

470. *The Conductivity of Solutions in which the Solvent Molecule is "Large." Part II.\* Solutions of Tetrapentylammonium Picrate in some Phthalate Esters.*

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The conductances of tetra-*n*-pentylammonium picrate in dibutyl, dipentyl, dioctyl, and dinonyl phthalate have been measured at 25°, 35°, and 45° over the concentration range 0.099—54.13 × 10<sup>-4</sup> mole l.<sup>-1</sup>.

A tendency towards the formation of minima in some of the conductance curves is observed. The general shape of the curves is that expected from modern theories of conductance in media of fairly low dielectric constant.

Variations in the value of the Walden product  $\lambda_0\eta$  with solvent and temperature can be explained on the theory of solvent-solvent and solvent-ion interaction as for the corresponding tetraethylammonium salts in the same series of solvents.

MEASUREMENTS of electrical conductance in solvents having large molecules have been carried out by Battacharyya and Nakhate<sup>1</sup> and by Fuoss and Elliott.<sup>2</sup> The latter authors found that for solutions of tetrabutylammonium picrate in tritolyphosphate the Walden product  $\lambda_0\eta$  was about 40% greater than the expected value. The explanation offered for this result did not, however, account for the high Walden product obtained in solutions in certain smaller solvents such as aniline<sup>3</sup> and pyridine.<sup>4, 5</sup> The present authors,<sup>6</sup> investigating the conductance of tetraethylammonium picrate in a series of phthalic esters, put forward an alternative hypothesis on the bases of solvent-solvent and solvent-ion interaction. In order to test this hypothesis further, to extend the range of data on conductance of solutions in solvents having large molecules, and to examine also the effect of the size of the solute ion, the conductance of solutions of tetrapentylammonium picrate in a series of dialkyl phthalates was also measured.

#### EXPERIMENTAL

Solvents were purified by the methods and conductance measurements made by means of the apparatus described earlier.<sup>6</sup>

Tetra-*n*-pentylammonium picrate was prepared as follows: Tri-*n*-pentylamine and *n*-pentyl iodide were refluxed for 100 hr. in toluene, the hydrocarbon was then distilled off, and the residual crude tetra-*n*-pentylammonium iodide washed with ether, reprecipitated from an alkaline alcoholic solution by water, again washed with ether, and recrystallised 5 times from absolute alcohol-light petroleum. Tetra-*n*-pentylammonium picrate was then prepared by interaction between exactly equivalent quantities of tetrapentylammonium iodide and silver picrate, both dissolved in hot 50% aqueous alcohol, the silver picrate being prepared as before.<sup>6</sup> The resulting picrate, recrystallised 5 times from aqueous alcohol, and dried in an oven at 50°, had m. p. 73.75—74° (lit.,<sup>7, 8</sup> 73°, 74°).

*Results.*—The Figure illustrates the change in equivalent conductance with concentration of tetrapentylammonium picrate in the four solvents used at 25°, the curves at 35° and 45° being similar. The detailed experimental data are shown in Table 1.

In Table 2 are given the values of  $\lambda_0$  and of the equilibrium constant *K* for ion-pair formation, both obtained by Shedlovsky's graphical extrapolation method.<sup>9</sup> Also in this Table are the values of the Walden product  $\lambda_0\eta$  for the various systems studied here. Finally, Table 2 gives

\* Part I, *J.*, 1956, 1424.

<sup>1</sup> Battacharyya and Nakhate, *J. Indian Chem. Soc.*, 1947, **24**, 1, 99.

<sup>2</sup> Fuoss and Elliott, *J. Amer. Chem. Soc.*, 1939, **61**, 294.

<sup>3</sup> Walden and Audrieth, *Z. phys. Chem.*, 1933, **165**, A, 11.

<sup>4</sup> Walden, Audrieth, and Birr, *ibid.*, 1932, **160**, A, 337.

<sup>5</sup> Pickering and Kraus, *J. Amer. Chem. Soc.*, 1949, **71**, 3288.

<sup>6</sup> French and Singer, *J.*, 1956, 1424.

<sup>7</sup> Vernon and Masterson, *J. Amer. Chem. Soc.*, 1942, **64**, 2822.

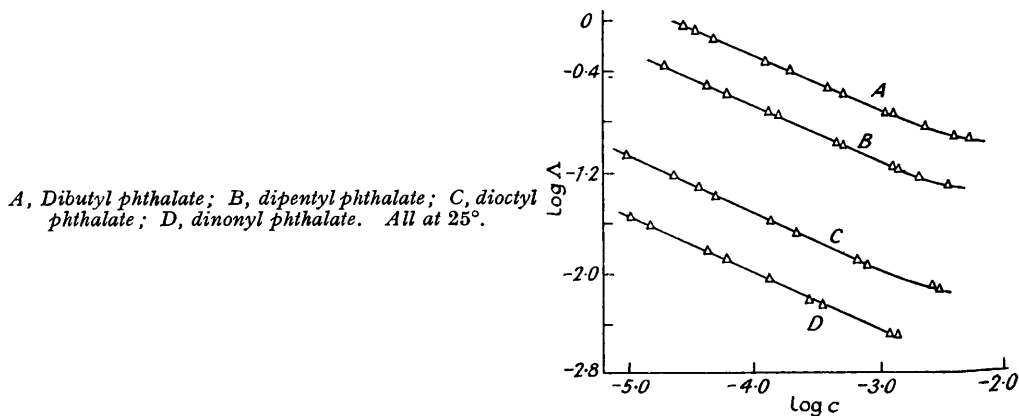
<sup>8</sup> Tucker and Kraus, *ibid.*, 1947, **69**, 454.

<sup>9</sup> Shedlovsky, *J. Franklin Inst.*, 1938, **225**, 739.

an estimate of the size of the ion pairs in the various solutions obtained by the graphical method described earlier.<sup>6</sup>

#### DISCUSSION

The  $\lambda\sqrt{c}$  curves for all these systems are of the usual exponential form, although both these curves and the  $\log \lambda - \log c$  curves tend to show minima in the more concentrated regions, as indicated in the Figure. Unfortunately the exact position of the minima could not be explored further owing to the very limited solubility of the salt in these solvents. The theory of ion-pair formation will account, in the more dilute region, for the shape of the  $\log \lambda - \log c$  curves and also for the deviations from the theoretical Debye-Hückel-Onsager curve. In the somewhat more concentrated region the occurrence of minima can again be explained on the basis of triple-ion formation.



As in the case of the tetraethylammonium picrate so with the tetrapentylammonium salt, the Walden product varies both with solvent and with temperature, although the latter variation is not as great.

The solvent association resulting from the close approach of two solvent molecules with their high electrical dipoles, postulated earlier,<sup>6</sup> will decrease from dibutyl to dinonyl phthalate, owing to the steric effect of the increasingly large alcohol residue. Solvation of the ions, by the loose association of a number of solvent molecules with each ion, owing to the coulombic attraction between the charge on the ions and the dipoles of the solvent, will therefore increase as the size of the alcohol residue increases. The ions will thus be increasingly hindered in their passage through solution, and  $\lambda_0\eta$  should decrease, as found experimentally (Table 2). All four solvents used in this series have very large molecules and, as might therefore be expected, the Walden product in all four is less than found for solvents with smaller molecules.

As in the system recorded in Part I<sup>6</sup> so here the large size of the tetrapentylammonium ion and of the solvent molecules results in a small interaction energy between them. Hence a decrease in the Walden product with decrease in temperature may be expected and is again found experimentally with the three largest solvents, as shown in Table 2. The absence of temperature effect for dibutyl phthalate exactly parallels the result for this solvent but with tetraethylammonium picrate as solute.

Comparison of the data presented in Part I<sup>6</sup> with those now recorded shows that the conductance curves for tetraethylammonium picrate fall below those for tetrapentylammonium in both dioctyl and dinonyl phthalate, although the reverse would be expected from the relative sizes of the bare ions. It appears therefore that in these two solvents, in contrast to solutions in dibutyl and dipentyl phthalate, the solvation of the tetraethylammonium ion is greater than that of the tetrapentylammonium ion by an amount that makes the solvated tetraethylammonium ion larger than the solvated tetrapentylammonium ion. This is confirmed by a comparison of the sizes of the ion pairs in the four solvents

TABLE I. *The equivalent conductance\* of tetrapentylammonium picrate in the solvents named.*

Dibutyl phthalate		Dipentyl phthalate		Diocetyl phthalate		Dinonyl phthalate	
10 <sup>4</sup> c	λ	10 <sup>4</sup> c	10λ	10 <sup>4</sup> c	10 <sup>4</sup> λ	10 <sup>4</sup> c	10 <sup>4</sup> λ
<i>At 25°</i>							
54.13	0.1211	32.28	0.5097	29.70	0.7336	12.29	0.3243
39.35	0.1294	20.62	0.5920	26.76	0.7747	11.57	0.3234
23.05	0.1508	13.66	0.6859	8.066	1.125	3.473	0.5439
12.59	0.1854	12.89	0.6973	6.728	1.251	2.756	0.6007
11.43	0.1875	4.995	1.029	2.244	1.960	1.319	0.8612
5.149	0.2640	4.934	1.042	1.371	2.555	0.5908	1.221
3.864	0.2912	1.523	1.742	0.5007	3.948	0.4109	1.458
1.928	0.3998	1.308	1.868	0.3629	4.859	0.1462	2.356
1.249	0.4714	0.6129	2.621	0.2362	5.837	0.1084	2.719
0.4795	0.7183	0.4214	3.096	0.1005	8.326		
0.3443	0.8333	0.1932	4.368				
0.2805	0.9042						
<i>At 35°</i>							
53.71	0.1811	34.94	0.8095	29.48	1.295	12.20	0.6045
39.04	0.1934	20.42	0.9394	26.50	1.364	11.49	0.6053
22.87	0.2251	13.53	1.088	8.006	1.979	3.448	1.283
12.49	0.2768	12.76	1.113	6.678	2.198	2.736	1.148
11.34	0.2801	4.947	1.631	2.228	3.628	1.309	1.615
5.110	0.3933	4.887	1.645	1.360	4.464	0.5865	2.340
3.834	0.4337	1.508	2.754	0.4970	6.979	0.4080	2.791
1.913	0.5961	1.296	2.943	0.3602	8.479	0.1451	4.435
1.239	0.7016	0.6070	4.155	0.2345	10.04	0.1076	4.998
0.4758	1.073	0.4174	4.917	0.09973	14.51		
0.3425	1.206	0.1870	6.742				
0.2783	1.319						
<i>At 45°</i>							
53.29	0.2563	34.57	1.210	29.27	2.110	12.11	1.033
38.74	0.2742	20.20	1.402	26.31	2.224	11.41	1.035
22.70	0.3185	13.39	1.618	7.947	3.457	3.423	1.746
12.40	0.3923	12.63	1.658	6.629	3.577	2.716	1.999
11.25	0.3965	4.895	2.435	2.211	5.608	1.300	2.745
5.070	0.5582	4.835	2.457	1.350	7.259	0.5822	4.028
3.804	0.6126	1.492	4.129	0.4933	11.33	0.4050	4.748
1.898	0.8431	1.282	4.406	0.3575	13.76	0.1440	7.525
1.229	0.9894	0.6006	6.154	0.2327	16.65	0.1069	8.684
0.4721	1.518	0.4130	7.312	0.09900	24.64		
0.3390	1.711	0.1893	10.04				
0.2762	1.841						

\* *c* is given in moles l.<sup>-1</sup>, and λ in ohm<sup>-1</sup> cm.<sup>2</sup>.

TABLE 2.

Solvent	Temp.	Dibutyl phthalate	Dipentyl phthalate	Diocetyl phthalate	Dinonyl phthalate
λ <sub>0</sub> .....	25°	3.33	1.47	0.371	0.162
	35	4.88	2.89	0.763	0.367
	45	8.83	4.40	1.36	0.634
10 <sup>7</sup> K .....	25	23.39	16.37	5.14	3.61
	35	23.07	15.42	4.99	2.94
	45	22.80	14.59	4.23	2.92
λ <sub>07</sub> .....	25	0.551	0.407	0.216	0.126
	35	0.545	0.492	0.257	0.158
	45	0.543	0.506	0.291	0.172
ion-pair size (10 <sup>-8</sup> cm.) } .....	25	6.01	6.52	6.90	7.24
	35	6.05	6.53	6.87	7.06
	45	6.03	6.45	6.75	7.06

used in the present series with those for tetraethylammonium picrate in the same solvents and shown in Table 3 of Part I.<sup>6</sup>

The authors thank the Chemical Society, the Central Research Fund Committee of the University of London, and the Royal Society for grants which have in part defrayed the cost of materials and apparatus.

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[Received, January 30th, 1956.]