56. *The Conductance of Solutions in which the Solvent Molecule is "Large." Part VII.*[1] *Solutions in Triaryl Phosphites.*

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The conductances of four quaternary ammonium toluene-*p*-sulphonates in four triaryl phosphites at 15°, 25°, 45°, and 65°, over a concentration range $6{\cdot}0 \times 10^{-6}$ to $7{\cdot}9 \times 10^{-3}$N are reported, together with the characteristic P–O–C(aryl) bond-stretching frequencies in the infrared spectra of the phosphites. Simple theories of ion-pair and triple-ion formation account for the general pattern of the conductance data. Ion-atmosphere effects are negligible. Ion-dipole and ion-pair–solvent interactions depending on both the dipole moment and the geometry of the solvent molecules, are suggested to account for the extremely low conductances in these systems, and for certain apparently anomalous variations in ion-pair dissociation constants.

Recent work on the conductance of systems in which the solvent molecules and solute ions do not differ markedly in size, and both are large compared with the molecules of a more usual solvent which may be treated conventionally as a homogeneous continuum, has included the use of dialkyl phthalates,[2] dialkyl alkylphosphonates,[1] and trialkyl and triaryl phosphates [3,4] as solvents. For reasons already enumerated [5] it proved impossible generally to compare the conductance relations of solutions in trialkyl phosphites and phosphates, but the possible influence of solvent structure on conductometric behaviour was thought to be of sufficient interest for measurements to be made in triaryl phosphites as well as in tritolyl phosphite, previously studied.[3] However, in view of the readiness with which many phosphorous acid esters are oxidised, it was deemed advisable to use, as solutes, quaternary ammonium salts other than picrates which are commonly employed in these investigations, and as the toluene-*p*-sulphonates could readily be prepared these were chosen for the present work.

Experimental

Conductances were measured as previously described [1] by means of the Jones and Josephs type bridge for the most highly conducting solutions, and by the Schering bridge for the more poorly conducting ones. Cells of both conventional parallel-plate design, and with 3 concentric platinum electrodes were employed. Cell constants K were determined by Deitz and Fuoss's method,[6] from the air capacitance of the cells measured by the Schering bridge, and checked by the capacitance of the cells filled with standard liquid (benzene or carbon tetrachloride). K for the 3-electrode cell $= 6{\cdot}658 \times 10^{-4}$; constants of the various parallel-plate cells employed were of the order of 10^{-3}.

Dielectric constants were determined at 10^6 c./sec. as previously described,[1] benzene ($\varepsilon^{25} = 2{\cdot}274$) being used as standard. The refractive index of each solution of the phosphite in benzene was also measured at 25° by means of an Abbé refractometer, and the dipole moments of the phosphorous acid ester molecules were calculated by using the relation given by Smith [7] for benzene as solvent at 25°, *viz.*, ${}_{\mu}P_2 = 0{\cdot}18811M_2\alpha - 0{\cdot}19064M_2\nu$, where M_2 is the molecular weight of the phosphorous acid ester, and α and ν are the limiting values at infinite dilution of $\delta\varepsilon/\delta w_2$ and $\delta n^2/\delta w_2$ respectively, w_2 being the weight fraction of the ester in the solution. From this we have

$$\mu = ({}_{\mu}P_2{\cdot}9\boldsymbol{k}T/4\pi\mathbf{N})^{\frac{1}{2}}$$

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[1] Parts V and VI, French and Hart, *J.*, 1960, 1671, 1679.
[2] French and Singer, *J.*, 1956, 1424, 2428.
[3] French and Muggleton, *J.*, 1957, 5064.
[4] French, Hart, and Muggleton, *J.*, 1959, 358.
[5] French and Hart, *J.*, 1960, 3161.
[6] Dietz and Fuoss, *J. Amer. Chem. Soc.*, 1938, **60**, 2394.
[7] Smith, "Electric Dipole Moments," Butterworths, London, 1955, p. 61.

The tetra-alkylammonium toluene-*p*-sulphonates * used as solutes were all prepared by one or both of the two alternative procedures: (1) Refluxing the appropriate tertiary amine in benzene with the corresponding ester of toluene-*p*-sulphonic acid, itself prepared by the interaction at −5° to −10° of dry pyridine solutions of recrystallised toluene-*p*-sulphonyl chloride and the appropriate alcohol.[8] The time of refluxing depended on the ester used (2 hr. for ethyl, 20 hr. for n-propyl, and 100 hr. for n-butyl ester). Cooling resulted in the deposition of tetraethyl- and tetra-n-propyl-ammonium toluene-*p*-sulphonates, but the tetra-n-butylammonium salt had to be extracted with water which was then removed by vacuum distillation, and desiccation (P_2O_5). (2) Neutralising toluene-*p*-sulphonic acid with the appropriate quaternary ammonium hydroxide in aqueous or aqueous-ethanolic solution. In the case of the tetra-n-propylammonium salt the solvent was then removed by vacuum distillation and desiccation (P_2O_5). With the three lower homologues, water was removed by refluxing with benzene in a Dean–Stark apparatus.

Purification of the toluene-*p*-sulphonates was effected by recrystallisation from aqueous solutions refluxed with benzene (Me_4NTos), from ethyl acetate and cooling in carbon dioxide–acetone (Et_4NTos), from benzene (Et_4NTos and Pr^n_4NTos), and from ethyl acetate (Bu^n_4NTos).

TABLE 1. *Solvent properties.**

	Triphenyl phosphite				*Tri-*m*-tolyl phosphite*			
B. p.	134°/0·14 mm. (lit.[9] 360°/760 mm., 200°/5 mm.)				174°/0·17 mm. (lit. 240—243°/10 mm.,[10] 248—250°/12 mm.[12])			
n_D^{20}	1·5900 (lit.[13] n_D^{25} 1·58801) [13]				1·5758			
μ^{25}	1·71				1·89			
Temp.	15°	25°	45°	65°	15°	25°	45°	65°
d_4^t	1·191	1·182	1·164	1·145	1·134	1·126	1·110	1·094
η	25·18	14·26	6·950	4·060	37·55	21·17	9·132	5·075
ε	3·79	3·75	3·67	3·57	3·67	3·61	3·53	3·49
$10^{10}\kappa$	4·597	8·961	24·85	45·72	2·083	5·706	20·50	49·70
	*Tri-*p*-tolyl phosphite*				*Tri-*p*-ethylphenyl phosphite*			
B. p.	180°/0·18 mm. (lit. 250—255°/10 mm.,[10] 285°/11 mm.[11])				180°/0·18 mm.			
n_D^{20}	1·5759				1·5650			
μ^{25}	2·05				2·08			
Temp.	15°	25°	45°	65°	15°	25°	45°	65°
d_4^t	1·134	1·127	1·111	1·095	1·104	1·096	1·082	1·066
η	35·23	20·17	8·794	5·017	30·23	18·80	9·047	5·274
ε	3·88	3·83	3·74	3·64	3·74	3·70	3·61	3·51
$10^{10}\kappa$	0·6275	1·602	6·840	16·78	0·2845	1·096	5·079	9·245

* μ = dipole moment (D); η = viscosity (cp.); ε = dielectric constant; κ = specific conductivity (ohm^{-1} $cm.^{-1}$).

The physical data and analyses of the *toluene-*p*-sulphonates* are as follows: Tetramethylammonium salt, m. p. 241—242°, d_4^{20} 1·21 (Found: C, 53·5; H, 7·3; N, 5·8; S, 13·25. $C_{11}H_{19}O_3NS$ requires C, 53·85; H, 7·8; N, 5·7; S, 13·1%), tetraethylammonium salt, m. p. 112°, d_4^{20} 1·15 (Found: C, 58·7; H, 9·0; N, 4·9; S, 10·8. $C_{15}H_{27}O_3NS$ requires C, 59·8; H, 9·0; N, 4·65; S, 10·6%); tetra-n-propylammonium salt, m. p. 106—107°, d_4^{20} 1·12 (Found: C, 63·75; H, 9·5; N, 3·9; S, 8·6. $C_{19}H_{35}O_3NS$ requires C, 63·8; H, 9·9; N, 3·9; S, 9·0%); tetra-n-butylammonium salt, m. p. 100—101°, d_4^{20} 1·09 (Found: C, 61·4; H, 9·8; N, 3·7; S, 7·6. $C_{23}H_{43}O_3NS$ requires C, 66·8; H, 10·5; N, 3·4; S, 7·75%).

The three larger solvents, tri-*p*-tolyl, tri-*m*-tolyl, and tri-*p*-ethyl-phenyl phosphite were prepared by mixing the appropriate phenol (after redistillation) with phosphorus trichloride in stoicheiometric quantities below 20°, raising the temperature to 160° during 6 hr., and distilling off the resulting phosphite. Subsequent purification of these esters and of triphenyl

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* This anion will be denoted in formulæ as " Tos."

[8] Tipson, *J. Org. Chem.*, 1944, **9**, 235.

[9] Beilstein, " Handbuch der Organischen Chemie," 4th Edn., Springer, Berlin, 1922, XI, p. 103.

[10] Michaels and Kühne, *Ber.*, 1898, **31**, 1048.

[11] Strecker and Grossman, *Ber.*, 1916, **49**, 63.

[12] Broeker, *J. prakt. Chem.*, 1928, **118**, 287.

[13] Lewis and Smyth, *J. Amer. Chem. Soc.*, 1940, **62**, 1529.

TABLE 2. *Equivalent conductivity* Λ (*ohm*$^{-1}$ *cm.*^{2}) *at concentration* c (*equiv./l.*).

15°				25°				45°				65°			
10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$
1. *Conductance in triphenyl phosphite of:*															
(*a*) Tetramethylammonium toluene-*p*-sulphonate															
23·83	0·4452	6·965	0·4681	23·65	0·8661	6·912	0·8926	23·29	2·696	6·807	2·420	22·91	5·818	6·696	5·075
14·71	0·4218	3·317	0·9135	14·60	0·8144	3·292	1·590	14·37	2·395	3·242	4·130	14·14	4·994	3·189	8·078
13·60	0·4193	1·870	1·517	13·50	0·8007	1·856	2·670	13·29	2·326	1·828	6·132	13·07	4·895	1·798	10·92
10·21	0·4098			10·13	0·7989			9·974	2·234			9·811	4·791		
(*b*) Tetraethylammonium toluene-*p*-sulphonate															
67·46	4·809	11·67	4·255	66·95	8·993	11·58	8·294	65·93	24·39	11·41	23·81	64·86	52·41	11·22	55·25
46·65	4·191	9·774	4·630	46·29	7·894	9·744	8·843	45·59	21·89	9·552	25·82	44·85	47·80	9·397	59·25
32·09	3·780	7·912	5·029	31·84	7·230	7·852	9·533	31·36	20·37	7·732	28·19	30·85	45·45	7·607	64·51
22·36	3·626	7·051	5·286	22·19	6·895	6·998	10·10	21·85	19·54	6·891	29·43	21·50	45·10	6·779	67·71
20·26	3·558	4·933	6·311	20·11	6·778	4·896	11·72	19·80	19·68	4·821	34·39	19·48	44·72	4·743	80·65
14·94	4·035	4·892	6·333	14·82	7·713	4·855	11·84	14·60	22·25	4·781	34·60	14·36	50·60	4·703	82·25
		3·193	7·579			3·169	13·94			3·121	41·49			3·070	95·02
(*c*) Tetra-n-propylammonium toluene-*p*-sulphonate															
76·69	6·980	10·00	4·027	76·11	12·79	9·928	7·733	74·94	33·15	9·776	21·75	73·73	68·62	9·617	50·22
46·64	5·281	6·589	4·609	46·29	9·754	6·539	8·489	45·58	26·06	6·439	23·71	44·85	55·09	6·335	54·65
30·24	4·292	6·336	4·719	30·01	8·261	6·288	8·542	29·55	22·78	6·192	23·84	29·08	49·17	6·092	55·02
25·95	4·243	4·347	5·374	25·75	8·012	4·314	9·277	25·36	22·38	4·248	27·12	24·95	48·78	4·179	64·20
19·30	3·911	3·957	5·722	19·15	7·546	3·927	9·745	18·86	21·77	3·868	27·90	18·55	48·15	3·805	65·20
15·78	3·947	2·961	6·930	15·66	7·522	2·938	11·40	15·42	21·17	2·893	31·50	15·17	47·75	2·846	74·31
10·54	4·013	2·323	7·667	10·46	7·697	2·305	12·49	10·30	21·66	2·270	35·32	10·13	49·17	2·233	83·03
		1·255	9·211			1·245	16·33			1·226	43·00			1·207	99·59
(*d*) Tetra-n-butylammonium toluene-*p*-sulphonate															
58·48	6·943	7·379	4·365	58·02	12·76	7·323	8·423	57·15	33·65	7·212	24·93	56·22	70·35	7·095	57·22
33·62	5·223	4·422	4·878	33·37	9·730	4·389	9·148	32·86	27·08	4·322	27·65	32·33	58·34	4·052	64·65
18·58	4·316	3·101	5·434	18·44	8·400	3·077	10·56	18·16	24·05	3·030	30·46	17·87	52·85	2·981	74·04
12·87	4·226	2·317	6·055	12·77	8·168	2·300	11·89	12·57	23·85	2·265	35·23	12·37	53·81	2·228	82·72
12·44	4·225	2·149	6·640	12·35	8·138	2·133	12·98	12·16	24·10	2·100	35·79	11·96	53·39	2·066	83·74
9·408	4·225	0·9110	9·391	9·336	8·206	0·9041	17·31	9·194	24·68	0·8903	46·00	9·045	56·66	0·8759	103·0
2. *Conductance in tri-*m*-tolyl phosphite of:*															
(*a*) Tetraethylammonium toluene-*p*-sulphonate															
2·450	0·9442	1·170	1·505	2·433	1·988	1·162	3·144	2·398	7·414	1·156	11·68	2·364	21·35	1·129	34·45
2·365	0·9809	0·8620	1·789	2·349	2·028	0·8559	3·800	2·315	7·439	0·8438	13·68	2·282	21·66	0·8316	40·87
1·310	1·400	0·6771	2·144	1·301	2·828	0·6723	4·651	1·282	10·52	0·6627	15·33	1·264	31·12	0·6532	48·98
(*b*) Tetra-n-propylammonium toluene-*p*-sulphonate															
15·11	1·757	1·575	1·269	15·00	3·572	1·564	2·822	14·79	10·27	1·542	10·64	14·57	24·78	1·469	31·01
7·936	1·390	1·523	1·270	7·880	2·774	1·512	2·884	7·768	9·001	1·491	11·00	7·656	21·03	1·012	41·86
6·262	1·301	1·049	1·291	6·218	2·677	1·042	3·083	6·129	8·805	1·027	12·32	6·041	21·36	0·6552	69·50
2·710	1·231			2·691	2·685			2·653	9·413	0·6648	19·55	2·615	25·58	0·3639	94·60
										0·3692	25·66	1·520	31·57		
(*c*) Tetra-n-butylammonium toluene-*p*-sulphonate															
10·04	1·400	0·8650	1·640	9·968	2·953	1·418	2·939	9·826	9·431	1·398	10·67	9·685	22·16	1·378	32·34
6·195	1·218	0·7514	1·859	6·151	2·685	0·8589	4·291	6·063	8·756	0·8467	16·49	5·976	20·52	0·8345	52·73
4·528	1·184			4·496	2·620	0·7461	4·519	4·432	8·595	0·7355	18·98	4·368	22·01	0·7249	59·59
2·977	1·181			2·956	2·574			2·914	8·937	0·5128	20·38	2·872	24·93	0·5054	70·35
2·703	1·192			2·684	2·607			2·646	9·184	0·5101	22·69	2·608	26·03	0·5028	77·31
1·428	1·327			1·532	2·873			1·510	10·50	0·3358	28·09	1·489	31·57	0·3310	101·1

TABLE 2. (*Continued.*)

3. *Conductance in tri-*p*-tolyl phosphite of:*

(*a*) Tetramethylammonium toluene-*p*-sulphonate

15°				25°				45°				65°			
10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$
1·029	2·155	0·1468	8·046	1·023	4·241	0·1459	15·14	1·008	13·16	0·1438	42·88	3·567	11·73	0·9940	30·63
0·4843	3·371	0·06207	13·64	0·4814	6·796	0·06169	25·43	0·4745	22·12	0·06081	68·52	2·607	12·61	0·4677	53·10
												1·560	20·82	0·1417	97·95
														0·05993	167·5

(*b*) Tetraethylammonium toluene-*p*-sulphonate

15°				25°				45°				65°			
10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$
15·70	1·586	2·520	2·256	15·61	3·527	2·504	4·722	15·39	10·71	2·469	16·33	15·16	24·06	2·433	45·69
12·19	1·579	2·360	2·400	12·12	3·351	2·346	4·999	11·95	9·762	2·313	17·23	11·78	23·35	2·279	47·99
8·254	1·571	1·359	3·193	8·203	3·261	1·351	6·678	8·086	10·63	1·332	24·37	7·970	26·32	1·312	72·05
7·175	1·605	0·7953	4·999	7·130	3·354	0·7904	10·29	7·029	11·61	0·7792	38·55	6·928	26·16	0·7680	111·7
4·576	1·734	0·5537	6·904	4·547	3·587	0·5503	13·10	4·483	12·58	0·5425	52·43	4·418	32·31	0·5346	152·5
4·377	1·774	0·3748	10·14	4·350	3·743	0·3725	19·33	4·289	13·05	0·3672	74·00	4·227	33·17	0·3619	215·3

(*c*) Tetra-n-propylammonium toluene-*p*-sulphonate

15°				25°				45°				65°			
10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$
18·29	1·996	2·788	2·061	18·18	4·181	2·770	4·563	17·92	11·86	2·731	16·87	17·66	27·92	2·692	43·04
14·74	1·767	1·531	2·769	14·65	3·728	1·521	6·166	14·44	10·93	1·500	22·34	14·23	26·24	1·478	58·13
10·58	1·710	1·059	3·584	10·51	3·596	1·052	7·786	10·36	11·22	1·037	30·18	10·21	27·59	1·022	70·61
6·973	1·667	0·7847	4·649	6·930	3·660	0·7798	10·42	6·831	11·70	0·7687	39·58	6·733	29·86	0·7577	103·3
5·866	1·742	0·4712	6·220	5·830	3·702	0·4683	13·05	5·747	11·82	0·4617	44·92	5·664	31·44	0·4550	115·7
2·810	2·056	0·4029	6·781	2·792	4·551	0·4004	14·25	2·753	16·75	0·3947	49·66	2·713	42·75	0·3890	123·0

(*d*) Tetra-n-butylammonium toluene-*p*-sulphonate

15°				25°				45°				65°			
10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$
14·33	2·922	1·266	5·385	14·25	5·722	1·258	11·27	14·04	17·17	1·240	35·89	13·84	39·70	1·223	78·54
9·511	2·750	0·9477	6·545	9·453	5·296	0·9419.	13·88	9·319	16·31	0·9285	42·77	9·184	37·80	0·9152	98·30
7·941	2·768	0·4701	10·11	7·892	5·400	0·4672	19·84	7·780	16·34	0·4606	58·53	7·668	38·77	0·4539	137·4
6·472	2·801	0·4601	10·19	6·432	5·602	0·4573	20·07	6·341	17·20	0·4508	59·57	6·249	40·96	0·4443	139·9
3·245	3·394	0·1447	18·66	3·225	6·680	0·1438	38·16	3·179	20·04	0·1418	114·8	3·134	48·76	0·1397	272·7
2·666	3·578			2·649	7·258			2·612	23·31			2·574	53·29		

4. *Conductance in tri-*p*-ethylphenyl phosphite of:*

(*a*) Tetraethylammonium toluene-*p*-sulphonate

15°				25°				45°				65°			
10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$
2·088	1·753	0·7741	3·838	2·074	3·430	0·7688	7·306	2·046	9·799	0·7587	21·74	2·016	24·32	0·7475	51·63
1·412	2·566	0·4517	4·933	1·403	5·009	0·4487	9·203	1·384	14·21	0·4427	29·44	1·364	33·56	0·4362	77·18
0·9268	3·479	0·3128	5·892	0·9205	6·653	0·3107	10·69	0·9083	19·05	0·3066	33·83	0·8950	46·11	0·3021	94·30

(*b*) Tetra-n-propylammonium toluene-*p*-sulphonate

15°				25°				45°				65°			
10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$
5·382	1·268	1·667	1·691	5·343	2·401	1·654	3·257	5·275	7·007	1·633	9·551	5·197	15·69	1·609	23·12
5·105	1·275	1·202	1·840	5·068	2·409	1·193	4·238	5·003	7·192	1·178	11·41	4·929	15·70	1·161	27·02
2·880	1·415	1·156	1·864	2·859	2·649	1·148	4·330	2·823	7·913	1·133	11·82	2·781	18·79	1·117	27·26
2·841	1·423	0·5890	2·744	2·820	2·682	0·5847	6·255	2·784	7·998	0·5773	16·34	2·743	18·80	0·5687	37·41
1·723	1·688	0·2462	4·950	1·711	3·167	0·2440	9·401	1·689	9·289	0·2413	27·69	1·664	22·49	0·2377	61·93

(*c*) Tetra-n-butylammonium toluene-*p*-sulphonate

15°				25°				45°				65°			
10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$	10^4c	$10^4\Lambda$
5·357	1·813	1·844	2·310	5·318	3·275	1·831	3·934	5·250	9·815	1·808	11·63	5·173	22·07	1·781	28·39
3·475	1·817	1·307	2·658	3·450	3·384	1·298	4·571	3·406	9·913	1·281	13·37	3·355	24·44	1·262	32·37
3·147	1·819	0·9619	3·150	3·124	3·445	0·9549	5·205	3·084	10·05	0·9427	15·44	3·039	25·09	0·9288	35·73
1·992	2·231	0·4716	4·157	1·978	3·829	0·4681	6·854	1·952	11·44	0·4622	20·08	1·924	27·53	0·4553	63·35

phosphite (purchased from Albright & Wilson Ltd.) was by distillation at reduced pressure in oxygen-free nitrogen. Physical data for the solvents are given in Table 1.

Results.—The variation in equivalent conductance with concentration at four temperatures for the systems studied is shown in Table 2.

DISCUSSION

The Λ–$c^{\frac{1}{2}}$ plots for all systems exhibited the expected marked curvature typical of weak electrolytes, and in many cases minima were observed in the more concentrated solutions. According to Walden,[14] $\varepsilon^3/c_{\text{min.}}$ = constant (approximately 3×10^4), and the data given in Table 3 show this empirical rule to be closely followed for solutions in triphenyl phosphite, but that increasingly great divergences are obtained with tri-*p*-tolyl and tri-*m*-tolyl phosphites. The low solubility of the solutes in tri-*p*-ethylphenyl phosphite prevented observation of the conductance minima in this solvent. It will also be noticed that in all cases, the value of $\varepsilon^3/c_{\text{min.}}$ decreases steadily with increase in temperature. The Λ–$c^{\frac{1}{2}}$ curves also demonstrate that the conductance of tetraethylammonium toluene-*p*-sulphonate is exceptionally low at all temperatures compared with that of the other toluene-*p*-sulphonates. A typical set of curves is shown in Fig. 1.

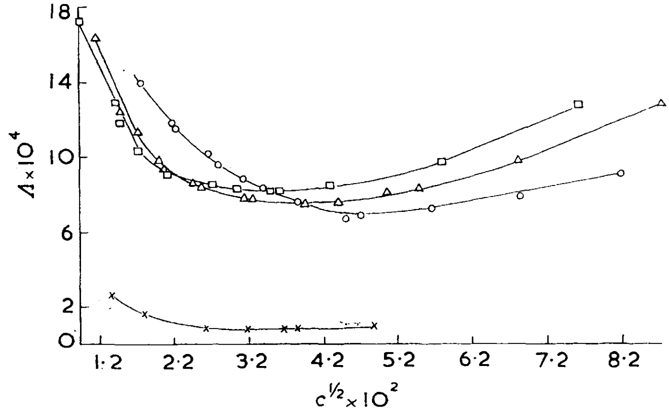

FIG. 1. *Solutions in triphenyl phosphite at* 25°.
× Me_4NTos. ○ Et_4NTos.
△ Pr_4NTos. □ Bu_4NTos.

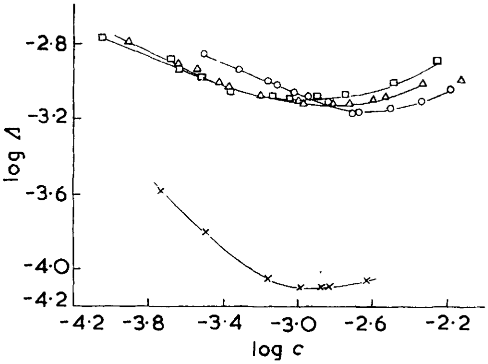

FIG. 2. *Solutions in triphenyl phosphite at* 25°.
(Key as in Fig. 1.)

log Λ–log c plots tended towards the ideal limiting case of straight line with slope $-\frac{1}{2}$ in the most dilute regions in most systems, but deviations from linearity occurred at concentrations considerably less than that of the minima in the curves (examples are given in Fig. 2), indicating appreciable triple-ion formation in this region. The existence of triple ions was further confirmed by the linearity of the $\Lambda c^{\frac{1}{2}}$–c plots down to concentrations of the order of 2—5 × 10^{-4}N.

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[14] Walden, *Z. phys. Chem.*, 1930, **147**, *A*, 1.

The Ostwald dilution function in the form given by Kraus and Bray [15] was employed to investigate further the equilibria in these systems. The plots of $1/\Lambda$ against $c\Lambda$ showed two distinct regions joined by a line of steep gradient. The lower end of the discontinuity occurs at concentrations of the order of $0{\cdot}5$—$1{\cdot}0 \times 10^{-4}$N, which is only a little greater than the value of $1{\cdot}2$—$1{\cdot}8 \times 10^{-5}$N for the critical concentration in these systems, predicted from the Fuoss relation $c_{\text{crit.}} \approx 3 \times 10^{-7} \times \varepsilon^3$. At concentrations up to the lower discontinuity, therefore, the free ion–ion-pair equilibrium appears to govern the magnitude of the conductance. The upper limit of the discontinuity occurs at concentrations of $1{\cdot}2 - 5{\cdot}5 \times 10^{-4}$N, where deviations from linearity of the $\Lambda c^{\frac{1}{2}}$–c graphs also appear, and above these concentrations triple-ion formation is thus well established. In the intermediate region of concentration between the discontinuity limits, there is a transition between the relative contributions of ion-pair and triple-ion equilibria, and, as expected, this region moves to lower concentrations as the dielectric constant of the solvent decreases.

TABLE 3. *Conductance minima, ion-pair dissociation constants, Bjerrum " a " parameters, and mean values of* ΔH^0.

Solute	Mean $\Delta H°$		15°	25°	45°	65°
1. *Solutions in triphenyl phosphite*						
		$10^{-4}\varepsilon^3/c_{\text{min.}}$	5·32	4·84	4·54	4·45
Me_4NTos	5·63	10^8K	0·177	0·267	0·505	0·747
		" a " (Å)	6·97	6·94	6·83	6·73
		$10^{-4}\varepsilon^3/c_{\text{min.}}$	2·57	2·44	2·82	1·98
Et_4NTos	6·53	10^8K	27·79	38·64	78·54	145·1
		" a " (Å)	9·89	9·94	10·08	10·28
		$10^{-4}\varepsilon^3/c_{\text{min.}}$	3·40	3·14	2·94	2·71
Pr_4NTos	6·07	10^8K	25·54	37·27	70·39	122·7
		" a " (Å)	9·83	10·10	9·83	10·11
		$10^{-4}\varepsilon^3/c_{\text{min.}}$	4·20	4·07	3·42	2·71
Bu_4NTos	7·10	10^8K	23·92	33·36	76·23	149·6
		" a " (Å)	9·76	9·80	10·03	10·32
2. *Solutions in tri-*m*-tolyl phosphite*						
		$10^{-4}\varepsilon^3/c_{\text{min.}}$	13·00	10·68	8·69	6·29
Pr_4NTos	8·49	10^8K	1·54	2·68	6·17	14·8
		" a " (Å)	8·21	8·35	8·44	8·49
		$10^{-4}\varepsilon^3/c_{\text{min.}}$	13·70	13·03	9·10	6·80
Bu_4NTos	8·94	10^8K	1·35	2·08	5·75	13·7
		" a " (Å)	8·14	8·20	8·38	8·45
3. *Solutions in tri-*p*-tolyl phosphite*						
		$10^{-4}\varepsilon^3/c_{\text{min.}}$	—	—	—	—
Me_4NTos	—	10^8K	—	—	—	4·97
		" a " (Å)	—	—	—	7·42
		$10^{-4}\varepsilon^3/c_{\text{min.}}$	6·08	5·66	4·40	3·83
Et_4NTos	6·88	10^8K	5·67	8·12	17·0	33·2
		" a " (Å)	8·40	8·48	8·55	8·62
		$10^{-4}\varepsilon^3/c_{\text{min.}}$	6·71	6·24	4·40	3·72
Pr_4NTos	7·92	10^8K	5·74	9·10	21·1	44·5
		" a " (Å)	8·47	8·55	8·62	8·85
		$10^{-4}\varepsilon^3/c_{\text{min.}}$	6·08	5·49	4·53	3·94
Bu_4NTos	6·28	10^8K	17·4	22·6	45·8	84·98
		" a " (Å)	9·13	9·19	9·32	9·45
4. *Solutions in tri-*p*-ethylphenyl phosphite*						
Pr_4NTos	7·03	10^8K	2·24	3·27	6·61	14·6
		" a " (Å)	8·23	8·22	8·25	8·34
Bu_4NTos	6·83	10^8K	3·36	5·33	10·2	20·5
		" a " (Å)	8·48	8·51	8·54	8·68

An accurate estimate of Λ_0 could not be obtained for the present systems since reliable extrapolations of conductance data to infinite dilution were not possible. This is due to the low specific conductance of solutions of dilutions at which binary equilibrium is dominant, and the consequent relatively high solvent conductance, ranging from 5 to 10%

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[15] Kraus and Bray, *J. Amer. Chem. Soc.*, 1913, **35**, 1315.

of that of the solution. It was, nevertheless, thought desirable to obtain some estimate of the order of magnitude of Λ_0 in these systems, and approximate values were therefore obtained as follows. Data from successive runs on each system fell on the same smooth curve when Λ was plotted against $c^{\frac{1}{2}}$, and interpolated points were taken in each case from the region of this graph more dilute than that of the lower discontinuity of the Ostwald plot of the original data. These points were used for plots of the Ostwald function. By applying the method of least squares to the interpolated points Λ_0 was calculated from the intercepts of these plots. (Ostwald plots are justified in the present solvents since the low dielectric constant results in ion-pair formation at high dilution, but in only very slight ion-atmosphere effects.) In these systems, where the relative size of the solvent conductance renders impracticable this treatment of the data in the dilute region, use was made of an earlier observation [2] that in homologous series of solvents with "large" molecules $\Lambda_0\eta$ decreases almost linearly with decrease in dielectric constant. Values of the Walden product obtained by graphical estimation of Λ_0 in tri-*p*-tolyl phosphite at 65° were therefore plotted against the dielectric constants of the solvents, and the data for the remaining systems calculated from the interpolated points. The resulting values of Λ_0 are shown in Table 4.

TABLE 4. *Limiting equivalent conductance* ($10^2\Lambda_0$).

Solvent	15°	25°	45°	65°	Solvent	15°	25°	45°	65°
Triphenyl phosphite	1·6	2·5	5·2	8·9	Tri-*p*-tolyl phosphite	1·0	1·8	4·1	7·2
Tri-*m*-tolyl phosphite	0·96	1·7	3·9	7·1	Tri-*p*-ethylphenyl phosphite	1·2	1·9	4·0	6·8

Examination of the data revealed, first, that the values of Λ_0 and hence of $\Lambda_0\eta$ for the three larger solutes in a given solvent and at a given temperature were identical within the limits of the method of determination. There are therefore no very great differences in solvation of the ions of the different solutes by the molecules of a given solvent. Although few data could be obtained, this is further shown by the virtual absence of temperature effect on the Walden product, the values obtained at 45° from limiting equivalent conductances in tri-*p*-tolyl phosphite being almost identical with those at 65°.

The second well-defined feature is the consistently higher values of Λ_0 at all temperatures in triphenyl phosphite than in the other three solvents. The close similarity of the values in the isomeric tritolyl phosphites is also noteworthy, that in the tri-*p*-tolyl ester being always a little higher than that in the *meta*-isomer. The cross-over in Λ_0 values in tri-*p*-ethylphenyl phosphite and its immediately preceding homologue as temperature increases from 15° to 65°, is associated with the lower temperature coefficient of viscosity of the former solvent. The temperature coefficient of conductance also decreases with increase in molecular weight of these solvents. Finally, of special interest is the extremely low order of magnitude of Λ_0 in all systems, implying a considerable retardation of movement of the ions in these solvents, occasioned perhaps by extensive even if loose solvation, or by steric hindrance due to particular configurations of the solvent molecules.

From these values of Λ_0 approximate values of the ion-pair dissociation constants K were obtained by using the relation for triple-ion formation (again with neglect of ion-atmosphere effects), *viz.*,

$$\Lambda = \Lambda_0 K^{\frac{1}{2}}/c^{\frac{1}{2}} + \lambda_0 (Kc)^{\frac{1}{2}}/K_3$$

where λ_0 is the sum of the limiting conductances of the two kinds of triple ion, and K_3 the triple-ion dissociation constant. By differentiation of this equation, imposing the conditions for a minimun (or maximum), and substitution of the resulting value of K_3 back into the original equation, we have

$$K = (c\Lambda^2)_{\text{min.}}/4(\Lambda_0)^2$$

In the three smaller solvents, K was estimated from the positions of the conductance minima by using this equation. This reduced the possible error due to the relative size of the solvent corrections which, at the conductance minima, were less than 1% of the solution conductances. The absence of well-defined minima in the concentration range studied in tri-*p*-ethylphenyl phosphite which was limited by the low solubility of the solutes in this ester, rendered this method impossible here, and K was accordingly deduced from the intercept $\Lambda_0 K^{\frac{1}{2}}$ of the plot of $\Lambda c^{\frac{1}{2}}$ against c. The values af K are given in Table 3.

Noteworthy features in the dissociation constants are, first, the very low values, which are 10—100 times less even than in several other " large " solvent molecule systems,[1-3] and secondly, that, as expected,[6] in solvents of low dielectric constant, K increases significantly with increase in temperature. This again is in contrast to the variable behaviour found in other systems in this series of investigations.[1-3] Certain well-marked tendencies are also discernible with change in cation size, but their significance is perhaps more easily discussed in terms of the ion-pair radius derived from K by means of the Bjerrum equation [17] and shown in Table 3. One apparent anomaly in K values should be noted. According to Bjerrum's equation K should decrease with decrease in dielectric constant, and this is observed for solutions in both the tritolyl and tri-*p*-ethylphenyl phosphites. However, if the structurally similar solvents, triphenyl, tri-*p*-tolyl, and tri-*p*-ethylphenyl phosphites are considered, the markedly larger K values in the first of these esters is unexpected in view of its smaller dielectric constant compared with that of the tolyl ester. The explanation for this phenomenon may nevertheless be related to ion-solvent interaction as discussed below.

A survey of the " a " values shows that, with the exception of tetramethylammonium toluene-*p*-sulphonate in triphenyl phosphite, there is a steady increase in ion-pair radius with increasing temperature, a phenomenon which is paralleled in other large solvent molecule systems.[1,3] In tri-*p*-tolyl and tri-*p*-ethylphenyl phosphites the slight increase in " a " in passing up the homologous series of toluene-*p*-sulphonates might be expected from the slight increase in cation size, and presents no anomaly. The virtual absence of change in " a " in the other two solvents if the tetramethylammonium salt is neglected (the variation in triphenyl phosphite being within the limits of accuracy of estimation in these systems) is perhaps a little surprising, but may be due to the insensitivity of the method of estimation in solvents of very low dielectric constant. Nevertheless, the markedly low " a " value for tetramethylammonium toluene-*p*-sulphonate compared with that of the higher homologues is interesting and suggests the possibility of an abrupt decrease in solvation of this salt.

Various of the characteristic features of the systems now discussed may be explained in terms of ion-solvent association. Since forces between dipoles are less than between ions and dipoles, the existence may be postulated in these systems of each ion surrounded by a close solvent molecule sheath of oriented dipoles. Beyond this first sheath the dipoles rapidly assume randon distribution, and the medium in this region may then be classed as a uniform dielectric. The conductance will thus be due to the movement of the ion-dipole complex under the influence of the applied field. Whether the complex moves as a whole or whether the ion alone moves to a neighbouring site by displacement of an adjacent solvent molecule which is of comparable size to itself, and this is followed by an immediate and consequent reorientation of solvent dipoles, the mobility of the ions will be reduced by the solvation sheath in a way not predicted by the macroscopic viscosity of the solvent. The measured conductance will thereby be greatly reduced, as is observed. Furthermore, this screening of each ion by the bulky solvent molecules is likely to be extremely effective so that, as suggested by Denison and Ramsay,[18] only ions which are in contact can be said to constitute ion-pairs. It is therefore interesting to observe that interionic distances calculated from models of the quaternary ammonium toluene-*p*-sulphonates (Me_4NTos, 7·5; Et_4NTos, 8·4; Pr_4NTos, 9·5; Bu_4NTos, 10·2 Å) do not differ

[16] Kraus, *J. Phys. Chem.*, 1956, **60**, 129.
[17] Bjerrum, *Kgl. danske Videnskab. Selskab*, 1926, **7**, No. 9, 18.
[18] Denison and Ramsay, *J. Amer. Chem. Soc.*, 1955, **77**, 2615.

widely from the Bjerrum "*a*" parameter shown in Table 3. Finally, efficient screening of this nature would tend to minimise ion-atmosphere effects, and explain the apparent applicability to these systems of equations in which the effect is neglected.

In view of this influence of screening, the dipole moments of the solvent molecules can be expected to be one of the important factors governing the relative magnitudes of conductances in these systems. If tri-*m*-tolyl phosphite, whose structure differs from that of the other phosphites is excluded, the dissociation constants for the salts in the other three structurally similar solvents are in the reverse order of the dipole moments of the solvent molecules, but are not simply related to the solvent dielectric constants (Table 1). However, since the latter also influence conductance, and it is difficult to separate the effect of each factor quantitatively, the overall result is likely to be complex in any given system. The determining part played by the dipole moment in the present systems is revealed owing to the very small variation between the dielectric constants of the solvents.

If the free ions alone were solvated, K should follow the dipole moments of the solvent molecules, and the reverse order observed here suggests that the solvated ion pairs are more stable structures than the solvated free ions in these systems. This is borne out also by the thermodynamic data; ΔG^0 (the free energy of dissociation) was calculated from the equation $\Delta G^0 = -\boldsymbol{R}T \ln K$, and plotted against the absolute temperature. Values of ΔH^0 obtained from the intercept of this graph are shown in Table 3 ($\Delta G^0 = \Delta H^0 - T\Delta S^0$), calculations showing that the 3% uncertainty in K, resulting from the method of estimation noted earlier, had a negligible effect on the ΔH^0 values. The use of $\ln K$–$1/T$ plots for determining ΔH^0 gives essentially the same ΔH^0 values, within the limits of graphical methods of estimation. It was shown by Stern and Martell[19] that when ΔH^0 is positive, as in all the present systems, solvated ion-pairs represent a more stable arrangement than solvated ions. Finally, an unexpectedly large variation in ΔS^0 from solvent to solvent was observed in these systems, although, as shown by Gurney,[20] none is expected when the temperature coefficient of the dielectric constant is the same, as is nearly true for the three structurally similar solvents here. This may be taken as further evidence of the failure of the simple macroscopic dielectric constant to account for the behaviour of this type of system.

Infrared spectra[21] and a study of atomic models suggest that there is a tendency for aryl phosphites to adopt a planar configuration with the lone pair of electrons on the phosphorus atom becoming progressively less shielded by the benzene rings as planarity increases. Data now presented (Table 5) for the O–C and P–O stretching frequencies in the present series of phosphorous acid esters demonstrate an increasing strain in the molecules as the substituents are placed nearer the P–O–C linkages, apparently caused by the mutual repulsion of the aryl groups, thus increasing the tendency to planarity. Models also indicate a restriction of free rotation of the aromatic groups even in triphenyl phosphite, *ortho*- and *meta*-substituents possibly increasing steric hindrance to rotation. This conclusion was substantiated by theoretical calculations by Lewis and Smyth,[13] who also pointed out that the P–O and C–O moments are screened by the phenyl groups. Thus, in addition to the factors already discussed, note must be taken of the effect on conductance and related quantities of the varying geometry of the solvent molecules, especially where

TABLE 5. P–O–C(*aryl*) *bond-stretching frequencies.*

Solvent	Absorption peaks (cm.$^{-1}$)		Solvent	Absorption peaks (cm.$^{-1}$)	
Triphenyl phosphite	1195	1025	Tri-*p*-tolyl phosphite	1199	1019
Tri-*m*-tolyl phosphite	1232	1007	Tri-*p*-ethylphenyl phosphite	1200	1018
Tri-*o*-tolyl phosphite	1224	1045			

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[19] Stern and Martell, *J. Amer. Chem. Soc.*, 1955, **77**, 1983.

[20] Gurney, "Ionic Processes in Solutions," McGraw-Hill, New York, 1953, p. 13.

[21] Bellamy and Beecher, *J.*, 1952, 475.

these are " large." Tri-*m*-tolyl phosphite has a lower dipole moment than that of tri-*p*-tolyl phosphite, and solutes in it might, by the arguments just adduced, be expected to have higher dissociation constants, but the reverse is actually observed. It is suggested that the introduction of *meta*-substituents has caused the mean position of the rings in the solvent molecules to become more planar than in the *ortho*-isomer. The P–O and C–O moments are then less efficiently screened in the *meta*-isomer, the effective ion–dipole and ion-pair–dipole interaction increased, and the K value for the ion-pair of the solute decreased below that expected from the measured dipole moment.

The anomalously low conductance of the tetramethylammonium compared with the other toluene-*p*-sulphonates could be associated with a closer approach of these quaternary ammonium ions to the localised dipoles of the solvent molecules. Models indicate that with triphenyl phosphite in a pyramidal form the tetramethylammonium ion can be completely surrounded by the aryl groups, and the centre of positive charge of the ion lies within 3·5 Å of the P–O and C–O bonds. The extent to which this occurs with the consequent reduction in ion mobility will clearly depend, in part at least, on the degree to which the aryl groups of the particular solvent molecule have achieved a planar configuration, and this in turn must affect the closeness of approach of the ions of the other solutes also. Thus movement of the ions will be retarded and conductance decreased by ion-dipole interaction, which depends both on the magnitude of the dipole moment and on the geometry of the ions and solvent molecules. This retarding effect cannot be fully described by the macroscopic viscosity of the solvent.

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