	15·4 §	0	0	0	0·51

Previous values for benzene solutions: * 17·8 D,[2] 20·8 D,[3] 15·1 D,[4] 15·70 D; [5] † 11·6 D,[2] 13·9 D; [3] ‡ 14·1 D; [2] § 15·4 D.[2]

The results are summarised in Table 2, where the subscripts M and D refer to the monomer and dimer, respectively. The dipole moments are of the same order of magnitude as the values reported previously for compounds which must exist as ion-pairs in benzene solution. For the salts with symmetrical anions the values increase progressively with increasing ionic size, but for tetra-n-butylammonium chloroacetate, benzoate, and picrate the moments are rather lower than would be expected relative to those of the other salts. The anions of these salts have permanent moments, however, which oppose the dipole moment of the ion-pair, and these should be taken into account when making comparisons.

From the results recorded in Table 2 it should be possible to derive approximate values of the charge separations, r, in the ion-pairs. Direct calculation by applying the relationship $\mu = er$ (where e is the electronic charge), as was used by Geddes and Kraus,[2] is highly inaccurate owing to the mutual polarisation of the ions. The expression $\mu = er(1 - \gamma/r^3)$ (where γ is the sum of the polarisabilities of the ions), which was used by Davies and Williams,[4] is an improvement, but neglects the effects of the induced dipoles on the opposite ions. These were included in Debye's treatment [8] of such systems as the hydrogen chloride molecule, but the theory is inadequate when either ion is itself dipolar. Debye's method can be extended to such ion-pairs if, as a first approximation, the following assumptions are made:

(*a*) The charges within each ion are so distributed that their effects on the other ion can be equated with those of point charges at the polarisable centres of the ions.

(*b*) The distances involved are large enough for the ions to be characterised by their polarisabilities.

(*c*) The ions are so oriented in the ion-pair that their dipoles act along the axis joining the charge centres of the ions and in the reverse sense to the resultant dipole.

The first two of these assumptions were also inherent in the Debye treatment.

On this basis, if the dipole moments of the constituent ions are μ_1 and μ_2, and their polarisabilities are γ_1 and γ_2, respectively, the total resultant dipole moment will be given, as a first approximation, by:

$$\mu = er - (\mu_1 + \mu_2) - (\mu_1' + \mu_2'),$$

where μ_1' and μ_2' are the moments induced in the two ions through polarisation by the

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[7] Smith, *Trans. Faraday Soc.*, 1950, **46**, 394.

[8] Debye, " Polar Molecules," Chemical Catalog Co., New York, 1929, p. 60.

fields E_1 and E_2 produced by the oppositely charged ions. These induced moments are given by

$$\mu_1' = \gamma_1 E_1 = \frac{\gamma_1}{\varepsilon}\left[\frac{e}{r^2} + \frac{2(\mu_2 + \mu_2')}{r^3}\right]$$

and

$$\mu_2' = \gamma_2 E_2 = \frac{\gamma_2}{\varepsilon}\left[\frac{e}{r^2} + \frac{2(\mu_1 + \mu_1')}{r^3}\right],$$

where ε is the dielectric constant of the intervening medium. Solution of these equations with respect to μ_1' and μ_2', followed by addition of the results, gives

$$\mu_1' + \mu_2' = \frac{er^4(\gamma_1 + \gamma_2)/\varepsilon + 2r^3(\gamma_1\mu_2 + \gamma_2\mu_1)/\varepsilon + 4\gamma_1\gamma_2 er/\varepsilon^2 + 4\gamma_1\gamma_2(\mu_1 + \mu_2)/\varepsilon^2}{r^6 - 4\gamma_1\gamma_2/\varepsilon_2}$$

For the tetrabutylammonium ion, μ_1 can be taken as zero, whilst for the cetylpyridinium ion, it is likely to be small and, for steric reasons, its axis is likely to be almost at right angles to the resultant moment of the ion-pair, so that its effect can again be neglected. Hence

$$\mu = er - \mu_2 - \frac{er^4(\gamma_1 + \gamma_2)/\varepsilon + 2r^3\gamma_1\mu_2/\varepsilon + 4er\gamma_1\gamma_2/\varepsilon^2 + 4\gamma_1\gamma_2\mu_2{}^2/\varepsilon^2}{r^6 - 4\gamma_1\gamma_2/\varepsilon^2} \qquad (3)$$

When the appropriate values of ε, γ_1, γ_2, and μ are introduced, this can be solved for r graphically.

The values of γ_1 and γ_2 can be deduced from the molar refractions, $[R]$, of the ions by use of the relationship $\gamma = 3[R]/4\pi N = 3{\cdot}964 \times 10^{-25}[R]$. For symmetrical anions, μ_2 is zero, when the expression reduces to that of Debye, but for other ions it is somewhat uncertain; it seems reasonable to assume that for the benzoate and picrate ions it may be approximately equal to that of nitrobenzene (4·0 D), and that for the chloroacetate ion it is about 3·0 D. The correct value for ε is also open to doubt. In similar problems arising for electrolyte solutions, it is customary to use the dielectric constant of the medium, but in the present instance it seems improbable that solvent penetrates between the ions. Hence it seems more reasonable to assume, with Debye, that ε is unity.

TABLE 3.

	μ (D)	$10^{24}\gamma_1$ (c.c.)	$10^{24}\gamma_2$ (c.c.)	μ_2 (D)	r (Å) (eqn. 3)	r (Å) (eqn. 4)	α (Å)
Tetra-n-butylammonium bromide	12·2	32·5	5·0	0	4·69	4·44	
,, ,, iodide	12·7	32·5	7·5	0	4·86	4·56	5·88
,, ,, perchlorate...	17·2	32·5	5·9	0	5·21	5·08	5·87
,, ,, chloroacetate	14·8	32·5	7·0	3·0	5·49	5·18	
,, ,, benzoate......	12·1	32·5	12·8	4·0	5·58	5·09	
,, ,, picrate	15·3	32·5	16·0	4·0	5·94	5·39	
Cetylpyridinium benzoate	7·5	41·8	12·8	4·0	4·97	4·78	

The intercharge distances, r, calculated in this way are given in Table 3, which also includes the values obtained by use of the simpler relationship

$$\mu = er(1 - \gamma/r^3) - \mu_2 \qquad (4)$$

which includes the moment of the dipolar ion, but neglects its polarising effect on the other ion and also the secondary effects of the induced dipoles on the opposite ions. It is evident that the omission of these effects makes an appreciable difference to the results. The values of r obtained by application of eqn. 3 are still smaller, however, than the sums of the ionic radii (*a*) derived by Kraus and his collaborators [9] from conductance measurements (shown in the last column of Table 3). This is not surprising, as the correct interpretation of the *a* value is not completely clear. Also, the measurements of the dipole moments were carried out in solution, so that the polarising effects of the ion-pairs upon the medium cause the observed values to be lower than the true values. Hence the *r* values should be slightly larger than those given here.

The relative values of *r*, however, increase reasonably with increasing size of the anion. An apparent exception arises in the case of cetylpyridinium benzoate. In this compound, however, the charge centre of the cation must lie near to the nitrogen atom whilst the carboxyl group of the anion probably lies in a plane at right angles to the axis of symmetry of the pyridine ring. Hence the charges will be able to approach one another more closely than they can in tetra-n-butylammonium salts. There is much uncertainty as to what value of the polarisibility should be taken for the highly anisotropic cetylpyridinium ion, so the charge separation calculated must be regarded as even more approximate than in the other cases. Unfortunately, simpler cetylpyridinium salts are too sparingly soluble in benzene for study by this method.

EXPERIMENTAL

Materials.—" Laboratory Reagent " grade tetra-n-butylammonium iodide was recrystallised from alcohol and dried in a vacuum; it had m. p. 145°. Tetra-n-butylammonium picrate was prepared by mixing equimolecular amounts of tetra-n-butylammonium hydroxide in water with picric acid in alcohol. The precipitated salt was recrystallised several times from benzene; it had m. p. 90°. Tetra-n-butylammonium chloracetate was prepared similarly by mixing the hydroxide with chloracetic acid, followed by evaporation in a vacuum. Solidification occurred only after prolonged storage in a vacuum over phosphorus pentoxide. Tetra-n-butylammonium benzoate and cetylpyridinium benzoate were both made by interaction of the iodide with a slight excess of silver benzoate in alcoholic solution. The silver iodide was separated and the solution evaporated in a vacuum. The cetylpyridinium salt was recrystallised twice, from benzene; it had m. p. 104°.

Benzene was purified as described previously.[10]

Measurements.—Dielectric constants were determined at 25·00° with the type of apparatus described previously,[10] but with the addition of an 8·5-pF standard micrometer condenser in parallel with the main measuring condenser. With the micrometer condenser at a predetermined setting, balance was attained with the main condenser whilst pure solvent was in the test condenser. The change in capacitance on replacing solvent by solution was then measured on the micrometer condenser.

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[9] Kraus, *J. Phys. Chem.*, 1956, **60**, 129.

[10] Few, Smith, and Witten, *Trans. Faraday Soc.*, 1952, **48**, 211.