# 289. *The Conductivity of Solutions in which the Solvent Molecule is "Large." Part I. Solutions of Tetraethylammonium Picrate in Some Phthalate Esters.*

By C. M. French and N. Singer.

The conductances of tetraethylammonium picrate in six dialkyl phthalates at 25°, 35°, and 45° have been measured over concentration ranges from $1{\cdot}03 \times 10^{-5}$ to $2{\cdot}516 \times 10^{-3}$ mole/l. The shapes of the resulting conductance curves agree with the theories of conductance in solvents of fairly low dielectric constant. Variations in the value of the Walden product $\lambda_0\eta$ from solvent to solvent, and with temperature are reported. These are accounted for by a theory of solvent–solvent and solvent–ion interaction.

Walden has shown that in a large number of solvents the product $\lambda_0\eta$ for tetraethylammonium picrate is a constant, independent of temperature, and with a value 0·563. This led to the suggestion that the solute ions are unsolvated in such solvents, solvation occurring only in those solutions where the product is less than 0·563. Thus for example the values in pyridine 0·635 (ref. 1) or 0·648 (ref. 2) and in aniline 0·635 (ref. 3) require explanation. In their work on tetrabutylammonium picrate in tritolyl phosphate, Fuoss and Elliott[4] obtained a higher value than expected; this, they attempted to explain on the assumption that, since the solvent molecules here are larger than in the usual solvents, certain configurations of them should exist that would allow the solute ions to slip between the solvent molecules without having to overcome the full macroscopic viscosity. This would naturally result in a greater ionic mobility and hence in an abnormally large $\lambda_0\eta$ value. This explanation is clearly not valid for solutions in pyridine and aniline. The only other recorded measurements in solvents having large molecules (triethanolamine, and *N*-ethyl-*N*-phenylethanolamine) are those by Bhattacharyya and Nakhate.[5] It was therefore thought to be of interest to investigate the conductance, in a series of closely related solvents of gradually increasing molecular size, of tetraethylammonium picrate which obeys Walden's rule accurately in a number of solvents of normal size. The solvents chosen for this purpose were in the first instance the dialkyl phthalates, measurement being carried out at 25°, 35°, and 45°.

## EXPERIMENTAL

The conductance of most of the solutions was measured by means of a Leeds and Northrup A.C. bridge of the Jones and Joseph type incorporating Wagner earthing. The source of alternating current was a tuned audiofrequency oscillator which was usually operated at 1000 cycles per sec. As detector a tuned audiofrequency amplifier was used in conjunction with a telephone of 30,000 ohms impedance at 1000 cycles. Leads were carefully screened.

The very high resistances obtained with the pure solvents and solutions of tetraethylammonium picrate in dioctyl and dinonyl phthalate were measured by means of a Schering bridge. The remainder of the ancillary apparatus was the same as before.

The cells used for the more highly conducting solutions were based on the design of Jones and Bollinger[6] and made of Pyrex. The electrodes were stout, circular, platinum discs, of about 3 cm. diameter and about 1·5 mm. apart. For the less conducting solutions the electrode system consisted of three concentric platinum cylinders, about 1 mm. apart, and was similar to that used by Fuoss and Kraus.[7] The cell itself consisted of an annular glass cylinder which contained the electrodes, and to the top of which were fused the tubes carrying the contact leads and the inlet tubes. This arrangement gave a cell with a small internal volume and,

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[1] Walden, Audrieth, and Birr, *Z. phys. Chem.*, 1932, **160**, *A*, 337.
[2] Pickering and Kraus, *J. Amer. Chem. Soc.*, 1949, **71**, 3288.
[3] Walden and Audrieth, *Z. phys. Chem.*, 1933, **165**, *A*, 11.
[4] Elliott and Fuoss, *J. Amer. Chem. Soc.*, 1939, **61**, 294.
[5] Bhattacharyya and Nakhate, *J. Indian Chem. Soc.*, 1947, **24**, 99.
[6] Jones and Bollinger, *J. Amer. Chem. Soc.*, 1931, **53**, 411.
[7] Fuoss and Kraus, *ibid.*, 1933, **55**, 3614.

because of the large surface area presented to the thermostat oil, led to a rapid attainment of temperature equilibrium. The cells were immersed in liquid white paraffin in a thermostat at 25° ± 0·02°. Between measurements, cells were cleaned by allowing them to stand in hot concentrated nitric acid, then steaming them out, rinsing them with acetone, and drying them in an oven. Cell constants were determined by the Ives and Sames's method,[8] with a standard solution of benzoic acid, usually $10^{-4}$N.

The solvents used were purified as follows: Dimethyl, diethyl, dibutyl, and dipentyl phthalate were washed first with sodium carbonate solution, then with distilled water, dried ($CaCl_2$), and distilled 3 times under reduced pressure, only the middle fraction being collected each time. The pure liquids were stored in a vacuum-desiccator ($P_2O_5$). Di-(2-ethylhexyl) and dinonyl phthalate were washed with sodium carbonate solution and then shaken with water; the resulting emulsion was broken by addition of ether. The ethereal solution was twice washed with water, dried ($CaCl_2$), and evaporated, and the residual liquid distilled 3 times under reduced pressure. The pure liquids were stored in a vacuum-desiccator ($P_2O_5$). The physical constants of these liquids are given in Table 1.

TABLE 1. *Physical properties of alkyl phthalates.* (The first row for each ester gives the values found; other rows give the values from the literature.)

| Phthalate | Sp. cond., κ, (mho) | $n_D^{20}$ | Viscosity, η (centipoises), at |  |  | $d_4^{25}$ | $d_4^{35}$ | $d_4^{45}$ | Dielectric const. at |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | 25° | 35° | 45° |  |  |  | 25° | 35° | 45° |
| $Me_2$ .............. | $8{\cdot}1 \times 10^{-9}$ | 1·5149 | 13·92 | 9·18 | 6·41 | 1·1865 | 1·1775 | 1·1674 | 8·37 | 8·25 | 8·11 |
|  |  | 1·5138 [a] | 13·8 [c] | 8·9 [d] | 6·3 [c] | 1·190 [e] | 1·1789 [d] |  |  |  |  |
|  |  | 1·5160 [b] |  | 9·2 [c] |  |  |  |  |  |  |  |
| $Et_2$ .............. | $1{\cdot}1 \times 10^{-9}$ | 1·5022 | 10·82 | 7·63 | 5·57 | 1·1160 | 1·1079 | 1·0991 | 7·53 | 7·34 | 7·13 |
|  |  |  | 10·6 [c] | 7·6 [c] | 5·5 [c] | 1·1172 [f] | 1·1083 [f] | 1·0995 |  |  |  |
|  |  |  | 10·06 [g] |  |  | 1·1142 [g] |  |  |  |  |  |
|  |  |  | 10·0 [e] |  |  | 1·118 [e] |  |  |  |  |  |
| $Bu_2$ .............. | $9 \times 10^{-11}$ | 1·4929 | 16·55 | 11·17 | 7·95 | 1·0426 | 1·0345 | 1·0264 | 6·36 | 6·17 | 5·99 |
|  |  | 1·49292 [h] | 16·7 [c] | 11·4 [c] | 8·1 [c] | 1·0416 [h] | 1·0331 [h] | 1·0256 [h] |  |  |  |
| $(C_5H_{11})_2$ ........ | $6{\cdot}2 \times 10^{-12}$ | 1·4885 | 27·58 | 17·03 | 11·51 | 1·0230 | 1·0132 | 1·0025 | 5·96 | 5·79 | 5·62 |
|  |  | 1·488 [e] |  |  |  | 1·022—1·025 [e] |  |  |  |  |  |
| $(CH_2{\cdot}CHEtBu)_2$ | $7{\cdot}4 \times 10^{-13}$ | 1·4863 | 58·22 | 33·67 | 21·40 | 0·9803 | 0·9731 | 0·9656 | 5·06 | 4·91 | 4·77 |
|  |  | 1·484—1·485 † [e] | 81·4 ‡ |  |  | 0·986 [d] |  |  |  |  |  |
| $(C_9H_{19})_2$ * ...... | $9{\cdot}6 \times 10^{-14}$ | 1·4825 | 77·90 | 43·14 | 27·12 | 0·9640 | 0·9570 | 0·9501 | 4·89 | 4·65 | 4·52 |

* Mixture of isomers, mostly 3 : 5 : 5-trimethylhexyl. † At 25°. ‡ At 20°.

[a] Gardner and Brewer, *Ind. Eng. Chem.*, 1937, **29**, 179. [b] Von Auwers and Heinze, *Ber.*, 1919, **52**, 600. [c] Jones, "Plasticizers, Fillers, Catalysts and Accelerators," Inst. Plastics Ind., 1947, No. 11, p. 24. [d] Swirbely, Eareckson, Matsuda, Pickard, Solet, and Tuemmler, *J. Amer. Chem. Soc.*, 1949, **71**, 507. [e] Buttrey, "Plasticizers," Cleaver-Hulme Press Ltd., London, 1950, pp. 5, 6, 11, 13. [f] Perkin, *J.*, 1896, **69**, 477. [g] Baker, *J.*, 1913, **103**, 166. [h] Berko and Bradley, *Proc. Roy. Soc.*, 1949, *A*, **198**, 226.

Conductivity water was prepared by running distilled water through a Biodeminrolit ion-exchange resin column. The resulting water had a specific conductance of 0·8—1·0 × $10^{-6}$ mho.

"AnalaR" benzoic acid was further purified by recrystallisation and sublimation at about 110°; it had m. p. 122° (lit., 122·38° [9]).

Tetraethylammonium picrate was prepared by interaction between hot aqueous solutions of the recrystallised tetraethylammonium bromide and silver picrate (prepared by the addition of picric acid to a suspension of silver oxide). The resulting salt was recrystallised 4 times from alcohol–ether, dried at 80°, and stored in a vacuum-desiccator ($P_2O_5$). It had m. p. 256·5—257° (lit., 255·8° [10]).

*Results.*—Table 1 records physical properties for the solvents, and recorded values where available.

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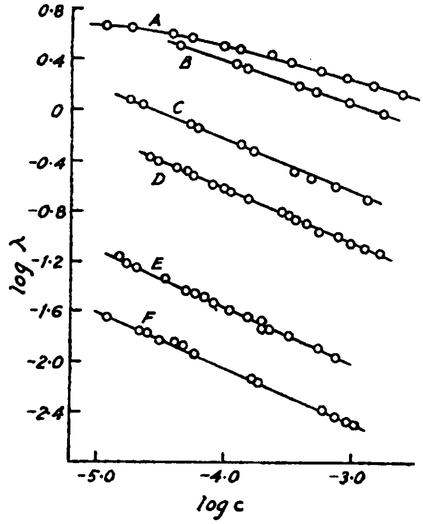
[8] Ives and Sames, *J.*, 1943, 511.

[9] Swab and Vickers, *J. Res. Nat. Bur. Stand.*, 1941, **34**, 333.

[10] Walden, Ulich, and Laun, *Z. phys. Chem.*, 1925, **114**, *A*, 286.

The Figure illustrates the variation in equivalent conductance, with concentration, of tetraethylammonium picrate in the six solvents at 25°. The curves at the other temperatures are similar. The exact experimental data for all systems are given in Table 2.



*Phthalates : A, dimethyl; B, diethyl; C, dibutyl; D, dipentyl; E, di-(2-ethylhexyl) ; F, di " nonyl."*

DISCUSSION

In all cases the shapes of the $\lambda$–$\sqrt{c}$ curves (where $\lambda$ is the equivalent conductance, and $c$ is the concentration in moles/l.) can be completely explained on the basis of the formation of ion pairs in the dilute regions, and of triple ions in the more concentrated solutions. The progressive decrease in slope of the linear (log $\lambda$–log $c$) plots to a limiting value of $-\frac{1}{2}$ with decrease in dielectric constant expected on this basis was obtained in all the systems studied. Thus the slopes decrease from about —0·28 for solutions in dimethyl phthalate of dielectric constant 8·6, to —0·46 for solutions in dinonyl phthalate of dielectric constant 4·9, both at 25°. Similar results are obtained at the other temperatures.

A value for the limiting equivalent conductance and for the dissociation constant for ion-pair formation in each system, was obtained by Shedlovsky's graphical extrapolation method,[11] and the results are shown in Table 3 together with the corresponding values of the Walden product.

Points requiring explanation are : (1) $\lambda_0\eta$ decreases with increasing size of the solvent molecule, being greater than the " normal " value in dimethyl—dipentyl phthalate, and less in the other two solvents. The direction of this change is the reverse of that expected on the basis of Fuoss and Elliott's[4] explanation. (2) $\lambda_0\eta$ increases with increase in temperature when the solvent molecule is large. The critical size of the solvent molecule at which this effect occurs may depend also on the size of the solute ions and, for the system reported here, it is only present in the three largest solvents, as seen from Table 3. (3) The equilibrium constant for ion-pair formation decreases less rapidly from dimethyl to dinonyl phthalate than expected from the dielectric constants of these solvents. These variations can be accounted for in a general way by ion-solvent interaction. In a dipolar solvent, a solute ion will be surrounded by, and associated with, a number of solvent molecules. All types of solvation from chemical binding to the formation of a labile complex due to Coulomb forces between the charge on the ion and the dipoles of the solvent are generally possible. In the present systems solvation would be restricted to the loose association of a number of solvent molecules with each ion, with the consequent hindering of its passage through solution. The extent of such solvation would depend on the dipole

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[11] Shedlovsky, *J. Franklin Inst.*, 1938, **225**, 739.

TABLE 2. *Equivalent conductance* (λ) *of tetraethylammonium picrate in alkyl phthalates.*

| $Me_2$ phthalate | | $Et_2$ phthalate | | $Bu_2$ phthalate | | $(C_5H_{11})_2$ phthalate | | $(C_8H_{17})_2$ phthalate | | $(C_9H_{19})_2$ phthalate | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^4c$ | $\lambda$ | $10^4c$ | $\lambda$ | $10^4c$ | $\lambda$ | $10^4c$ | $10\lambda$ | $10^4c$ | $10\lambda$ | $10^4c$ | $10^2\lambda$ |
| | | | | | *Temperature* : 25°. | | | | | | |
| 25·16 | 1·294 | 18·03 | 0·8735 | 13·72 | 0·1950 | 16·81 | 0·6943 | 7·618 | 0·1080 | 10·09 | 0·3086 |
| 14·58 | 1·497 | 9·456 | 1·105 | 7·651 | 0·2436 | 13·17 | 0·7505 | 5·446 | 0·1246 | 9·354 | 0·3184 |
| 8·730 | 1·728 | 5·206 | 1·330 | 4·976 | 0·2856 | 9·996 | 0·8669 | 3·183 | 0·1561 | 7·305 | 0·3663 |
| 5·725 | 1·956 | 3·880 | 1·516 | 3·812 | 0·3254 | 8·117 | 0·9318 | 2·203 | 0·1823 | 5·928 | 0·3940 |
| 3·211 | 2·297 | 1·470 | 2·064 | 1·699 | 0·4506 | 5·604 | 1·065 | 2·048 | 0·1909 | 1·905 | 0·6548 |
| 2·235 | 2·545 | 1·227 | 2·275 | 1·368 | 0·5060 | 3·689 | 1·297 | 1·977 | 0·1953 | 1·873 | 0·6597 |
| 1·270 | 2·922 | 0·4339 | 3·183 | 0·5916 | 0·7103 | 3·250 | 1·404 | 1·551 | 0·2188 | 1·763 | 0·6845 |
| 0·9253 | 3·175 | | | 0·5465 | 0·7315 | 3·061 | 1·439 | 1·116 | 0·2539 | 0·5861 | 1·120 |
| 0·5274 | 3·550 | | | 0·2207 | 1·066 | 1·526 | 1·934 | 0·7936 | 0·2961 | 0·4622 | 1·269 |
| 0·3818 | 3·773 | | | 0·1806 | 1·142 | 1·067 | 2·280 | 0·6840 | 0·3183 | 0·3975 | 1·328 |
| 0·1732 | 4·277 | | | | | 1·018 | 2·305 | 0·5783 | 0·3400 | 0·3091 | 1·480 |
| 0·1169 | 4·435 | | | | | 0·8239 | 2·450 | 0·5074 | 0·3621 | 0·2398 | 1·655 |
| | | | | | | 0·5481 | 2·984 | 0·3489 | 0·4390 | 0·2248 | 1·697 |
| | | | | | | 0·4993 | 3·107 | 0·2353 | 0·5054 | 0·1187 | 2·241 |
| | | | | | | 0·4409 | 3·327 | 0·1676 | 0·5593 | | |
| | | | | | | 0·3011 | 3·863 | 0·1484 | 0·6310 | | |
| | | | | | | 0·2724 | 4·002 | 0·1030 | 0·7439 | | |
| | | | | | *Temperature* : 35°. | | | | | | |
| 24·96 | 1·943 | 17·90 | 1·247 | 13·61 | 0·2921 | 16·65 | 1·108 | 7·561 | 0·1919 | 10·02 | 0·5863 |
| 14·46 | 2·255 | 9·386 | 1·578 | 7·591 | 0·3658 | 13·04 | 1·228 | 5·405 | 0·2217 | 9·286 | 0·6029 |
| 8·658 | 2·595 | 5·168 | 1·898 | 4·938 | 0·4439 | 9·901 | 1·396 | 3·160 | 0·3204 | 7·252 | 0·6793 |
| 5·679 | 2·952 | 3·85 | 2·171 | 3·783 | 0·4875 | 8·040 | 1·507 | 2·187 | 0·3210 | 5·885 | 0·7423 |
| 3·185 | 3·464 | 1·459 | 2·949 | 1·686 | 0·6727 | 5·550 | 1·763 | 2·033 | 0·3393 | 1·891 | 1·196 |
| 2·217 | 3·847 | 1·218 | 3·251 | 1·358 | 0·7541 | 3·653 | 2·082 | 1·962 | 0·3452 | 1·859 | 1·199 |
| 1·259 | 4·408 | 0·4308 | 4·535 | 0·5870 | 1·067 | 3·218 | 2·220 | 1·540 | 0·3764 | 1·750 | 1·257 |
| 0·9177 | 4·799 | | | 0·5423 | 1·068 | 3·032 | 2·277 | 1·108 | 0·4367 | 0·5818 | 2·106 |
| 0·5231 | 5·359 | | | 0·2190 | 1·594 | 1·512 | 3·056 | 0·7877 | 0·5096 | 0·4589 | 2·313 |
| 0·3787 | 5·730 | | | 0·1792 | 1·742 | 1·057 | 3·556 | 0·6789 | 0·5625 | 0·3946 | 2·499 |
| 0·1717 | 6·489 | | | | | 1·009 | 3·626 | 0·5740 | 0·6084 | 0·3069 | 2·786 |
| 0·1160 | 6·746 | | | | | 0·8160 | 3·930 | 0·5036 | 0·6451 | 0·2381 | 3·106 |
| | | | | | | 0·5429 | 4·712 | 0·3463 | 0·7389 | 0·2231 | 3·204 |
| | | | | | | 0·4945 | 4·902 | 0·2335 | 0·9174 | 0·1179 | 4·264 |
| | | | | | | 0·4366 | 5·167 | 0·1663 | 0·9590 | | |
| | | | | | | 0·2983 | 6·070 | 0·1472 | 1·088 | | |
| | | | | | | 0·2698 | 6·393 | 0·1022 | 1·283 | | |
| | | | | | *Temperature* : 45°. | | | | | | |
| 24·76 | 2·725 | 17·76 | 1·694 | 13·50 | 0·4157 | 16·47 | 1·661 | 7·503 | 0·3165 | 9·942 | 1·011 |
| 14·34 | 3·174 | 9·312 | 2·148 | 7·532 | 0·5224 | 12·90 | 1·842 | 5·364 | 0·3657 | 9·219 | 1·043 |
| 8·589 | 3·645 | 5·128 | 2·583 | 4·899 | 0·6058 | 9·795 | 2·088 | 3·135 | 0·4561 | 7·200 | 1·176 |
| 5·634 | 4·161 | 3·821 | 2·951 | 3·753 | 0·6990 | 7·954 | 2·260 | 2·170 | 0·5296 | 5·842 | 1·279 |
| 3·159 | 4·877 | 1·448 | 4·009 | 1·673 | 0·9528 | 5·491 | 2·644 | 2·017 | 0·5570 | 1·877 | 2·136 |
| 2·199 | 5·434 | 1·209 | 4·415 | 1·347 | 1·074 | 3·614 | 3·119 | 1·947 | 0·5701 | 1·738 | 2·223 |
| 1·249 | 6·233 | 0·4274 | 6·147 | 0·5824 | 1·516 | 3·184 | 3·329 | 1·528 | 0·6377 | 0·5776 | 3·672 |
| 0·9104 | 6·788 | | | 0·5381 | 1·519 | 3·000 | 3·415 | 1·099 | 0·7402 | 0·4552 | 4·000 |
| 0·5189 | 7·569 | | | 0·2173 | 2·265 | 1·496 | 4·573 | 0·7817 | 0·8639 | 0·3918 | 4·333 |
| 0·3756 | 7·990 | | | 0·1778 | 2·425 | 1·045 | 5·333 | 0·6737 | 0·9251 | 0·3047 | 4·930 |
| 0·1704 | 9·136 | | | | | 0·9978 | 5·439 | 0·5696 | 0·9995 | 0·2363 | 5·537 |
| 0·1150 | 9·502 | | | | | 0·8073 | 5·944 | 0·4997 | 1·056 | 0·2215 | 5·724 |
| | | | | | | 0·5371 | 7·069 | 0·3436 | 1·254 | 0·1169 | 7·459 |
| | | | | | | 0·4893 | 7·354 | 0·2317 | 1·510 | | |
| | | | | | | 0·4320 | 7·751 | 0·1651 | 1·757 | | |
| | | | | | | 0·2951 | 9·108 | 0·1461 | 1·847 | | |
| | | | | | | 0·2669 | 9·539 | 0·1014 | 2·179 | | |

TABLE 3.

| | $10^7K$ at | | | $\lambda_0$ (ohm$^{-1}$ cm.$^2$) at | | | $\lambda_0\eta$ at | | |
|---|---|---|---|---|---|---|---|---|---|
| Phthalate | 25° | 35° | 45° | 25° | 35° | 45° | 25° | 35° | 45° |
| $Me_2$ ............... | 467·7 | 497·7 | 494·3 | 5·05 | 7·73 | 10·96 | 0·703 | 0·710 | 0·703 |
| $Et_2$ .................. | 158·1 | 168·3 | 159·2 | 6·52 | 9·30 | 12·63 | 0·705 | 0·710 | 0·704 |
| $Bu_2$ ............... | 18·32 | 21·14 | 18·58 | 5·92 | 5·81 | 8·15 | 0·649 | 0·648 | 0·655 |
| $(C_5H_{11})_2$ ......... | 10·64 | 8·53 | 7·91 | 2·08 | 3·57 | 5·54 | 0·574 | 0·608 | 0·639 |
| $(C_8H_{17})_2$ ......... | 8·87 | 5·78 | 4·41 | 0·276 | 0·588 | 1·12 | 0·162 | 0·198 | 0·239 |
| $(C_9H_{19})_2$ ............ | 7·31 | 5·58 | 3·13 | 0·117 | 0·263 | 0·465 | 0·092 | 0·114 | 0·126 |

moment of the solvent, the size of the ion, the distance of closest approach of the ion to the solvent dipole, and the dielectric constant of the solvent.

Although Walden ascribed the observed constancy of $\lambda_0\eta$ in solvents of dielectric constant 10—35 to non-solvation, uniform solvation would lead to the same result. Considerations just noted suggest that large ions such as $Et_4N^+$ are solvated, so that a " normal " value of $\lambda_0\eta$ here may be due to a mutual compensation of changes in the above factors within certain limits. It might then be expected that the Walden product would be subject to specific solvent effects.

TABLE 4.

| | Ion-pair size ($10^{-8}$ cm.) at | | | | Ion-pair size ($10^{-8}$ cm.) at | | |
|---|---|---|---|---|---|---|---|
| Phthalate | 25° | 35° | 45° | Phthalate | 25° | 35° | 45° |
| $Me_2$ ............ | 5·86 | 5·70 | 5·65 | $(C_5H_{11})_2$ ...... | 6·03 | 5·85 | 5·85 |
| $Et_2$ ............ | 5·80 | 5·85 | 5·83 | $(C_8H_{17})_2$ ...... | 7·33 | 7·00 | 6·81 |
| $Bu_2$ ............ | 5·84 | 5·82 | 5·85 | $(C_9H_{19})_2$ ...... | 7·62 | 7·49 | 7·21 |

Dimethyl phthalate has a large dipole moment[12] (2·3; 2·8 D), and its dielectric constant is low. It may therefore be assumed that the pure ester is associated in such a way that the dipoles are as close together as possible and will be shielded from close approach by, or interaction with, the solute ions. The solute ions may accordingly be regarded as practically unsolvated in this solvent [and also in diethyl phthalate (dipole moment 2·4; 2·7; 2·8)]. As the bulk of the alcohol residue in the ester increases, it will become increasingly difficult for two solvent molecules to approach each other closely, and their interaction energy will therefore decrease. This type of solvent association will decrease progressively from dibutyl to dinonyl phthalate. Ion solvation will then increase and $\lambda_0\eta$ decrease in the same direction. Further, $\lambda_0\eta$ will be smaller in these large molecule solvents than in normal systems.

The large size of the ions and of the solvating molecules in these systems will result in a small interaction energy between the two. A slight increase in temperature will therefore be sufficient to decrease the amount of solvation significantly. The $\lambda_0\eta$ product should thus increase with increase in temperature, as is found with the three largest solvents (Table 3). The absence of this temperature effect in the two smallest solvents would be consistent with the suggestion above, that the solute ions are practically unsolvated in these solvents. Dibutyl phthalate thus appears to be the solvent molecule of critical size for these phenomena in the present systems.

Comparison of the present $\lambda_0\eta$ values with those of similar systems further supports the explanation offered here. Thus $\lambda_0\eta$ for tetraethylammonium picrate in both pyridine[1] ($\varepsilon_{25}$ 12·01) and aniline[2] ($\varepsilon_{25}$ 7·2) is of the order of 0·650. Although both these solvents and the phthalates have strong localised dipoles, yet if solvent association occurs shielding of the dipoles in the latter systems will be more complete, and $\lambda_0\eta$ might therefore be expected to be correspondingly greater. This is verified experimentally with dimethyl and diethyl phthalate as solvent. Conversely, a normal result would be expected, and is found, in ethylene dichloride[13] ($\varepsilon_{25}$ 10·1; $\lambda_0\eta$ 0·545) and ethylidene chloride[14] ($\varepsilon_{25}$ 10·00; $\lambda_0\eta$ 0·542), where, even if solvent association occurs, the geometry of the molecule precludes shielding of the dipole from an approaching ion. Fuoss and Elliott's results[4] are explicable on the same basis, tritolyl phosphate having a strong localised dipole which is shielded if solvent association occurs.

This kind of solvent association will only occur if the solvent is of fairly low dielectric constant, when the forces between the dipoles will be large. Thus a normal $\lambda_0\eta$ value would be expected, and is found, in such solvents as nitrobenzene[15] (0·586) and in acetophenone[16] (0·591).

[12] Wesson, " Tables of Electric Dipole Moments," Technology Printers, Cambridge, Mass., 1949.
[13] Walden and Busch, *Z. phys. Chem.*, 1929, **140**, *A*, 89.
[14] Healey and Martell, *J. Amer. Chem. Soc.*, 1951, **73**, 3296.
[15] Taylor and Kraus, *ibid.*, 1947, **69**, 1731.
[16] Walden and Birr, *Z. phys. Chem.*, 1933, **165**, *A*, 32.

Finally the theory of ion-pair formation leads to the familiar equation for the equilibrium constant:

$$\frac{1}{K} = \frac{4\pi N}{1000}\left[\frac{\varepsilon^2|Z_1Z_2|}{DkT}\right]^3 \cdot Q(b)$$

where $b = \frac{|Z_1Z_2|\varepsilon^2}{aDkT}$ and $a$ is the radius of the ion pair and the other symbols have their usual significance. By using these two equations, a graph of log $b$ against log $Q(b)$, and the values of $K$ given in Table 3, the $a$ values in the various solvents may be computed. The results are shown in Table 4, and demonstrate the gradual increase in size of the ion pair in the series of solvents from dimethyl to dinonyl phthalate.

The suggestions offered here are clearly an over-simplification, but nevertheless they afford a qualitative explanation for differences in behaviour of a number of systems, including those in which the solvent molecule is large. It is hoped that further work on large solvent molecule systems now in progress will clarify other points.

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Department of Chemistry, Queen Mary College,
Mile End Road, London, E.1.

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