408. *The Conductivity of Some Quaternary Ammonium and Amine Picrates in Acetonitrile at 25°.*

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The conductivity, in acetonitrile at 25°, of three tetra-*n*-alkylammonium and two amine picrates has been investigated in the concentration range $4{\cdot}77 \times 10^{-6}$ to $6{\cdot}25 \times 10^{-3}$N, and the limiting equivalent conductance Λ_0 computed for each salt. In $<10^{-3}$N-solutions, tetraethyl-, tetra-*n*-butyl-, and tetra-*n*-pentyl-ammonium picrate conformed to the Debye–Hückel–Onsager equation, the plots of Λ against $c^{0{\cdot}5}$ being linear. For $>10^{-3}$N-solutions the plots become convex to the concentration axis. Aniline picrate dissociates simultaneously into ionic and molecular species, and the magnitudes of the respective dissociation constants indicate that the non-ionic process predominates. Tribenzylamine picrate, however, appears to exist in acetonitrile almost exclusively in an ionic form, in contrast to its behaviour in other solvents. Dissymmetry in the cation markedly reduces the dissociation constant. The effect of the solvent on these several equilibria cannot adequately be expressed solely in terms of the macroscopic dielectric constant.

The present theory of conductivity is based, in part, on the assumptions that the solvent medium is continuous and isotropic, and that its influence on ionic processes can be described in terms of a macroscopic dielectric constant and macroscopic viscosity. It has been pointed out, however, that if the solvent is composed of large molecules the above assumptions can no longer be justified and anomalous effects may arise.[1] In work, to be

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[1] Fuoss and Elliott, *J. Amer. Chem. Soc.*, 1939, **61**, 294.

reported later, on the conductance of certain tetra-*n*-alkylammonium and amine picrates in non-aqueous media having large molecules, it was deemed necessary to use an additional solvent as a reference standard with which to compare the conductance–concentration relations of these systems. Acetonitrile was chosen since its molecule is very small, and the solvent may here be presumed to approximate to the ideal isotropic continuum; further, its dielectric constant is high enough for direct extrapolation of experimental data so as to provide reasonably accurate values for the limiting conductances of the various salts. The behaviour of these electrolytes in acetonitrile is broadly in agreement with current theory and with other published results. Certain points, however, require comment since there is some evidence of solvent effects which cannot adequately be explained in terms of the present theory.

EXPERIMENTAL

Conductance was measured by the method, and with the equipment, described earlier[2] for the more highly conducting dialkyl phthalate solutions.

The dielectric constant of acetonitrile was measured on a low-voltage Schering bridge in a cell previously calibrated with air and benzene.

Solvent viscosity was determined in an Ostwald viscometer of standard pattern.

Materials were prepared and purified as follows: acetonitrile was allowed to stand over solid potassium hydroxide, then over calcium chloride, refluxed over phosphoric oxide for 50 hr., and repeatedly distilled from fresh portions of this oxide. It was not possible to reproduce Walden and Birr's observation[3] that the phosphoric oxide eventually remained colourless: our experience is similar to that of Smith and Witten.[4] The solvent was fractionated from anhydrous potassium carbonate through a 75 cm. column packed with Fenske helices, first and last fractions (each 10% of the whole) being rejected. The purified material was twice redistilled, only the middle fraction being collected. At all stages the solvent was protected with phosphoric oxide from atmospheric contamination. Our product had b. p. 81·7°/760 mm., n_D^{20} 1·3438, d_4^{25} 0·7767, ε_{25} 36·2, η_{25} 0·34376 centipoise, κ_{25} 5·41 × 10^{-8} mho (lit., b. p. 81·7°/760 mm.,[4] n_D^{20} 1·3438,[5] d^{25} 0·7767,[4] 0·77683,[3] η_{25} 0·3437$_6$,[3] κ_{25} 5·39—8·60 × 10^{-8} mho[3]).

Tetraethylammonium picrate was prepared in two ways from recrystallised tetraethylammonium bromide: (*a*) This salt was shaken with an aqueous suspension of freshly prepared silver oxide at 45°, the whole then filtered through sintered glass and neutralised with the calculated quantity of picric acid; the product was recrystallised several times from conductivity water. (*b*) The bromide was treated with silver picrate in alcohol. The organic picrate was twice precipitated from hot alcohol by addition of water and of ethyl acetate severally. The two products dried at 110° and stored in a vacuum desiccator over phosphoric oxide had identical physical properties, *viz.*, m. p. 255·8° (lit., m. p. 255·5—255·8°,[6] 255·8°,[7] 256° [8]).

Tetra-*n*-butyl- and tetra-*n*-pentyl-ammonium picrate were obtained by metathesis of silver picrate in hot alcoholic solution with the corresponding quaternary ammonium bromide which had been prepared by Ostwald and Roederer's method.[9] In each case the tetra-alkylammonium picrate was repeatedly crystallised from alcohol, the final product being dried for some weeks *in vacuo* over phosphoric oxide. Tetra-*n*-butylammonium picrate had m. p. 89·5° (lit., m. p. 89°,[3] 89·5° [10]). Tetra-*n*-pentylammonium picrate had m. p. 74° (lit., m. p. 73°,[11] 73—74° [6]).

Aniline picrate was prepared by mixing hot alcoholic solutions of freshly distilled aniline and picric acid. The solution was evaporated until crystallisation commenced, and was then

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[2] French and Singer, *J.*, 1956, 1424.

[3] Walden and Birr, *Z. phys. Chem.*, 1929, **144**, 269.

[4] Smith and Witten, *Trans. Faraday Soc.*, 1951, **47**, 1304.

[5] Partington and Cowley, *Nature*, 1935, **135**, 474.

[6] Tucker and Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 454.

[7] Walden, Ulich, and Laun, *Z. phys. Chem.*, 1924, **114**, 275.

[8] *Idem, ibid.*, 1923, **106**, 49.

[9] Ostwald and Roederer, *Kolloid Z.*, 1938, **82**, 174.

[10] Mead, Fuoss, and Kraus, *Trans. Faraday Soc.*, 1936, **32**, 594.

[11] Vernon and Masterson, *J. Amer. Chem. Soc.*, 1942, **64**, 2822.

rapidly chilled in ice. The product, purified by recrystallisation from alcohol and dried *in vacuo* over phosphoric oxide, had m. p. 178—179° (decomp.) [lit., m. p. 175—177° (decomp.) [1]].

Tribenzylamine picrate was obtained by interaction of the base with a slight excess of picric acid in hot alcohol. The precipitated salt was recrystallised several times from 7 : 3 ethyl alcohol–acetone and dried at 100° before storage *in vacuo* over phosphoric oxide. The product had m. p. 191° (lit., m. p. 191° [1]).

" AnalaR " benzoic acid, recrystallised several times from hot conductivity water, dried by prolonged storage over phosphoric oxide, and sublimed at about 110°, had m. p. 121·7° (lit., m. p. 121·7° [12]).

Conductivity water was prepared from the laboratory supply of distilled water in a Bousfield still equipped with a block-tin condenser. It had κ_{25} 1 × 10^{-6} mho.

Results.—The variation in equivalent conductance with concentration for all the systems is recorded in Table 1. A solvent correction applied to the experimental readings consisted simply of subtracting the solvent conductance from that of the solution.

TABLE 1. *Conductances of the picrates in acetonitrile at* 25°.

Et_4NX		Bu_4NX		$(C_5H_{11})_4NX$		$(CH_2Ph)_3NHX$		$Ph{\cdot}NH_3X$	
10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
36·927	142·63	45·760	118·84	38·953	111·81	60·476	87·343	62·530	46·742
27·683	144·92	21·355	123·89	24·605	115·21	40·159	93·651	38·951	51·087
17·795	148·71	16·608	126·18	16·755	118·72	29·880	98·332	22·922	55·520
12·545	151·22	13·445	127·60	11·011	121·92	21·818	102·73	17·015	57·683
9·7144	152·90	12·321	128·23	8·7616	123·20	15·505	106·55	15·178	58·054
8·1863	153·69	10·662	129·11	6·0398	125·28	10·881	110·16	10·613	60·105
7·3296	154·40	7·2590	131·18.	4·7112	126·65	9·5736	111·03	7·5686	61·648
6·2305	155·29	6·4312	131·84	3·7006	127·74	7·2593	113·24	6·4043	62·255
4·4496	156·80	4·4029	133·53	2·2969	129·37	4·4323	116·63	5·5066	62·887
3·2844	157·61	2·4718	135·49	1·8118	129·80	3·8097	117·21	3·3066	64·461
1·8389	159·55	1·6574	136·66	0·77174	131·93	2·3430	119·30	2·3094	65·226
1·0065	160·95	1·3762	137·06	0·50590	132·52	1·9358	121·25	1·5985	66·198
0·33567	162·49	0·66736	138·41	0·34599	133·18	0·94702	122·76	0·92535	67·325
0·10210	163·40	0·33841	139·36	0·047712	134·49	0·28205	124·81	0·38423	68·097
						0·17620	125·63		

DISCUSSION

As with the similar series of salts measured by Walden and Birr,[3] the plots of Λ against $c^{0.5}$ for the various systems are almost linear over a concentration range up to 2 × 10^{-3}N for the tetra-alkylammonium picrates, and up to 3 × 10^{-3}N for the amine salts. In all cases the observed slope of the line is somewhat greater than the theoretical Onsager value, owing presumably to ion-pair association. Each of the five salts gave linear Fuoss plots ($c\Lambda f^2/F$ versus F/Λ) from which the limiting conductance Λ_0 and ion-pair dissociation constant K were computed. Relevant data are recorded in Table 2. At concentrations in excess of 10^{-3}N the slopes of the Λ–$c^{0.5}$ plots are less than required by theory, as is usually the case in systems of this type.

TABLE 2.

Picrates	Et_4N	Bu_4N	$(C_5H_{11})_4N$	$(CH_2Ph)_3NH$	$Ph{\cdot}NH_3$
Λ_0	164·5	141·2	135·2	126·5	70·0
10^4K	1508	706·8	339·8	144·4	—

TABLE 3.

Solvent	$CH_3{\cdot}CHCl_2$ [a]	$(CH_2Cl)_2$ [b]	$Ph{\cdot}NO_2$ [c]	MeOH [d]	$COMe_2$	MeCN [f]
$\Lambda_0\eta$	0·451	0·451	0·505	0·471	0·463	0·485
$\Lambda_0^+\eta$	0·206	0·206	0·212	0·202	0·204	0·207

[a] Healey and Martell, *J. Amer. Chem. Soc.*, 1951, **73**, 3296. [b] Ref. 6. [c] Taylor and Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 1731. [d] Evers and Knox, *ibid.*, 1951, **73**, 1739. [e] Reynolds and Kraus, *ibid.*, 1948, **70**, 1709. [f] This work.

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[12] International Critical Tables, Vol. I, McGraw-Hill Book Co. Inc., New York, 1926.

The limiting conductance of tetra-*n*-butylammonium picrate found in the present experiments may be used to compute the ion conductances of other tetra-*n*-alkylammonium ions in the same solvent. Table 3 shows that tetra-*n*-butylammonium picrate obeys Walden's rule fairly closely in a number of solvents, and a mean value of 0·207 ± 0·005 may be accepted for $\Lambda_0^+\eta$. Since the viscosity of acetonitrile at 25° is 0·0034376, it follows that Λ_0^+ should have the value 60·2 and, since $(\Lambda_0^+ + \Lambda_0^-) = 141{\cdot}1$, Λ_0^- for the picrate ion in this solvent must be 80·9. It is then possible to calculate limiting conductances for the whole series of tetra-*n*-alkylammonium ions by subtracting the value for the picrate ion (80·9) from the limiting conductance of the appropriate salt. By combining the present results with Walden and Birr's for tetramethylammonium and tetra-*n*-propylammonium picrate,[3] it can be seen from the second line of Table 4 that the cation conductances in acetonitrile decrease irregularly with increasing number of carbon atoms. Walden and Birr's values for the equivalent conductance of tetraethylammonium picrate, the only solute common to both investigations, are slightly but not significantly lower than ours over the whole range of concentration and result in a correspondingly slightly lower value of Λ_0 (163·8). The use of Walden and Birr's values of Λ_0 for the first three solutes referred to in Table 4, while giving a slightly different value for the increments as shown in the third line of the Table, do not alter the conclusions noted above. The reason for the abnormally large decrease in conductance from ethyl to propyl is not fully understood, but is a phenomenon observed in certain other solvents also.

TABLE 4.

Cation	Me_4N		Et_4N		Pr_4N		Bu_4N		$(C_5H_{11})_4N$
Λ_0^+ difference		5·9		18·7		4·8		6·1	
Λ_0^+ difference (Walden)		6·7		17·9					

Fuoss and Elliott [1] and Witschonke and Kraus [13] have shown that some amine picrates exist in certain solvents as a mixture of molecularly and ionically dissociating species, and the low value of Λ_0 for aniline picrate obtained now can similarly be explained on the basis of two equilibria in acetonitrile:

$$C_6H_5{\cdot}NH_3Pic \rightleftharpoons C_6H_5{\cdot}NH_3^+ + Pic^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (a)$$

$$C_6H_5{\cdot}NH_3Pic \rightleftharpoons C_6H_5{\cdot}NH_2 + HPic \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (b)$$

The equilibrium constants of reactions (*a*) and (*b*) will be denoted by K and k respectively. A value of the true (ionic) limiting conductance was estimated in the following way. The limiting cation conductance Λ_0^+ is approximately a function of the number n of carbon atoms present. Λ_0^+ for tetramethylammonium ($n = 4$) and for tetraethylammonium ($n = 8$) in acetonitrile is 89·6 and 83·7 respectively, the latter value being somewhat smaller than expected. A value of 87·0 may therefore be adopted for anilinium ($n = 6$). Λ_0 for aniline picrate in acetonitrile at 25° will then be (87·0 + 80·9). When this value is used, a plot of $\frac{1}{f}\left(\frac{F}{\Lambda} - \frac{1}{\Lambda_0}\right)$ against $c\Lambda f/F$, where f is the mean ion activity coefficient and F the Fuoss function, is linear over a considerable concentration range. A slight deviation occurring in very dilute solution may possibly result from the rather large solvent correction (approx. 2%) applied in this region. The ionic and molecular dissociation constants evaluated from the slope and intercept of the linear portion of the plot were found to be $K = 10{\cdot}43 \times 10^{-4}$ and $k = 23{\cdot}46 \times 10^{-4}$. It is of interest to compare these values with the corresponding figures in nitrobenzene,[13] where $K = 0{\cdot}554 \times 10^{-4}$ and $k = 0{\cdot}163 \times 10^{-4}$. The difference is particularly striking since the dielectric constants of the two solvents are very similar (acetonitrile ε 36·2; nitrobenzene ε 34·5), and it illustrates the importance of solvent properties other than the dielectric constant in conductance phenomena. It is also worthy of note that k is larger than K in acetonitrile, indicating that the non-ionic

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[13] Witschonke and Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 2472.

molecular dissociation predominates, although the reverse condition exists in nitrobenzene.

The Λ-$c^{0.5}$ plot for tribenzylammonium picrate was again linear over a considerable concentration range—at least up to $2{\cdot}5 \times 10^{-3}$N, with a slope slightly greater than theoretical, although it has been suggested elsewhere that this solute may be expected to behave as a weak electrolyte. Fuoss and Elliott,[1] on the other hand, observed that the picrates of the aromatic amines such as tribenzylamine also gave conductance curves suggesting that they exist, in certain solvents, in two modifications, one of which cannot furnish ions. This does not appear to be true for tribenzylamine picrate in acetonitrile however; or at most the ionic form appears to be present in very considerable excess. Thus the value of Λ_0 obtained from the Fuoss plot is 126·9, which gives $\Lambda_0^+ = 46{\cdot}0$ for the tribenzylammonium ion since Λ_0^- for the picrate iòn is 80·9. It will be observed (Table 2), that the element of dissymmetry in the tribenzylammonium ion, as compared with the tetra-*n*-pentylammonium ion, has brought about a marked reduction in the dissociation constant. The relative importance of the two dissociation processes discussed above with reference to aniline picrate and tribenzylamine picrate is clearly dependent both on the structure of the ions involved and on the nature of the solvent medium. This suggests that solvent–solute interaction, which is specifically ignored in the current theory of conductivity, may be an important factor in conductance processes.

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