

**719.** *The Conductance of Solutions in which the Solvent Molecule is "Large." Part IV.<sup>1</sup> Amine Picrates in Triethyl Phosphate.*

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The conductances in triethyl phosphate at 40° of three quaternary ammonium picrates and two amine picrates have been measured in the concentration range  $4.59 \times 10^{-6}$  to  $6.10 \times 10^{-4}$ N. One of the systems was studied also at 25° and 55°. All solutes behaved as moderately strong electrolytes. The ratios to each other of the limiting equivalent conductances of the three quaternary ammonium picrates were fairly close to the values in solvents having smaller molecules, *e.g.*, acetonitrile. Walden products were unexpectedly high, and anomalies were encountered in the ion-pair dissociation constants. Ionic rather than molecular dissociation was observed for the two amine picrates.

TRITOLYL and trioctyl phosphates have already been used to study the electrical conductance of non-aqueous systems where the solvent molecules are larger than those of common solvents, and the work has now been extended to solutions in triethyl phosphate. This solvent has much smaller molecules than the phosphoric esters employed earlier<sup>1</sup> so that the effect of chemical nature and structure, as opposed to mere molecular size, might become dominant factors. Conductance relationships in this solvent might therefore be expected to approximate to those of solutions in solvents of conventional size.

#### EXPERIMENTAL

Solutes were purified and conductances measured as described earlier.<sup>1</sup>

Triethyl phosphate was dried ( $\text{Na}_2\text{SO}_4$ ), and distilled under reduced pressure. The middle fraction (~80%) was stored for several weeks over anhydrous sodium sulphate, again fractionated, and repeatedly distilled under reduced pressure until the specific conductance reached a constant

<sup>1</sup> Part III, French and Muggleton, *J.*, 1957, 5064.

low value [b. p. 216°/760 mm. (lit.,<sup>2</sup> 216°/760 mm.), 70.5°/4 mm. (lit.,<sup>3</sup> 75.5°/5 mm.);  $n_D^{20}$  1.40527 (lit.,<sup>2</sup>  $n_D^{20}$  1.4053);  $d_4^{25}$  1.06826 (lit.,<sup>2</sup> 1.0686),  $d_4^{40}$  1.05332 (lit.,<sup>2</sup> 1.0532),  $d_4^{55}$  1.03841 (lit.,<sup>2</sup> 1.0378); viscosity  $\eta^{25}$  2.147,  $\eta^{40}$  1.684,  $\eta^{55}$  1.376 cP; dielectric constant  $\epsilon^{15}$  13.43,  $\epsilon^{25}$  12.94,  $\epsilon^{45}$  11.91,  $\epsilon^{55}$  10.93; specific conductance  $\times 10^8$ ,  $\kappa^{25}$  1.19,  $\kappa^{40}$  1.68,  $\kappa^{55}$  2.89 ohm<sup>-1</sup> cm.<sup>-1</sup>].

Difficulties were encountered in measuring the dielectric constant of triethyl phosphate because the ester appears to have a high dielectric loss. The Schering bridge previously used failed because the capacitance to be measured ( $C_p$ ) will be equal to  $-\Delta C_1$ , the change in capacitance of the variable condenser  $C_1$  (in parallel with the test cell) which is required to restore balance when the test cell is introduced into the circuit, only if  $R_p \gg R_4$ , where  $R_p$  is the resistance of the test cell, and  $R_4$  the resistance in parallel with a small variable capacitance  $C_4$ , itself in series with  $C_1$ . When the conductance of the liquid in the test cell is high,  $-\Delta C_1 < C_p$ , and the measured dielectric constant will be too small. A precise estimate cannot be given of the conductance of the liquid above which the method fails, but experience suggests that a specific conductance of  $5 \times 10^{-10}$  ohm<sup>-1</sup> cm.<sup>-1</sup> is probably near the limit. Extrapolation of measurements made by a high-frequency technique also gave unacceptable results.

The dielectric constant of triethyl phosphate was finally measured by a resonance method, in an apparatus built by Mr. Fairbourne of this Department according to his modification of

TABLE I. *Equivalent conductance in triethyl phosphate.*

Et <sub>3</sub> NPic at 25°									
10 <sup>4</sup> c	Λ	10 <sup>4</sup> c	Λ	10 <sup>4</sup> c	Λ	10 <sup>4</sup> c	Λ	10 <sup>4</sup> c	Λ
61.032	20.591	17.132	25.361	6.3999	28.672	1.7836	33.732	0.27158	36.071
36.696	22.426	12.216	26.565	3.8992	30.488	1.5161	33.187	0.050588	37.549
22.451	24.323	7.8264	28.063	2.9085	31.390	0.81695	34.448		
Et <sub>3</sub> NPic at 40°									
46.423	27.010	18.197	31.146	6.0198	36.551	1.7897	40.823	0.82821	43.162
40.939	27.426	12.372	33.193	5.2246	37.004	1.4314	41.504	0.33193	45.333
27.650	29.471	8.8596	34.750	3.5424	38.711	0.96780	42.927	0.17942	46.861
								0.11885	47.394
Et <sub>3</sub> NPic at 55°									
39.531	32.947	9.4458	41.503	2.4734	48.800	0.81734	53.052	0.15565	56.112
21.525	36.239	5.7580	44.427	1.5478	50.648	0.64240	53.468	0.045871	57.668
17.798	37.554	4.5970	45.876						
Bu <sub>3</sub> NPic at 40°									
34.448	24.657	18.219	27.704	7.1039	31.618	2.6077	35.526	0.55098	39.569
31.359	25.163	11.467	29.643	3.7666	34.385	2.0081	36.540	0.51470	39.446
28.147	25.535	7.1945	31.837	2.6515	35.635	1.0270	38.173	0.31270	40.121
(C <sub>5</sub> H <sub>11</sub> ) <sub>4</sub> NPic at 40°									
34.620	23.667	15.173	27.384	7.5455	30.361	2.5062	34.506	0.35425	38.825
26.041	24.813	11.336	28.512	5.2900	31.822	1.8893	35.261	0.27157	39.250
22.779	25.598	9.8013	29.285	4.9109	32.278	0.92391	37.352		
(Ph-CH <sub>2</sub> ) <sub>3</sub> NHPic at 40°									
31.038	22.074	7.2938	27.193	1.1827	36.465	0.78434	39.180	0.19501	42.425
16.763	23.701	5.0410	28.579	0.80032	39.154	0.44933	40.591	0.12341	42.644
11.425	25.376	2.9751	31.092						
Ph·NH <sub>3</sub> Pi at 40°									
56.928	17.974	15.116	22.804	7.0898	27.061	1.9315	34.306	0.66991	38.352
34.807	19.163	12.172	23.870	4.4991	29.790	1.2969	36.114	0.31233	40.358
25.932	20.340	8.9941	25.508	3.1022	31.897	0.98275	37.209	0.06540	42.723
19.195	21.747								

Le Fèvre and Calderbank's circuit.<sup>4</sup> A test cell as described by Smith<sup>5</sup> was used, the leads to it being unshielded and kept as short as possible. Ethylene dichloride, purified by refluxing over activated alumina and fractionation, was used for calibration, its dielectric constant at 25° being taken as 10.25.<sup>6</sup> It was not practicable to measure the dielectric constant at the three

<sup>2</sup> Sugden, Read, and Wilkins, *J.*, 1925, **127**, 1525.

<sup>3</sup> Vogel and Cowan, *J.*, 1943, 16.

<sup>4</sup> Le Fèvre and Calderbank, *J.*, 1948, 1951.

<sup>5</sup> Smith, "Dipole Moments," Butterworths, London, 1956.

<sup>6</sup> Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 3614.

temperatures used in the conductance experiments, but a plot of dielectric constant against temperature was linear, so that values at 40° and 55° were interpolated ( $\epsilon^{40}$  12.18,  $\epsilon^{55}$  11.43).

*Results.*—The equivalent conductance in triethyl phosphate of the five picrates at various concentrations is shown in Table 1.

#### DISCUSSION

The specific conductance of solutions in triethyl phosphate varied almost linearly with concentration. This resembled the behaviour of solutions of the same salts in acetonitrile<sup>7</sup> but was unlike that of solutions in the phosphoric esters with larger molecules.<sup>1</sup> As in the case of solutions in tritoyl phosphate, however, the variation in equivalent conductance with concentration was small for all electrolytes. The  $\Lambda-c^{\dagger}$  plots were again shallow curves typical of moderately strong electrolytes, and could be extrapolated to give approximate values of  $\Lambda_0$  from which the final values of  $\Lambda_0$  shown in Table 2 were obtained by Shedlovsky's extrapolation method.<sup>8</sup> Consideration was also given to the modified derivation of constants from conductance data suggested recently by Fuoss,<sup>9</sup> but in view of the low ion-pair dissociation constants ( $\leq 10^{-3}$ ) of all solutes in triethyl phosphate, and the fact that the size of the ionic species was comparable with that of the solvent, his treatment was not employed. As expected, no minima were observed in the  $\Lambda-c^{\dagger}$  plots since Walden's empirical rule  $\epsilon^3/c_{\min.} = 3 \times 10^4$ , indicated that these should occur at concentrations in excess of  $10^{-2}N$ , and hence outside the present range.

The ratios of  $\Lambda_0$  for the three tetra-alkylammonium picrates resemble those in acetonitrile<sup>7</sup> and other solvents with small molecules [ $\text{Et}_4\text{NPic} : \text{Bu}^n_4\text{NPic} : (\text{n-C}_5\text{H}_{11})_4\text{NPic}$  1 : 0.878 : 0.860], but differ markedly from the corresponding values in the other phosphoric esters. For the tetra-alkylammonium picrates in triethyl phosphate  $\Lambda_0$  values differ considerably from those in tritoyl and trioctyl phosphates, and are of the order of 100 times larger, approximating more closely to values in conventional solvents. The Walden products (Table 2) are very high compared with the average values in a large number of other common solvents of conventional size, where  $\Lambda_0\eta$  at 25° is 0.560 for  $\text{Et}_4\text{NPic}$  and is somewhat lower for the larger solutes. However, as with solutions in dialkyl phthalates<sup>10</sup> where the solvent molecules are comparatively large, the Walden product decreases with increasing size of quaternary ammonium ions, whilst  $\Lambda_0\eta$  for a given salt appears to decrease with increasing solvent size. It has been suggested<sup>10</sup> that a "normal" Walden product may be due to uniform solvation, so that the high Walden products found in the triethyl phosphate systems indicate very limited solvation. This suggests that, as with dimethyl phthalate, the solvent molecules may be oriented with their dipoles close together and shielded from interaction with the solute ions. The large hydrocarbon residues in trioctyl and tritoyl phosphates might, however, diminish loose dipolar association of solvent molecules and hence favour increased ion solvation, thus producing the observed lowering of the Walden product. Limited solvation of the tetra-alkylammonium ions in triethyl phosphate is consistent with the fact that temperature has little effect on the Walden product, which suggests that increased ion mobility is associated simply with decreased viscosity of the solvent.

Ion-pair radii, the Bjerrum "a" parameter, calculated from the equation where  $K$  is the ion-pair dissociation constant (see Table 2):

$$\frac{1}{K} = \frac{4\pi N}{1000} \left[ \frac{e^2 |z_1 z_2|}{\epsilon k T} \right]^3 \cdot Q(b)$$

are given in Table 3 together with the corresponding values in the other phosphoric esters<sup>1</sup> and in acetonitrile.<sup>7</sup> The magnitude of "a" for tetraethylammonium picrate in triethyl phosphate, the smallest of the phosphoric esters, approximates closely to that in the small

<sup>7</sup> French and Muggleton, *J.*, 1957, 2131.

<sup>8</sup> Shedlovsky, *J. Franklin Inst.*, 1938, **225**, 739.

<sup>9</sup> Fuoss, *J. Amer. Chem. Soc.*, 1957, **79**, 3301.

<sup>10</sup> French and Singer, *J.*, 1956, 1424, 2428.

solvent acetonitrile at the only temperature available for comparison, but differs markedly from that in the other two phosphates. Thus, if this parameter is taken as indicating the size of an ion, the variation in value seems to indicate that the tetraethylammonium ion is solvated in each of the solvents, and perhaps also that there are differences in degree of solvation, and/or to reflect the size of the solvating molecules. Nevertheless, the change

TABLE 2.

	25°	Et <sub>4</sub> NPic 40°	55°	Bu <sub>4</sub> NPic 40°	(C <sub>8</sub> H <sub>17</sub> ) <sub>4</sub> NPic 40°	(Ph·CH <sub>2</sub> ) <sub>3</sub> NHPic 40°	Ph·NH <sub>3</sub> Pic 40°
Λ <sub>0</sub> .....	37.3	47.45	57.6	41.7	40.8	44.25	43.5
Λ <sub>0</sub> η .....	0.801	0.799	0.793	0.702	0.687	0.745	0.732
10 <sup>4</sup> K ...	11.55	10.97	10.16	12.59	10.81	5.30	4.19

TABLE 3. *Ion-pair size (Å).*

Solvent	Solute				
	25°	Et <sub>4</sub> NPic 40°	55°	Bu <sub>4</sub> NPic 40°	(C <sub>8</sub> H <sub>17</sub> ) <sub>4</sub> NPic 40°
Triethyl phosphate .....	6.15	7.00	7.92	7.90	6.78
Trioctyl phosphate .....	9.10	8.41	7.86	10.60	10.64
Tritolyl phosphate .....	9.59	11.50	16.00	36.04	38.09
Acetonitrile .....	6.00				

in "a" with temperature indicates that other factors must also be involved. The interaction energy between a large ion and the solvent will be small so that a slight increase in temperature should produce a significant decrease in solvation. However, "a" increases with temperature in both triethyl and tritolyl phosphate although the expected decrease is observed in trioctyl phosphate. Finally the ion-pair radius in triethyl phosphate increases slightly on passing from tetraethyl- to tetrabutyl-ammonium picrate and then decreases although this does not occur in the other two solvents. This again suggests a very small degree of solvation of quaternary ammonium ions in triethyl phosphate, the observed difference of 0.92 Å in "a" between the tetraethyl- and tetrabutyl-ammonium picrates possibly representing the difference in sizes of the actual quaternary ammonium ions (the difference calculated by Robinson and Stokes<sup>11</sup> from models is 0.94 Å), the smaller value of the third salt corresponding to a decrease in solvation. These arguments do not exclude the possibility that the picrate ion also is solvated in these solvents, and some of the phenomena just discussed may be due in part, at least, to this cause. Nevertheless, since the picrate ion is common to all solutes here used, solvation of this ion cannot account for all the variations in "a" noted.

These data may also be considered in terms of the ion-pair dissociation constants, and these, for all three quaternary ammonium salts in triethyl phosphate, are similar to those in tritolyl phosphate, but differ considerably from those in trioctyl phosphate. The low dissociation constant of tetrapentylammonium picrate compared with that of the preceding homologue may clearly be associated with the decreased solvation of the cation discussed above, and the consequent possibility of closer approach of the two ions of the ion pair. The increase in *K* between tetraethyl- and tetrabutyl-ammonium picrate parallels qualitatively the effects in the other two phosphoric esters,<sup>1</sup> although the ratio of *K* for the two salts in triethyl phosphate approaches much more nearly the value in conventional solvents. Finally, contrary to Kraus's suggestion,<sup>12</sup> *K* and ε decrease with increasing temperature for solutions in both triethyl and trioctyl phosphates.

It is noteworthy that, in triethyl phosphate, Λ<sub>0</sub> for both tribenzylammonium and anilinium picrates is similar to the values for the quaternary ammonium picrates. It seems therefore, that the acid-base (*i.e.*, molecular) dissociation which has been postulated to account for the conductimetric behaviour of these two amine picrates in most other solvents

<sup>11</sup> Robinson and Stokes, "Electrolyte Solutions," Butterworths, London, 1955.

<sup>12</sup> Kraus, *J. Phys. Chem.*, 1956, **60**, 129.

is negligible in triethyl phosphate. Tribenzylammonium picrate in acetonitrile<sup>7</sup> is also an exception, and Marryott,<sup>13</sup> by dielectric measurements, failed to find evidence of acid-base dissociation of this electrolyte in benzene. It appears also that the mobility of the tribenzylammonium ion, with 24 carbon atoms, is greater than that of the tetrapentylammonium ion with only 22 carbon atoms,  $\Lambda_0$  for the two picrates being 44.2 and 40.8 respectively. However, the Shedlovsky plots for tribenzylammonium picrate were somewhat less reliable than in the other cases, deviations from linearity occurring at a considerably lower concentration.

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<sup>13</sup> Marryott, *J. Res. Nat. Bur. Stand.*, 1948, **41**, No. 1, 7.

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