337. *The Conductance of Solutions in which the Solvent Molecule is "Large." Part VI.* Solutions in Heptane–Phosphonate Ester Mixtures.*

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The conductance of tetrabutylammonium picrate has been measured in three mixtures of heptane with diethyl ethyl- and dibutyl butyl-phosphonate over the concentration range 9×10^{-3} to $5{\cdot}5 \times 10^{-6}$N at 15°, 25°, 45°, and 65°. The conductometric behaviour of the solutions depends, not on the size of the solvent molecule, but on the formation of a dipolar atmosphere round the solute ion, which in turn is governed partly by the dielectric constant of the medium. Specific influences are also shown to be operative. Shedlovsky plots proved again to be unsatisfactory in solvents of dielectric constant of the order of 5 or less.

Earlier work on the conductometric behaviour of systems in which the solvent molecule is " large " has been chiefly confined to solutions in homologous series of pure single esters. In the ascent of each series, however, in addition to the increasing size of the solvent molecule whereby the solvent becomes even further removed from the ideal of a dielectric continuum, other properties such as viscosity and dielectric constant change. Furthermore, the dipole moment of any polar groupings may change. Thus, as the size of the solvent for a series of esters is increased, the polar ester groups are diluted by the increase in the size of the non-polar hydrocarbon residue. It was therefore decided to eliminate the changes in some of these factors, and this was done by adding the same proportion of hydrocarbon to polar group as in the higher pure ester but without its being attached to the polar group, *i.e.*, by the use of mixtures of ester and hydrocarbon as the solvent medium. In this case, provided the hydrocarbon molecule is smaller than that of the ester, there would be no increase in size of the solvent molecule, and viscosity would decrease with increasing hydrocarbon residue in contrast to the pure ester systems. The conductance relationships of tetrabutylammonium picrate in three solvent mixtures were accordingly investigated. Mixture I consisted of heptane and diethyl ethylphosphonate such that the ratio of $-PO(O-)_2$ to hydrocarbon was the same as in dibutyl butylphosphonate. Mixture II contained the same constituents in the ratio corresponding to di-(2-ethylhexyl) 2-ethylhexylphosphonate, and the latter was also simulated by mixture III, composed of the appropriate proportions of heptane and dibutyl butylphosphonate.

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* Part V, preceding paper.

Experimental.—Physical measurements were carried out as described in Part V.

Heptane was purified by fractionation and distillation from activated alumina. Other materials were prepared and purified as before. The physical data for the mixtures are given in Table 1.

TABLE 1.* *Physical data for solvent mixtures.*

Temp.	15°	25°	45°	65°	15°	25°	45°	65°	15°	25°	45°	65°
	Mixture I. $EtPO(OEt)_2$: C_7H_{16} = 166·16 : 84·15				*Mixture* II. $EtPO(OEt)_2$: C_7H_{16} = 166·16 : 252·45				*Mixture* III. $BuPO(OBu)_2$: C_7H_{16} = 250·31 : 168·30			
η (cP)	0·803	0·686	0·544	0·437	0·566	0·500	0·400	0·330	0·956	0·653	0·519	0·424
d ((g./ml.)	0·8785	0·8699	0·8510	0·8326	0·7922	0·7834	0·7657	0·7439	0·8276	0·8197	0·8037	0·7876
ε	5·80	5·62	5·30	5·07	3·60	3·54	3·45	3·27	3·06	2·98	2·83	2·71
$10^{10}\kappa$	60	66	78	100	2·4	2·8	3·4	4·1	0·17	0·32	0·48	1·07

* η = Viscosity, d = density, ε = dielectric constant, κ = specific conductivity. Proportions of constituents are by weight.

Results.—The equivalent conductance of tetrabutylammonium picrate at various concentrations in the three solvent mixtures is given in Table 2.

DISCUSSION

In all cases the Λ–$c^{\frac{1}{2}}$ plots were steep curves typical of weak electrolytes, and exhibited definite minima.

In general, the log Λ–log c plots were similar to those in the pure esters, showing both

TABLE 2. *Equivalent conductivity* Λ *at concentration* (c) *of tetrabutylammonium picrate in various mixtures* (*see text*).

15°		25°		45°		65°	
(a) *Mixture* I							
10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
89·52	1·710	88·64	1·992	86·72	2·596	84·84	3·230
83·14	1·704	82·33	1·977	80·54	2·643	45·04	3·393
47·52	1·757	47·05	2·049	46·03	2·692	28·22	3·770
29·77	1·941	29·48	2·265	28·84	2·977	19·70	4·088
20·79	2·084	20·58	2·434	20·13	3·215	13·35	4·835
14·09	2·397	13·95	2·801	13·65	3·698	7·900	5·524
8·335	2·812	8·254	3·294	8·074	4·347	4·268	7·214
3·996	3·706	4·459	4·268	4·362	5·667	3·787	7·373
2·884	4·262	3·957	4·347	3·871	5·774	2·732	8·450
1·205	6·076	1·194	7·129	2·794	6·612	1·142	12·03
				1·168	9·435		
(b) *Mixture* II							
10^4c	10Λ	10^4c	10Λ	10^4c	10Λ	10^4c	10Λ
84·69	1·549	83·75	1·790	81·85	2·325	72·52	2·842
77·22	1·453	76·37	1·681	74·64	2·212	14·36	2·533
19·86	1·181	15·12	1·427	14·78	1·928	4·485	3·895
15·29	1·215	4·723	2·194	4·617	2·946	3·380	4·104
4·776	1·839	3·560	2·281	3·479	3·093	1·423	5·995
3·600	1·942	1·499	3·342	1·465	4·512	0·5557	9·636
1·516	2·846	0·5852	5·403	0·5720	7·257	0·5066	9·676
0·5917	4·600	0·5335	5·451	0·5214	7·314	0·1590	19·15
0·5394	4·638	0·1680	9·738	0·1642	13·12	0·09887	19·68
0·1699	8·305	0·1041	10·89	0·1018	15·01	0·05227	25·60
0·1053	9·42	0·05504	16·15	0·05380	18·88		
0·05566	13·89						
(c) *Mixture* III							
10^4c	$10^3\Lambda$	10^4c	$10^3\Lambda$	10^4c	$10^3\Lambda$	10^4c	$10^3\Lambda$
39·48	8·477	39·12	10·99	38·35	17·83	37·58	20·03
29·26	8·135	28·99	10·17	28·43	16·59	27·86	18·08
13·96	6·407	13·84	7·941	13·57	13·50	13·29	20·99
5·897	6·509	5·859	8·468	5·725	14·01	5·385	22·43
3·362	17·29	3·329	9·543	3·264	16·12	3·198	25·74
0·6877	13·06	0·6813	17·47	0·6680	29·46	0·6547	46·48
0·4837	15·06	0·4790	20·86	0·4696	34·77	0·4602	55·06
0·2822	19·34	0·2797	25·10	0·2742	45·95	0·2687	72·91
0·1157	29·2	0·1147	37·49	0·1124	66·01	0·1102	92·65

a linear portion at low concentrations and a well-defined minimum at higher ones. As with solutions in pure di-(2-ethylhexyl) 2-ethylhexylphosphonate so here, the Shedlovsky plots were somewhat unsatisfactory, could not be extrapolated to Λ_0 in mixture III, and yielded values of Λ_0 and K in the other two mixtures only of the same order of accuracy as for pure di-(2-ethylhexyl) 2-ethylhexylphosphonate (preceding paper). This is, of course, to be expected, since, in order to obtain the requisite data for these plots in the region where triple-ion formation is negligible, when the dielectric constant of the medium is as low as 5, measurements must be made in the concentration region 10^{-6}—10^{-7}M. Solvent conductance forms an appreciable part of the total solution conductance at these concentrations and this, coupled with the uncertainty in the nature of the solvent correction that should be applied to particular organic systems, renders Shedlovsky plots difficult to construct and of decreased reliability. Approximate values of Λ_0 and K in mixtures I and II are given in Table 3.

TABLE 3.

	15°		25°		45°		65°	
	10^6K	a	10^6K	a	10^6K	a	10^6K	a
Mixture I	1·80	6·71	2·25	6·85	1·69	6·60	1·99	6·56
Mixture II	0·178	9·96	0·059	8·95	0·037	8·25	0·022	7·87
	Λ_0	$\Lambda_0\eta$	Λ_0	$\Lambda_0\eta$	Λ_0	$\Lambda_0\eta$	Λ_0	$\Lambda_0\eta$
Mixture I	44·5	0·358	47·1	0·323	70·4	0·383	80·0	0·350
Mixture II	7·50	0·452	15·5	0·0775	26·5	0·105	44·1	0·145

It has already become clear that, where the solvent molecule is larger than usual, neither the macroscopic dielectric constant nor the bulk viscosity can be employed satisfactorily in conductance relationships, and in the case of mixtures the latter property may bear little relation to the frictional force encountered by the moving ion. Nevertheless, although the Walden product cannot, therefore, be expected to remain constant, the trends of this quantity in conjunction with other data are of some qualitative interest.

It will be observed that in mixture I the limiting equivalent conductance is comparable with, but owing to the lower solvent viscosity a little higher than, the corresponding values in the pure dibutyl butylphosphonate which the mixture simulates. The Walden products, however, while in no sense anomalous, are significantly lower than in dibutyl butylphosphonate itself, implying somewhat more extensive solvation. In mixture II the decrease in solvent viscosity, as compared with pure di-(2-ethylhexyl) 2-ethylhexylphosphonate, results again in a substantial increase in Λ_0, although the Walden products remain anomalously low. That this is due, in part at least, to solvation is shown by the higher ion-pair radii in mixture II than in I, and by the increase in $\Lambda_0\eta$ and decrease in a in mixture II as temperature rises. It is noteworthy also, that the effect of increase of temperature on a, indicating a decrease of solvation in the latter solvent, is the reverse of that in the pure ester to which II corresponds, whence very specific solvent effects can be inferred.

Finally, and alternatively to the ion-pair radii, one may note appreciably lower ion-pair dissociation constants in both solvent mixtures I and II than in the pure esters they represent, and again the opposite effect of temperature on K in mixture II when compared with the corresponding values in di-(2-ethylhexyl) 2-ethylhexylphosphonate. The decrease in magnitude of K may be ascribed to the lower dielectric constants of the media.

The most interesting fact that emerges from these measurements is that where there is a difference in the order of magnitude of a property such as K or $\Lambda_0\eta$ between the pure esters, the values in the mixtures resemble those in the esters they represent and not those of which they are constituted. The size in itself of the solvent molecule can therefore have little effect on conductance, and the explanation for various phenomena must be sought in terms of properties common to the solvent mixtures and to the pure solvents they represent, and these are few. Notable among them are the presence of a polar group surrounded by non-polar hydrocarbon groups, and comparable dielectric constants. As suggested in the preceding paper the presence of a dipolar " atmosphere " round a solute ion will have a marked influence on its conductometric behaviour, and the formation of the atmosphere will be influenced both by the moment of the polar group of the solvent, and by the dielectric constant of the medium. This view is further supported by the present results, for it may be assumed that solvation in the mixtures is almost exclusively due to the phosphonate molecules, whence the effect of the moment of the polar group becomes identical with that in solutions of the pure constituent ester. The dielectric constant of each mixture, however, is very similar to that of the ester it represents, but is considerably less than that of the ester it contains. This lowered dielectric constant will (*a*) affect conductance relations in a manner which may be predicted from conventional theory and leads to increased ion association, and (*b*) result in a more marked formation of a dipolar atmosphere round the ions than when the solvent consists of pure ester alone.

In conclusion, it must still be stressed that there are also very specific effects observable which vary from system to system, and for which no explanation is yet available. Thus, in addition to the anomalies already noted in the current work, marked differences may also be observed between the two mixtures corresponding to di-(2-ethylhexyl) 2-ethylhexylphosphonate. The equivalent conductances at finite concentrations in mixture III containing dibutyl butylphosphonate are appreciably lower than those at the same concentrations in mixture II containing diethyl ethylphosphonate, and the Λ–$c^{\frac{1}{2}}$ graphs show a very much sharper minimum and at a lower concentration in III than in II. These differences are greater than could be accounted for by the small change in dielectric constant and viscosity.

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