336. *The Conductance of Solutions in which the Solvent Molecule is "Large." Part V.* Solutions in Dialkyl Alkylphosphonates.*

By C. M. French and P. B. Hart.

Conductances of four quaternary ammonium picrates in three dialkyl alkylphosphonates at 15°, 25°, 45°, and 65° have been measured in the concentration range 10^{-2}—10^{-6}N. Limiting equivalent conductances and ion-pair dissociation constants have been estimated for all except two systems. Shedlovsky plots failed to show linearity in these two cases. In a number of respects the conductometric behaviour of solutions in phosphonate esters is found to resemble that in phosphoric acid esters, and anomalies have again been observed. A qualitative theory is advanced to account for certain effects in terms of the formation of an "atmosphere" of oriented solvent dipoles round the solute ions.

In 1939, Elliot and Fuoss [1] commenced work on conductance relations in solutions where, because of the large size of its molecules, the solvent can no longer be regarded as a homogeneous continuum whose structure may be ignored except insofar as it determines its viscosity and dielectric constant. This work was extended in earlier papers in the present series.[2-5] All investigations have revealed abnormalities in such properties as ionic mobilities and ion-pair dissociation constants in these systems which are not amenable to the treatment applied to classical systems. To obtain more results in an attempt to assess the influence of various structural features of large solvent molecules on conductivity, measurements have been made in dilute solutions of four quaternary ammonium picrates of gradually increasing size, in three dialkyl alkylphosphonates, again of varying size, and at several temperatures. The results are now presented.

Experimental

The larger conductances were measured with the apparatus described earlier [2] except for the replacement of the telephone used previously for detection of current, in conjunction with the Gambrell bridge, by a single-beam cathode-ray oscilloscope, Model 2300, made by Industrial Electronics Ltd. This oscilloscope was used as a vertical deflection amplifier. Solvent conductances and those of the more dilute and therefore poorly conducting solutions in di-(2-ethylhexyl) 2-ethylhexylphosphonate were measured by means of the Schering bridge.

Bright platinum electrodes were employed when polarisation was undectable, but very lightly platinised electrodes were essential for solutions in diethyl ethylphosphonate where the concentrated solutions were subject to polarisation if bright platinum electrodes were used, but where dilute solutions gave the same results irrespective of the nature of the platinum electrodes.

A solvent correction was always applied, and consisted of subtraction of the specific conductance of the solvent from that of the solution. This correction varied in magnitude from approximately 0·01% of the solution conductance for the most concentrated solutions, to 2% for the most dilute.

Measurements of the constants of the cells with bright platinum electrodes (which are generally to be preferred for organic solutions in view chiefly of the possibility that platinised electrodes might catalyse an otherwise negligible undetected reaction in the cell solution) and with potassium chloride [6] or benzoic acid [7] revealed the occurrence of small but significant polarisation errors. Accordingly, the conventional two-electrode parallel plate cells were calibrated by an intercomparison method, those with platinised electrodes first being standardised with potassium chloride and with benzoic acid, and then used for the measurement

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* Part IV, *J.*, 1959, 3582.

[1] Elliot and Fuoss, *J. Amer. Chem. Soc.*, 1939, **61**, 294.
[2] French and Singer, *J.*, 1956, 1424.
[3] French and Singer, *J.*, 1956, 2428.
[4] French and Muggleton, *J.*, 1957, 5064.
[5] French, Hart, and Muggleton, *J.*, 1959, 3582.
[6] Jones and Bradshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780.
[7] Ives and Sames, *J.*, 1943, 511.

of the resistance of dilute solutions of some tetra-alkylammonium picrates in dibutyl butylphosphonate which seemed to be unaffected by the platinum black. These solutions were then taken as secondary standards for the calibration of cells with bright electrodes. The constant of the three-electrode cell was calculated from the capacitance measured on the Schering bridge, by using the relation [8]

$$\text{Capacitance} = 8{\cdot}842 \times 10^{-14}/(\text{cell constant})$$

The constants for the various cells used were as follows:

(I) *Two-electrode parallel plate cells*

(a) Platinised electrodes: (1) 0·1167, (2) 0·06971, (3) 0·03932

(b) Bright electrodes: (1) 0·2360, (2) 0·05075, (3) 0·02510, (4) 0·008200

(II) *Three-electrode cell:* $6{\cdot}657 \times 10^{-4}$.

Dielectric constants were measured by the resonance method and with the apparatus described earlier.[5]

The quaternary ammonium picrates were prepared by interaction between recrystallised " AnalaR " picric acid and the appropriate quaternary ammonium hydroxide, itself prepared (except for tetraethylammonium hydroxide, which was commercially available) from the tertiary amine and alkyl iodide *via* the corresponding quaternary ammonium iodide. The m. p.s of the final picrates, after recrystallisation from water for the two lower homologues, and from ethyl acetate for the two higher ones, were as follows: tetraethylammonium 256° (lit., 255·8°,[9] 256·0° [10]); tetra-n-propylammonium 115·8° (agreeing closely with the more recent literature value, 116·0°,[11] cf. 120·0° [12]); tetra-n-butylammonium 89° (lit., 89°,[13] 89·5° [14]); tetra-n-pentylammonium 73—73·5° (lit., 73°,[15] 73—74° [16]).

The three dialkyl alkylphosphonates used as solvents were obtained from the Virginia-Carolina Chemical Corp. and were purified as follows. The two lower homologues were first distilled to remove low-boiling impurities, and then fractionated. They were next refluxed for some hours over activated alumina, and finally distilled. Because of the observed thermal

TABLE 1. *Physical data for solvents.*

Property	15°	25°	45°	65°	Property	15°	25°	45°	65°
(I) Diethyl ethylphosphonate: B. p. 54°/0·3 mm.; $n_D^{17\cdot5}$ 1·4165 (lit., b. p. 62°/2 mm.; [16a] n_D^{18} 1·4172,[17] 1·4148 [18]).									
η (cP.)	1·627	1·330	0·9689	0·7431	ε	11·00	10·57	9·86	9·17
d (g./ml.) ...	1·026	1·019	1·004	0·9880	$\kappa \times 10^8$	3—5	5—7	7—9	8—9
(II) Dibutyl butylphosphonate: B. p. 104°/0·1 mm.; n_D^{20} 1·4330 (lit.,[17] b. p. 127—128°/2·5 mm.; n_D^{20} 1·4310).									
η (cP.)	4·368	3·173	2·061	1·623	ε	6·96	6·76	6·36	6·01
d (g./ml.)	0·9520	0·9436	0·9281	0·9108	$\kappa \times 10^9$	0·8—2	1·1—3·2	1·4—5·3	2—9
(III) Di-(2-ethylhexyl) 2-ethylhexylphosphonate: B. p. 155°/0·1 mm.; $n_D^{17\cdot5}$ 1·4489 (lit.,[17] b. p. 160—161°/0·25 mm.; n_D^{20} 1·4480).									
η (cP.)	18·31	11·98	6·000	3·609	ε	4·35	4·27	4·09	3·94
d (g./ml.) ...	0·9126	0·9052	0·8912	0·8770	$\kappa \times 10^{11}$	3·6—9	2—8	5—17	12—26

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[8] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 3614.

[9] Walden, Ulich, and Loun, *Z. phys. Chem.*, 1924, **114**, 275.

[10] Walden and Ulich, *Z. phys. Chem.*, 1923, **106**, 49.

[11] Taylor and Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 1731.

[12] Walden, Ulich, and Birr, *Z. phys. Chem.*, 1927, **130**, 495, 515.

[13] Cox, Kraus, and Fuoss, *Trans. Faraday Soc.*, 1935, **31**, 749.

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

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

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

[16a] Ford-Moore and Williams, *J.*, 1947, 1465.

[17] " Dialkyl Alkyl Phosphonates," Virginia-Carolina Chemicals Corp., 1953.

[18] Arbuzov and Vinogradova, *Doklady Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1947, 459.

instability of higher phosphonates, the di-(2-ethylhexyl)-2-ethylhexylphosphonate was purified simply by a number of successive, slow distillations, generous head and tail fractions being discarded each time. The physical constants for the three solvents are given in Table 1.

Results.—The variation of equivalent conductance with concentration and temperature in the 12 systems is recorded in Table 2.

TABLE 2. *Equivalent conductivity* (λ) *at concentration c.*

(I) *In diethyl ethylphosphonate*:

15°		25°		45°		65°	
$c \times 10^4$	λ	$c \times 10^4$	λ	$c \times 10^4$	λ	$c \times 10^4$	λ
(*a*) Tetraethylammonium picrate							
151·0	10·36	149·5	12·39	147·3	16·59	145·0	21·01
84·70	11·75	83·69	13·65	82·46	18·34	81·14	23·40
41·63	13·12	41·23	15·65	40·62	21·08	39·97	26·97
32·10	13·27	32·66	15·87	32·18	21·28	31·66	27·28
29·23	13·98	28·94	16·73	28·52	22·00	28·06	28·97
13·33	16·58	13·20	19·88	13·01	26·96	12·80	34·30
12·72	16·51	12·60	19·77	12·41	26·62	12·22	34·35
8·911	17·96	8·824	21·53	8·695	29·27	8·556	37·68
4·210	20·52	4·169	24·72	4·107	33·71	4·042	43·40
2·160	22·57	2·139	27·38	2·107	37·52	2·074	48·45
0·7441	25·3						
(*b*) Tetrapropylammonium picrate							
83·04	10·62	81·58	12·66	81·02	16·88	79·73	21·87
60·24	11·30	59·18	13·63	58·77	18·29	57·84	23·13
38·89	12·20	38·20	14·71	37·94	19·76	37·34	25·31
7·744	17·29	7·608	20·95	7·556	28·35	7·434	36·40
1·959	21·69	1·925	26·21	1·912	35·71	1·881	46·34
1·487	22·56	1·461	27·35	1·451	37·24	1·428	48·42
0·8513	23·94	0·8363	29·16	0·8306	39·77	0·8174	51·74
0·4423	25·37	0·4345	30·75	0·4315	41·83	0·4246	55·10
0·1670	27·8	0·1642	33·6	0·1629	45·8	0·1604	60·29
(*c*) Tetrabutylammonium picrate							
118·6	9·511	117·8	11·38	116·0	15·35	114·2	19·67
109·6	9·725	108·9	11·58	107·2	15·37	105·6	19·12
53·47	11·14	53·10	13·28	52·32	17·95	51·49	22·94
29·72	12·72	29·52	15·23	29·10	20·62	28·62	26·47
20·72	13·56	20·58	16·26	20·27	21·96	19·95	27·81
5·849	17·68	5·809	21·16	5·724	28·90	5·633	37·37
4·217	18·81	4·188	22·55	4·132	30·73	4·060	39·88
1·634	21·62	1·623	26·06	1·599	35·70	1·574	46·27
1·104	22·92	1·097	27·49	1·070	38·00	1·063	49·03
0·3629	24·33	0·5589	29·22	0·5563	40·40	0·5423	52·78
(*d*) Tetrapentylammonium picrate							
85·92	9·750	85·69	11·66	84·20	15·77	82·90	20·14
72·74	10·08	72·03	12·07	70·97	16·26	69·84	20·93
14·44	14·13	14·37	16·90	14·14	22·92	13·94	29·34
9·880	15·53	9·784	18·61	9·640	25·19	9·487	32·49
5·339	17·43	5·318	20·80	5·231	28·38	5·151	36·48
2·245	20·20	2·223	24·30	2·191	33·81	2·156	42·95
1·053	22·26	1·048	26·54	1·031	37·48	1·015	47·42
(II) *In dibutyl butylphosphonate*:							
(*a*) Tetraethylammonium picrate							
120·1	0·4409	119·0	0·5856	117·0	0·9393	114·9	1·377
36·76	0·4997	36·43	0·6643	35·83	1·069	35·17	1·574
9·510	0·764	9·425	1·018	9·271	1·644	9·098	2·375
3·414	1·151	3·384	1·527	3·328	2·462	3·266	3·622
1·071	1·911	1·061	2·556	1·044	4·106	1·025	6·001
0·2346	3·58	0·2325	4·065	0·2287	7·591	0·2244	11·15
0·07102	5·60	0·07039	7·473	0·06924	12·09	0·06794	17·21

TABLE 2. (*Continued.*)

15°		25°		45°		65°	
$c \times 10^4$	λ	$c \times 10^4$	λ	$c \times 10^4$	λ	$c \times 10^4$	λ
(*b*) Tetrapropylammonium picrate							
99·39	0·6022	98·51	0·8010	96·88	1·274	95·09	1·851
37·81	0·6784	37·48	0·8973	36·86	1·429	36·18	2·082
18·81	0·8315	18·64	1·100	18·34	1·752	18·00	2·541
10·14	1·025	10·05	1·350	9·884	2·156	9·700	3·146
8·622	1·075	8·545	1·428	8·405	2·255	8·248	3·292
2·546	1·719	2·523	2·285	2·482	3·618	2·435	5·195
2·157	1·858	2·138	2·459	2·103	3·917	2·064	5·581
0·6874	2·873	0·6812	3·802	0·6701	6·060	0·6576	8·733
0·5456	3·182	0·5407	4·195	0·5319	6·655	0·5220	9·720
0·3129	3·876	0·3101	5·118	0·3051	8·168	0·2994	11·87
0·1368	5·172	0·1358	6·795	0·1334	10·76	0·1309	15·60
0·1062	5·536	0·1052	7·34	0·1035	11·58	0·1016	16·86
(*c*) Tetrabutylammonium picrate							
117·5	0·6708	116·4	0·8857	114·5	1·407	112·4	2·045
85·03	0·6902	84·27	0·9112	82·89	1·454	81·34	2·089
29·45	0·8127	29·18	1·085	28·71	1·726	28·17	2·500
8·421	1·262	8·346	1·663	8·209	2·642	8·056	3·832
6·146	1·412	6·092	1·861	5·992	2·959	5·880	4·281
4·583	1·542	4·542	2·039	4·468	3·250	4·385	4·693
4·390	1·572	4·351	2·075	4·279	3·295	4·200	4·774
2·252	2·007	2·231	2·653	2·195	4·383	2·154	6·058
0·8857	2·897	0·8778	3·846	0·8634	6·083	0·8473	8·821
0·1633	5·122	0·1618	6·786	0·1592	10·77	0·1562	15·52
0·08602	6·089	0·08525	8·082	0·08385	12·81	0·08229	18·41
(*d*) Tetrapentylammonium picrate							
72·81	0·6900	72·16	0·9148	70·98	1·427	69·68	2·052
54·37	0·7181	53·89	0·9438	53·00	1·486	52·02	2·132
29·17	0·8200	28·91	1·089	28·44	1·702	27·91	2·448
9·844	1·164	9·756	1·510	9·597	2·420	9·488	3·429
8·624	1·222	8·548	1·611	8·408	2·538	8·251	3·667
2·609	1·903	2·585	2·502	2·543	3·623	2·496	5·717
2·048	2·089	2·030	2·741	1·996	4·325	1·959	6·243
1·067	2·664	1·058	3·520	1·040	5·567	1·021	7·949
0·7156	3·065	0·7094	4·047	0·6977	6·390	0·6847	9·286
0·3240	4·04	0·3213	5·319	0·3160	8·396	0·3101	12·15

(III) *In di-(2-ethylhexyl) 2-ethylhexylphosphonate*:

$c \times 10^4$	$\lambda \times 10^3$	$c \times 10^4$	$\lambda \times 10^3$	$c \times 10^4$	$\lambda \times 10^3$	$c \times 10^4$	$\lambda \times 10^3$
(*a*) Tetraethylammonium picrate							
24·26	3·974	24·06	7·085	23·68	16·89	23·29	33·90
14·53	4·195	14·40	7·430	14·17	17·79	13·95	35·51
8·910	4·850	8·842	8·376	8·702	20·98	8·560	42·17
4·977	5·935	4·935	10·48	4·862	25·68	4·781	51·32
3·752	6·668	3·722	11·51	3·662	28·71	3·602	56·23
0·6664	14·74	0·6613	25·60	0·6504	66·87	0·6397	129·4
0·5203	17·18	0·5162	28·71	0·5077	77·60	0·4996	147·4
0·4302	18·81	0·4269	31·72	0·4202	83·20	0·4132	162·4
(*b*) Tetrapropylammonium picrate							
67·06	5·267	66·52	8·596	65·49	20·13	64·45	39·26
44·82	4·818	44·45	8·407	43·77	18·89	43·07	37·13
43·78	4·646	43·43	7·847	42·76	18·80	42·07	35·97
14·44	4·500	14·32	7·835	14·10	18·77	13·88	36·27
5·058	6·787	5·017	11·46	4·939	26·65	4·861	53·63
1·335	13·37	1·324	20·18	1·303	49·82	1·283	97·90
0·8401	15·28	0·8332	25·94	0·8204	63·86	0·8073	125·1
0·1666	36·56	0·1652	60·35	0·1627	153·9	0·1601	303·8
0·05674	64·66	0·05628	90·0	0·05541	239·0	0·05452	481·3

TABLE 2. (*Continued.*)

15°		25°		45°		65°	
$c \times 10^4$	$\lambda \times 10^3$	$c \times 10^4$	$\lambda \times 10^3$	$c \times 10^4$	$\lambda \times 10^3$	$c \times 10^4$	$\lambda \times 10^3$
(*c*) Tetrabutylammonium picrate							
107·5	6·223	106·7	10·21	105·0	23·34	103·3	44·58
80·50	5·445	69·62	8·485	78·62	20·47	77·37	39·59
70·18	5·130	31·94	7·733	68·54	19·63	67·45	37·93
32·20	4·646	10·29	9·815	31·45	18·21	30·95	35·73
26·00	4·827	6·820	11·63	25·39	18·54	24·99	36·34
10·37	6·118	3·604	14·93	10·13	23·05	9·712	46·73
10·11	6·049	2·422	18·08	9·869	23·27	6·607	55·62
6·875	7·029	1·848	19·62	6·714	27·42	3·492	71·99
3·633	9·072	1·081	24·89	3·548	35·38	2·346	82·76
2·441	10·84	0·6284	32·25	2·384	41·31	0·6088	150·4
1·863	12·75	0·5890	33·10	1·819	46·77	0·1345	298·4
1·090	15·68	0·1388	63·96	1·065	59·19	0·02694	588·3
0·6335	19·92	0·02781	138·9	0·6187	75·24		
0·1399	38·70			0·5798	78·53		
0·02804	89·97			0·1366	147·2		
				0·02738	299·5		
(*d*) Tetrapentylammonium picrate							
115·9	6·280	114·9	10·24	113·2	23·10	111·4	53·96
56·62	4·498	50·18	7·417	49·43	17·16	48·65	33·16
47·26	4·281	46·88	7·035	46·15	15·52	45·42	31·53
23·14	4·478	25·44	7·280	25·05	15·96	24·65	30·38
8·542	8·866	8·339	11·10	8·258	23·21	8·127	45·76
0·9266	17·78	0·9190	26·61	0·9048	63·63	0·8904	125·1
0·3280	25·63	0·3848	39·55	0·3789	94·33	0·3728	189·8
0·1148	45·59	0·1139	68·69	0·1121	181·2	0·1103	326·7

DISCUSSION

Earlier work in solvents having large molecules [2-5] has shown that some conductance phenomena are governed by the existence of a dipole " atmosphere " of solvent molecules round the solute ions. It is therefore pertinent to consider structural aspects which may affect the formation of such an atmosphere.

The mean radius (in Å) of each dialkyl alkylphosphonate as calculated from molar-volume data is diethyl ethyl- 3·95, dibutyl butyl- 4·71, and di-(2-ethylhexyl) 2-ethylhexyl-phosphonate, 5·67, Courtauld models indicating that the P=O group is probably prominent and not shielded to any significant extent by the alkyl chain. Furthermore, the dipole moments of these solvent molecules may be expected to be high; the moment of the P=O group has been extimated as 2·66 D [21] with the negative end of the dipole on the oxygen atom, and the P–O–C and P–C bonds seem likely to increase the moment of the O·PO·O group. The dielectric constants of the phosphonates decrease both with temperature and with molecular size, increasing linearly at all temperatures with increasing number of these polar molecules per unit volume, thus showing a " dilution effect " with increasing length of alkyl chain. Finally, the energy of viscous flow, E_v, was estimated graphically by using the relation [22] $\eta = A \exp (E_v/kT)$, and the results are shown in Table 3.

TABLE 3. *Energy of viscous flow* (E_v in kcal.).

Solvent	15°	25°	45°	65°
DEEP	4·03	3·79	3·10	2·81
DBBP	5·54	5·26	3·51	2·17
DOOP	7·09	7·09	6·18	5·17

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[19] Arbuzov and Arbuzova, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1533.
[20] Kosolapoff, *J. Amer. Chem. Soc.*, 1945, **67**, 1180.
[21] Hunter, Phillips, and Sutton, *J.*, 1945, 146.
[22] de Guzman, *Anales real Soc. españ. Fiz. Quim.*, 1913, **11**, 353.

As expected, E_V decreases both with decrease in molecular size, although not in direct proportion to it, and with increase in temperature, the latter effect indicating some breakdown in structure of the solvent as temperature increases. Of great interest is the relatively small value of E_V and of its temperature coefficient when compared with the corresponding quantities in strongly hydrogen-bonded solvents, and it would appear that any solvent association in the dialkyl alkylphosphonates is fairly loose.

One further factor of importance in ion–solvent interaction is the charge density at the surface of the ion. This must be low for the quaternary ammonium ions with their spherical symmetry and large radii, and especially low for the higher homologues used in the present work. [The radii (in Å) estimated by Robinson and Stokes [23] from a Catalin model for the first ion, and from molar volumes for the higher homologues are: $(C_2H_5)_4N^+$ 4·00; $(C_3H_7)_4N^+$ 4·52; $(C_4H_9)_4N^+$ 4·94; $(C_5H_{11})_4N^+$ 5·29.]

The λ–$c^{\frac{1}{2}}$ plots gave evidence of ion association in all three solvents, and the extent of curvature of these graphs increased very considerably with increase in size of the solvent molecules. Thus, in diethyl ethylphosphonate the plots became linear at low concentrations but with slope greater than theoretical; in the butyl compound moderately steep curves extended over the whole concentration range studied, while in di-(2-ethylhexyl) 2-ethylhexylphosphonate the curves were very steep and showed pronounced minima at about 5×10^{-3}N.

Plots of log λ against log c over a wide range of concentration for solutions in non-aqueous solvents may be expected to exhibit certain distinct regions, which can be explained in terms of ion association. In the most dilute region there is curvature towards the concentration axis, changing to a linear portion as concentration increases, owing to the effect of ion-pair formation. This is succeeded by an increasing curvature in the opposite direction and the ultimate appearance of a minimum as concentration increases still further and ion triplets are formed. Ultimately, in the most concentrated regions the curve rises again owing to the extensive formation of ion triplets and higher aggregates. Low solubility at higher concentrations, and uncertainties in the most dilute solutions due to the high proportion of the total conductance represented by that of the solvent, frequently prevent the whole curve from being observed in a single system. In the present work all regions of the curve can be examined by considering systems in the three solvents used. In general, as these solvents increase in size and the dielectric constant decreases, the whole curve is shifted towards lower concentrations. In diethyl ethylphosphonate only the initial curvature and linear portion were detectable, but in the butyl compound both this region and the subsequent curvature were observed, and although there was no minimum there were indications that this might be expected at about 10^{-2}—10^{-1}N, which is outside the range studied. The curvature was absent from the most dilute region of the four systems studied in the 2-ethylhexyl compound, but the other features including the minimum, were obtained.

Limiting equivalent conductances (accurate to within ±0·5% in diethyl ethyl- and dibutyl butyl-phosphonate), and ion-pair dissociation constants K, were obtained from Shedlovsky plots which were linear to a fairly high concentration (1—2 × 10^{-3}N in the ethyl, and only slightly less in the butyl compound). In the 2-ethylhexyl compound Shedlovsky plots could not be obtained for tetraethyl- or tetrapropyl-ammonium picrate since the graphs were not linear over any part of the concentration range, and λ_0 and K could not be determined. For the other two solutes in this solvent linearity was obtained only in the most dilute region, the ion-atmosphere term was large, and the accuracy of the resulting value of λ_0 is only ±5%, and of K is ±15%. These quantities are given in Tables 4 and 5, together with the corresponding Walden products $\lambda_0\eta$ and ion-pair radii (the Bjerrum " a " parameter).

It will be observed that in the two smaller solvents λ_0 resembles the corresponding

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[23] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955.

TABLE 4. *Limiting equivalent conductances* (λ_0) *and Walden products* ($\lambda_0\eta$).

	15°		25°		45°		65°	
Solute	λ_0	$\lambda_0\eta$	λ_0	$\lambda_0\eta$	λ_0	$\lambda_0\eta$	λ_0	$\lambda_0\eta$
(I) In diethyl ethylphosphonate								
Et_4NPi	29·3	0·477	38·1	0·506	50·5	0·489	65·3	0·485
Pr_4NPi	28·4	0·462	34·7	0·461	46·3	0·448	62·3	0·463
Bu_4NPi	27·8	0·452	33·4	0·444	45·9	0·444	59·8	0·444
$Pent_4NPi$	27·0	0·439	32·5	0·432	47·0	0·455	59·4	0·444
(II) In dibutyl butylphosphonate								
Et_4NPi	13·0	0·567	17·5	0·555	23·9	0·493	37·5	0·609
Pr_4NPi	10·3	0·449	15·3	0·486	22·5	0·464	32·4	0·526
Bu_4NPi	10·3	0·449	13·7	0·435	21·5	0·443	30·0	0·487
$Pent_4NPi$	9·1	0·397	12·4	0·393	19·4	0·399	28·0	0·454
(III) In di-(2-ethylhexyl) 2-ethylhexylphosphonate								
Bu_4NPi	0·165	0·0302	0·513	0·0614	0·74	0·0414	0·90	0·0275
$Pent_4NPi$	0·245	0·0449	0·595	0·0712	1·12	0·0672	0·80	0·0245

TABLE 5. *Ion-pair dissociation constants* ($K \times 10^6$), *radii "a"* (Å), *and Bjerrum critical parameter* (q).

	15°		25°		45°		65°	
(I) In diethyl ethylphosphonate								
10^8q	$26{\cdot}0_5$		$26{\cdot}2_0$		$26{\cdot}3_2$		$26{\cdot}6_3$	
Solute	10^6K	a	10^6K	a	10^6K	a	10^6K	a
Et_4NPi	545	$6{\cdot}9_5$	373	$6{\cdot}1_7$	412	$6{\cdot}4_1$	395	$6{\cdot}4_6$
Pr_4NPi	474	$6{\cdot}6_0$	428	$6{\cdot}4_2$	564	$7{\cdot}2_4$	379	$6{\cdot}3_9$
Bu_4NPi	443	$6{\cdot}4_3$	456	$6{\cdot}5_8$	436	$6{\cdot}5_4$	372	$6{\cdot}3_4$
$Pent_4NPi$	460	$6{\cdot}5_3$	435	$6{\cdot}4_7$	337	$6{\cdot}0_2$	360	$6{\cdot}2_8$
(II) In dibutyl butylphosphonate								
10^8q	$41{\cdot}1_7$		$40{\cdot}9_7$		$40{\cdot}8_1$		$40{\cdot}6_3$	
Et_4NPi	2·06	$5{\cdot}4_0$	2·03	$5{\cdot}3_6$	2·68	$5{\cdot}4_8$	2·38	$5{\cdot}3_9$
Pr_4NPi	5·93	$6{\cdot}0_0$	4·35	$5{\cdot}7_7$	5·23	$5{\cdot}8_4$	5·12	$5{\cdot}7_9$
Bu_4NPi	6·51	$6{\cdot}0_3$	6·84	$6{\cdot}0_5$	6·61	$5{\cdot}9_7$	7·22	$6{\cdot}0_2$
$Pent_4NPi$	7·97	$6{\cdot}1_9$	8·41	$6{\cdot}1_8$	8·45	$6{\cdot}1_5$	8·23	$6{\cdot}1_0$
(III) In di-(2-ethylhexyl) 2-ethylhexylphosphonate								
10^8q	$65{\cdot}8_8$		$64{\cdot}8_6$		$63{\cdot}4_6$		$61{\cdot}9_8$	
Bu_4NPi	1·03	$9{\cdot}2_6$	2·24	$9{\cdot}8_6$	5·53	$10{\cdot}7_8$	9·34	$11{\cdot}4_6$
$Pent_4NPi$	0·429	$8{\cdot}5_1$	0·199	$7{\cdot}8_0$	0·266	$7{\cdot}7_9$	1·99	$9{\cdot}1_5$

values in other solvents of moderate size such as triethyl phosphate.[5] These mobilities also decrease with increasing cation size, the greatest change usually being between the tetraethyl- and tetrabutyl-ammonium picrates as in the case of many other organic solvents. Correspondingly, the Walden products of all solutes in these two solvents are of normal magnitude, although in most cases slightly lower than the average values of 0·560, 0·506, 0·471, and 0·449 for tetra-ethyl-, -propyl-, -butyl-, and -pentyl-ammonium picrates in conventional solvents. This might imply a slightly higher degree of solvation in the present solvents, although the negligible effect of temperature on $\lambda_0\eta$ indicates that solvation is not extensive. It should nevertheless be remarked that in dibutyl butylphosphonate there is an ultimate tendency above 45° for $\lambda_0\eta$ to increase; presumably at these temperatures thermal agitation becomes sufficiently vigorous to reduce or destroy the loose solvation.

Mobilities in di-(2-ethylhexyl) 2-ethylhexylphosphonate are abnormally low λ_0 for the two solutes where it can be evaluated being of the order of 50 times smaller than in the other two phosphonates, but resembling closely the corresponding values in trioctyl phosphate.[4] These data would seem to indicate, as in this earlier case, considerable solvation here by the molecules of di-(2-ethylhexyl) 2-ethylhexylphosphonate. This is consistent with the relatively large increase in mobility with increase in temperature, especially from 15° to 25°, and also with the increase in mobility with increase in cation size, since the smaller ions are usually more highly solvated. The low mobilities in this solvent lead in turn to abnormally low values of $\lambda_0\eta$, and of particular interest is the pronounced maximum in the Walden product over the temperature range 15—65°, which again parallels experience with the phosphate esters.[4]

A survey of values of the Bjerrum " *a* " parameter shows these to be somewhat larger in the phosphonates, and especially so in the 2-ethylhexyl compound, than in more conventional solvents such as ethylidene chloride where the ion-pair radius of tetraethylammonium picrate, given by the data of Stern, Healey, and Martell[24] at 25° is 4·37 Å. They are, however, slightly smaller than the values calculated by Robinson and Stokes from models, and from molar volumes, and do closely resemble those in triethyl and trioctyl phosphates. Although the variation in " *a* " with cation size and with temperature is somewhat irregular even if small in diethyl ethylphosphonate, both the regular but small increase in " *a* " with increase in cation size in the butyl compound, and the virtual absence of temperature effect in this solvent, indicate that the ions are only very slightly solvated in dibutyl butylphosphonate. The quite marked increase in " *a* " on passing to the 2-ethylhexyl compound is further evidence of solvation in this solvent, and as expected, the larger tetrapentylammonium ion appears to be less solvated, and consequently the ion-pair radius is smaller than that of the tetrabutylammonium ion. The most obvious feature here is, however, the steady increase in " *a* " for tetrabutylammonium picrate in di-(2-ethylhexyl) 2-ethylhexylphosphonate as temperature increases, and although there is no ready explanation for this phenomenon it is noteworthy that it also occurs in triethyl[5] and tritolyl[4] phosphates.

An alternative approach to the variation in " *a* " for a given solute in different solvents is to regard it as a measure of the dissociation of the salt in various media (the effect of ion size will still be reflected in the " *a* " parameter since the smaller ions will tend to be more associated).

The values of the dissociation constants shown in Table 5 can be compared with the corresponding data for the systems studied earlier.[2-4] Whereas in the smaller solvents in all series, K is of the order of 10^{-4}, this has decreased by a factor of approximately 100 in the larger solvents, the change occurring gradually with increasing size of the phthalic esters, but abruptly in passing from the ethyl to the butyl ester in the present series. It would be of interest, therefore, to examine this effect in more detail in the phosphoric esters. It has been noted[4] that the direction of change of K with cation size shows specific solvent effects, and this is further emphasised here where K consistently increases with increase in cation size in dibutyl butylphosphonate, and exhibits the reverse behaviour in the 2-ethylhexyl compound as far as the limited data indicate, and also in the ethyl compound at the highest temperatures. The appearance of a maximum value of K for the cations of intermediate size in diethyl ethylphosphonate at 25° and 45° and a minimum at 15° again emphasizes the complexity of the factors operating and producing specific effects in each particular system. This is further illustrated, as with the phosphates, by the temperature-dependence of K. No general relation covering solutions in all the " large " solvent molecule systems can yet be deduced, the variation in K depending on both solute and solvent, but increasing markedly in magnitude in the largest solvent of the present series.

In partial explanation of some of these phenomena it is reasonable to assume that solvent dipoles will interact with the electric field due to the ions. One can postulate a

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[24] Stern, Healey, and Martell, *J. Phys. Chem.*, 1951, **19**, 1114.

" time-average dipole atmosphere " oriented in the field of an ion, which is dependent on the dipole moments of the solvent molecules and of the solute ion, the effective dielectric constant between ion and solvent dipole, the size of the ion, and the temperature. The presence of such a dipole atmosphere which represents a loose association of ion and solvent, could affect the mobility of the ion, since this structure will have to be broken down before the ion can flow. Secondly, it could affect the dissociation constant. If the ion-pair radius (4·37 Å) of tetraethylammonium picrate in ethylidene chloride at 25° ($\varepsilon = 10{\cdot}00$), where the moment of the C–Cl bond is appreciably less than that of the P=O bond, is taken as a " normal " value for this solute, then the corresponding " normal " ion-pair dissociation constant at 25° in diethyl ethylphosphonate ($\varepsilon = 10{\cdot}57$) would be some six times less than its experimental value.

Clearly, more data are required, and further work on this type of system is in progress.

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