

CHAPTER-VII

Ion-Solvent Interactions in Mixed Non-Aqueous Solvents:
Conductance Measurements of Tetraalkylammonium Bromides,
 NaBPh_4 and Bu_4NBPh_4 in Propylene Carbonate + Methanol
Mixtures at 25°C

Studies on the transport properties of electrolytes in different solvents are of great importance to obtain information on the behaviour of ions in solution. Recently, attempts have been made to study ion-solvent interactions in different dipolar aprotic media¹⁻³ having extensive use as solvents and solubilizing agents in different electrochemical investigations⁴⁻⁷. These factors have also stimulated some interest for the study of their binary aqueous mixtures^{3,8-9}. The transport properties in non-aqueous binary mixtures having propylene carbonate (PC) as one of the components have not been extensively studied barring a few^{3,10-11} (PC and water are not miscible at all proportions¹²). In the previous sections [Chapters IV and V], we have reported the transport properties of some tetraalkylammonium bromides and tetraphenyl salts in PC from their viscosity and conductance data. In the present chapter, we report the behaviour of tetraalkylammonium bromides, NaBPh_4 and Bu_4NBPh_4 in the binary mixed solvents of PC with methanol from their conductance measurements.

Experimental

The purifications of propylene carbonate and methanol have been described in Chapters II and VI. Salts were purified in accordance with the procedure given earlier (Chapters II and IV).

Solvent mixtures were prepared by weight and in practice, four sets of solvent mixtures of different mole fractions of PC viz. 0.10, 0.20, 0.40 and 0.60 were prepared. Physical properties of the solvent mixtures have been given in Table 1. Freshly distilled solvents were always used and solvent mixtures were prepared immediately prior to use.

A stock solution for each salt in the appropriate solvent mixture was prepared by weight and the working solutions were obtained by weight dilution. The molar concentrations of the solutions were calculated from molality and density values. Viscosity and density of the solvent mixtures were determined in the same way as described earlier [Chapters II & IV]. Dielectric constants of mixtures were taken from the literature¹³.

A Pye-Unicam conductivity meter (PW 9509) was used for measuring the conductances of the solutions at a frequency of 2 kHz with a dip-type cell of cell constant 0.751 cm^{-1} and having an accuracy of $\pm 0.1\%$. The measurements were carried out in a thermostatic oil bath maintained at $25 \pm 0.005^\circ\text{C}$. Conductance values of all salt solutions were corrected to avoid the contribution of the solvent.

Results

The measured equivalent conductances (Λ) of electrolyte solutions as a function of molar concentrations (c) have been reported in Table 2.

The experimental results have been analysed by the Fuoss 1978 conductance equation¹⁴ in the same way as described previously (Chapter-IV). The values of Λ^0 , K_A , R and σ have been recorded in Table 3.

Discussion

Table 1 shows that viscosity of PC + CH₃OH mixtures increases with increase in PC content of the mixture. Densities of the solvent mixtures also gradually increase with increase in the amount of PC in the mixture. The present observations indicate the possible absence of any heteroassociation or structure formation or any other type of specific interaction between unlike molecules.

The variation of limiting equivalent conductance, Λ^0 , with the solvent composition is represented in Fig. 1. The limiting equivalent conductance decreases with the corresponding increase in the viscosity of the mixture. Although, it is evident that the variations in Λ^0 do not exactly compensate each other to give the

Walden product a constant value (Fig. 2) but the changes in Walden products for an electrolyte in different solvent compositions are sufficiently small compared to other binary mixed solvent systems. It thus reflects that the differences in solvation of ions are not primarily responsible for the observed changes in ionic mobility or Λ° of the electrolytes.

The assumption that the dielectric constant is not involved in affecting the values of Λ° is untenable as the change in Λ° values is not due to any change in the number of ions. The difference in the mobilities of ions is actually responsible for the change in λ_+° and λ_-° of the ions. The cations and anions are moving in the opposite directions, the attractive forces of the opposite ions decrease with increasing dielectric constant of the solvent medium and the mobilities of the ions are inversely proportional to the dielectric constant of the medium.

PC is a structureless dielectric having moderately high dielectric constant and large dipole moment (values are 64.40 and 4.98 D respectively)¹⁵. It is thus expected that the solvodynamic entity around the tetraalkylammonium salts are likely to be greater in PC than in methanol (dielectric constant¹³ 32.64 and dipole moment 1.70 D¹⁵). On the other hand, methanol molecules are associated through the intermolecular hydrogen bonding. From conductance¹⁶, viscosity¹⁷ and volumetric¹⁸ studies, it has been established that the tetraalkylammonium ions are not solvated in

methanol. However, unlike the cations, Br^- ion has been found to be solvated in this medium. It appears that very large size of tetraalkylammonium ions and hence their low charge densities and the low dipole moment of methanol molecules are primarily responsible for the weak ion-solvent interactions in this medium. The interaction energy (ion-solvent) appears to be too weak to break up the intermolecular H-bonding in methanol and thus can't orient solvent dipoles properly in its solvation sheath. Increased values of Λ^0 in methanol might be due to greater freedom of ions to move through this polar, hydrogen bonded solvent system and also due to the low viscosity of the medium.

It is well established that if the viscosities of the media differ widely, the conductance in the less viscous medium will be greater. In comparison to pure methanol, the transport process of ions is obviously difficult in PC + CH_3OH mixtures as the solvent viscosity is increased and the hydrogen bonded structure in methanol loosens or breaks up and most probably, the interstitial spaces are withdrawn. Another factor that also plays a vital role for the decrease in Λ^0 values of the electrolytes in PC + CH_3OH mixtures is the dielectric constant of the media. Since, the dielectric constant decreases in PC + CH_3OH mixtures from PC, the ionic mobilities increase and hence greater Λ^0 values are obtained in the mixture than in pure PC. The tetraalkylammonium ions generally remain unsolvated in PC medium (Chapter - IV). As the PC + CH_3OH mixture is enriched by PC, the viscosity and dielectric

constant increase further (compared to CH_3OH and methanol-rich regions) causing a general decrease in Λ^0 values, as observed.

The variation of Walden products of the tetraalkylammonium salts with solvent compositions is shown in Fig. 2. It is observed that the changes in Walden products of an electrolyte with compositions of the mixture are very small. Since the electrolytes are not solvated either in PC or in methanol so it is expected that these salts would also remain unsolvated in their binary mixtures. This is reflected by the very small variation in Walden product values. Results thus support the earlier view point that for large cations, the Walden product values are solvent independent and remain almost unchanged¹⁹.

From Table 3 we see that K_A values of the salts generally increase with increase in CH_3OH content in the mixture i.e. with the decrease in dielectric constant of the mixture. Among all the electrolytes studied here, tetrabutylammonium tetraphenylborate is seen to be associated to the greatest extent followed by sodium tetraphenylborate. Kay *et al*¹⁶ studied some tetraalkylammonium salts in methanol with the help of Fuoss-Onsager conductance equation and observed that among the bromides, only tetramethylammonium and tetraethylammonium salts are associated (K_A values are 14.0 and 10 respectively). However, Papadopoulos²⁰ reanalysed the conductance data of Kay *et al* for Pr_4NBr in CH_3OH at 25°C using Lee-wheaton conductance equation²¹. They obtained the K_A value of

24 whereas, Kay et al¹⁶ found it to be only 6.3. Thus, it appears that the association constants of the R_4NBr salts in CH_3OH as reported by Kay and coworkers may be much larger. Kay et al¹⁶ further observed that Bu_4NBPh_4 is much more associated than the R_4NBr salts in methanol. Since, the association constants of R_4NBr salts vary by small amounts from Me_4NBr to Hep_4NBr , so a regular trend in association constant values was difficult to obtain. K_A , is generally, a function of the parameters such as the size of the ions and the dielectric constant of the medium. Besides electrostatic forces, solvation forces also exist which are completely system specific and their contribution can not be predicted. Thus, specific solvent effects also play a vital role in the association process. Generally, useful results in binary mixed solvents can be obtained when the ions are solvated only by the polar component of the mixture. And when the polar compound is a hydrogen bonded solvent, the solvation energy is complicated by the solvent structural effects and the interpretation becomes difficult. As the sizes of the cation and anion increase, it is reasonable to anticipate that the specific interaction with the solvent molecules will become less important and then the association should be a function of dielectric constant of the medium only. However, association process in polar hydrogen bonded solvents like alcohol and so also in their binary mixtures is not so simple as anticipated. A comparison of the association constant values of Bu_4NClO_4 in two isodielectric solvents viz. acetone and propanol was made by Evans and Gardam.²²

Taking into consideration the dielectric constants of the two media, the ions of the salt, Bu_4NClO_4 is expected to be equally associated in accordance with the electrostatic theory. But K_A value for the large Bu_4NClO_4 salt in propanol is much greater than that in acetone. It is thus apparent that the simple solvation is not the major factor controlling the association process in propanol. Evans and Gardam further concluded that the alcohols appear to constitute a separate class of solvents, distinct in behaviour from many other non-aqueous solvents but similar in some respects to water. However difference with water exists in the presence of three-dimensional structures in water. In PC - CH_3OH solvent mixtures, the solvation energy is complicated by the solvent structural effects arising from the presence of alcohol in the mixture. It thus demands much more investigations on the solvent structures and the behaviour of different electrolytes in such types of binary non-aqueous solvent mixtures. Evans and coworkers²² have further shown that the ionic association in the hydrogen bonded solvents like ethanol and propanol does not exhibit the simple dependence upon ionic size as predicted by electrostatic theory. Among the tetraalkylammonium halides, although the bromides and chlorides exhibit K_A values in the manner predicted by the relative sizes of the cations in these two solvent systems but anomalous and large K_A values were obtained for the iodide salts. They have treated these K_A values as almost unchanged and concluded that the tetraalkylammonium iodides irrespective of their sizes

are equally associated in ethanol and propanol. One point that should be noted here is the fact that the decrease in K_A values from Me_4NBr to Bu_4NBr in either of these two solvent systems is not consistent enough. In fact Pr_4NBr and Bu_4NBr have got almost equal K_A values in ethanol (78 and 75 respectively) and propanol (270 and 266 respectively). Again in our case, K_A values of the tetraalkylammonium salts in PC - CH_3OH mixtures are small enough (Table 3) and the solvent mixture is quite complicated from structural point of view. It thus can be said that for any given composition of PC - CH_3OH mixtures, the R_4NBr salts are equally associated which is most likely due to peculiar nature of the alcohol (methanol here) present in the mixture and the complicated structural features of the mixture arising from it.

From Table 4, we see that for any particular composition of PC - CH_3OH solvent mixtures, the Walden products of the R_4NBr salts decrease in the order : $\text{Me}_4\text{NBr} > \text{Et}_4\text{NBr} > \text{Pr}_4\text{NBr} > \text{Bu}_4\text{NBr} > \text{Pen}_4\text{NBr} > \text{Hex}_4\text{NBr} > \text{Hep}_4\text{NBr}$. So, the lowest value is obtained for the largest molecule and it indicates the lack of solvation of these salts in these mixtures. The quantitative explanation for the variation of the Walden products with solvent composition is yet unknown though some attempts have been made to derive a satisfactory expression taking into account all types of ion-solvent interactions. In spite of some qualitative agreements, the complicated expression derived by Zwanzig²³ involving the (solvent) dielectric relaxation

time, the solvent viscosity, static and infinite frequency dielectric constant fails to predict quantitatively the variation of Walden product with composition. This is quite natural as no single mathematical expression can cover all the ions and their interactions with various solvents as the ion-solvent interaction is quite specific for an ion and a particular solvent. However, it is reasonable to believe like Hemes²⁴ that the variation of the Walden product with solvent composition is due to the variation of the electrochemical equilibrium between the ions and the solvent molecules at one hand and selective solvation of ions and complex formation between unlike solvent molecules on the other. It has already been mentioned that majority of the ions studied here lack selective solvation in PC - CH₃OH mixtures and also in either of these two components. Studies on thermodynamic properties in PC - CH₃OH mixtures (Chapter- VI) also indicate the lack of specific interaction or complex formation between unlike molecules. This has also been supported by the fact that the Λ^0 values of the salts do not exhibit any maxima or minima at any intermediate composition of the mixture. The change in Walden product from one composition to another in PC - CH₃OH mixtures is so small that no fruitful and definite conclusion should be drawn from it rather we think, the Walden product values should be treated as almost unchanged over the composition range.

In absence of transport number data in these mixed solvents, we have used "reference electrolyte" method for the division of into single ion values. Bu_4NBPh_4 ²⁵ has been used as the reference electrolyte. Bu_4NBPh_4 was utilized by Fuoss and Kirsch²⁶ to calculate the limiting ion conductances in several organic solvents assuming the equality:

$$\lambda_0(\text{Bu}_4\text{N}^+) = \lambda_0(\text{Ph}_4\text{B}^-) \quad (1)$$

But instead of equal division, we divided Λ^0 values using the method similar to that proposed by Krumgalz²⁷ for division of B values:

$$\frac{\lambda_0(\text{Bu}_4\text{N}^+)}{\lambda_0(\text{Ph}_4\text{B}^-)} = \frac{r(\text{Ph}_4\text{B}^-)}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} = 1.07 \quad (2)$$

The r values have been taken from the works of Gill et al^{28,29}. The virtual organic solvent independence of the solvation radii of large Bu_4N^+ and Ph_4B^- ions found by Krumgalz²⁷ (and Gill^{28,29}) suggests that these ions are unsolvated in organic solvents and therefore, their ionic radii calculated as

$$r_{\pm} = \frac{|z| F^2}{6\pi\eta_0 N \lambda_{\pm}^{\mp}} \quad (3)$$

correspond to their true dimensions in the solvent.

The limiting ionic conductances calculated from equation (2) are given in Table 5. Stokes radii of the ions from equation (3) are given in Table 6.

From Table 5, we see that the λ_i^0 values decrease as we go from Me_4N^+ to Hep_4N^+ in PC + CH_3OH mixtures and PC similar to those observed in methanol¹⁶ and water³⁰. If the R_4N^+ ions were solvated in PC or in its binary mixtures with methanol, then the λ_i^0 values for R_4N^+ ions should have been in the reverse order. Most studies for electrolyte solutions in the non-aqueous media involving different techniques indicate that the cationic solvation is strong while the anionic solvation is weak. But owing to the very large size of tetraalkylammonium ions, these are most likely not solvated either in PC or in PC + CH_3OH mixtures. However, Na^+ ion is substantially solvated both in PC and CH_3OH and also in their binary mixtures because of its small crystallographic radius and large charge density. Results thus indicate (Table 6) that the R_4N^+ ions in PC + CH_3OH mixtures remain almost as bare ions. For anions, Br^- ion is found to be solvated in methanol and also in PC + CH_3OH binary mixtures though the probability decreases as PC content in the mixture increases. However, BPh_4^- ion is found to be almost unsolvated in pure as well as in mixed solvents. Since, PC lacks a well-developed centre of positive charge, the anions appear to have

weak interactions with its molecules. Obviously, the decrease in size of the anion favours the solvation process.

More extensive studies, however, are required to arrive at reasonable conclusions about the conductance behaviour and about the nature of ion-solvent interactions in different non-aqueous organic mixtures, particularly in the mixtures in which a component is a hydrogen bonded organic solvent like alcohol.

Table 1. Solvent properties of PC + methanol mixtures at 25°C

Property	Mole fraction of PC					
	0.00	0.10	0.20	0.40	0.60	1.00
Density/g cm ⁻³	0.7866	0.8693	0.9346	1.0327	1.1036	1.1988
Viscosity/cP	0.544	0.626	0.719	0.975	1.297	2.471
Dielectric constant	32.64	39.20	44.10	51.30	57.30	64.40
Specific conductance /Scm ⁻¹	0.15x10 ⁻⁶	1.52x10 ⁻⁶	1.81x10 ⁻⁶	2.25x10 ⁻⁶	2.42x10 ⁻⁶	0.73x10 ⁻⁶

Table 2. Equivalent conductances of tetraalkylammonium bromides, NaBPh_4 and Bu_4NRPh_4 in PC + methanol mixtures at 25°C

$10^4 \text{C/mol dm}^{-3}$	$\wedge/\text{Scm}^2 \text{mol}^{-1}$	$10^4 \text{C/mol dm}^{-3}$	$\wedge/\text{Scm}^2 \text{mol}^{-1}$	$10^4 \text{C/mol dm}^{-3}$	$\wedge/\text{Scm}^2 \text{mol}^{-1}$
Me_4NBr		0.10 mole fraction of PC			
		Et_4NBr		Pr_4NBr	
120.214	89.47	120.047	85.34	120.519	75.11
105.491	90.96	105.304	86.67	105.215	76.46
90.312	92.405	90.261	88.03	90.336	77.81
75.134	94.17	75.217	89.54	74.926	79.35
59.955	96.06	60.174	91.23	60.047	81.03
45.536	96.12	45.130	93.27	45.168	82.92
30.357	100.68	30.087	95.42	29.758	85.22
10.625	105.34	15.043	98.39	14.879	88.23

Contd..

Table 2 (Contd..)

0.10 mole fraction of PC

	Bu ₄ NBr		Pen ₄ NBr		Hex ₄ NBr	
120.632	69.61	120.637	66.77	120.078	64.75	
105.230	70.94	105.496	67.99	105.007	65.95	
89.945	72.27	89.981	69.29	90.182	67.14	
75.248	73.78	75.088	70.78	75.358	68.67	
59.963	75.47	60.195	72.31	59.916	70.24	
45.267	77.32	45.301	74.07	45.091	72.08	
29.982	79.61	30.408	76.22	30.267	74.12	
15.285	82.47	12.411	79.73	12.354	77.58	

Contd..

Table 2 (Contd..)

	Hep ₄ NBr		NaBPh ₄		Bu ₄ NBPh ₄	
120.280	62.64	120.223	58.01	111.842	54.41	
105.183	63.81	105.607	59.13	95.649	55.83	
90.334	65.05	90.032	60.35	80.153	57.33	
75.484	66.37	75.139	61.71	60.022	59.56	
60.016	67.93	60.247	63.15	49.956	60.87	
45.164	69.68	45.354	64.82	39.890	62.24	
30.317	71.62	30.462	66.83	30.197	63.75	
12.374	74.94	12.184	70.06	20.131	65.52	
				10.065	68.03	

Contd..

Table 2 (Contd..)

0.20 mole fraction of PC					
	Me ₄ NBr		Et ₄ NBr		Pr ₄ NBr
170.471	77.64	170.052	74.63	169.965	65.26
149.864	79.01	155.751	75.41	154.719	66.02
130.121	80.39	140.117	76.23	139.990	66.87
115.165	81.46	120.214	77.46	120.227	68.05
100.208	82.63	100.311	78.77	100.464	69.29
90.017	84.38	79.612	80.28	80.700	70.77
70.503	85.22	59.709	81.90	60.113	72.51
59.826	86.38	39.806	83.79	40.350	74.42
40.382	88.74	19.903	86.41	20.586	76.97
20.191	91.66				
	Bu ₄ NBr		Pen ₄ NBr		Hex ₄ NBr
170.225	59.69	172.079	58.47	174.410	56.78
144.944	61.08	159.984	59.03	150.077	57.93
131.972	61.75	140.086	60.04	129.834	58.96
120.506	62.38	120.187	61.03	110.289	60.11
100.281	63.74	100.288	62.27	90.046	61.36
80.056	65.03	80.390	63.52	70.501	62.68
59.831	66.71	60.491	64.95	50.258	64.26
40.449	68.54	39.797	66.77	30.015	66.31
20.224	71.02	19.898	69.06	15.356	68.21

Contd..

Table 2 (Contd..)

		0.20 mole fraction of PC			
Hep ₄ NBr		NBPh ₄		Bu ₄ NBPh ₄	
170.144	55.51	170.283	49.72	131.370	48.48
155.738	56.18	154.827	50.46	110.790	49.77
140.410	56.94	140.233	51.23	91.547	51.19
120.588	58.01	120.199	52.31	70.964	52.76
90.939	59.21	100.166	53.49	60.177	53.72
80.116	60.50	80.133	54.76	49.958	54.75
60.294	61.89	60.099	56.24	40.023	55.84
40.471	63.61	40.066	58.03	30.088	57.02
20.813	65.82	20.033	60.31	20.152	58.48
				15.044	59.33
		0.40 mole fraction of PC			
Me ₄ NBr		Et ₄ NBr		Pr ₄ NBr	
250.935	61.23	269.917	57.58	270.393	51.10
230.304	61.90	246.389	58.38	245.943	51.81
210.567	62.68	220.335	59.21	229.770	52.28
190.736	63.31	201.260	59.91	209.176	52.92
170.199	64.26	180.384	60.63	190.417	53.50
130.923	66.01	140.433	62.23	149.795	54.89
100.374	67.50	110.167	63.60	120.597	56.00
69.825	69.28	79.901	65.17	90.131	57.39
44.732	71.08	50.846	66.95	59.664	59.01
25.093	72.84	30.265	68.59	30.466	60.97

Contd..

Table 2 (Contd..)

0.40 mole fraction of PC

	Bu ₄ NBr		Pen ₄ NBr		Hex ₄ NBr	
	270.317	46.21	268.821	43.78	271.259	42.75
	249.449	46.85	240.083	44.64	249.861	43.33
	230.734	47.48	210.216	45.58	230.341	43.96
	210.184	48.17	180.349	46.61	200.151	44.85
	180.158	49.26	160.537	47.33	169.960	45.70
	139.737	50.82	140.144	48.12	140.888	46.82
	110.866	52.10	110.277	49.37	110.698	48.03
	79.685	53.69	80.410	50.82	80.507	49.28
	49.658	55.52	50.543	52.62	55.908	50.75
	30.026	57.09	29.866	54.30	30.190	52.35
	Hep ₄ NBr		NaBPh ₄		Bu ₄ NBPh ₄	
	221.389	43.20	269.297	36.68	147.394	37.50
	180.263	44.31	249.834	37.17	131.376	38.19
	149.806	45.28	230.364	37.66	109.710	39.13
	129.881	45.98	201.036	38.46	90.062	40.07
	109.956	46.70	169.742	39.40	75.052	40.84
	90.031	47.52	139.982	40.31	60.123	41.70
	70.106	48.44	110.222	41.37	49.899	42.35
	55.347	49.21	80.462	42.59	40.163	43.03
	39.850	50.16	49.600	44.09	30.061	43.79
	19.925	51.64	25.351	45.69	19.878	44.81

Contd..

Table 2 (Contd...)

0.60 mole fraction of PC

	-Me ₄ NBr		Et ₄ NBr		Pr ₄ NBr	
190.613	48.82	353.944	43.69	346.817	38.74	
162.131	49.81	311.372	44.72	300.574	39.78	
124.840	51.07	278.333	45.50	260.834	40.74	
109.708	51.64	225.344	46.84	225.431	41.68	
90.252	52.47	175.792	48.27	174.564	43.12	
70.256	53.46	125.060	50.02	124.854	44.67	
50.260	54.63	89.665	51.36	90.172	46.10	
30.264	56.03	68.919	52.31	69.363	47.10	
15.132	57.42	47.342	53.56	49.710	48.02	
7.566	58.40	33.602	54.39	30.057	49.31	
	Bu ₄ NBr		Pen ₄ NBr		Hex ₄ NBr	
373.447	37.12	371.387	34.78	355.918	33.70	
300.002	38.55	302.884	35.97	279.988	35.13	
261.317	39.42	261.784	36.77	250.683	35.81	
225.313	40.32	225.617	37.57	220.669	36.51	
175.520	41.57	175.622	38.70	169.654	37.76	
124.482	43.10	125.627	40.09	125.757	39.02	
90.872	44.31	91.016	41.17	90.165	40.23	
69.710	45.15	70.505	41.94	69.997	40.96	
49.792	46.12	49.999	42.75	51.014	41.89	
31.120	47.21	30.766	43.79	31.926	42.89	

Contd.

Table 2 (Contd..)

0.60 mole fraction of PC

	Hep ₄ NBr		NaBPh ₄		Bu ₄ NBPh ₄	
373.723	32.69	325.739	27.52	231.946	27.60	
300.192	34.00	251.165	28.94	175.863	28.93	
261.935	34.69	175.986	30.57	149.793	29.62	
225.796	35.55	145.700	31.28	130.442	30.23	
174.894	36.57	120.325	32.06	110.374	30.84	
125.297	37.89	94.951	32.83	90.306	31.51	
90.057	38.94	75.306	33.50	71.671	32.26	
70.479	39.69	55.660	34.28	50.170	33.17	
50.902	40.42	35.197	35.19	30.102	34.28	
30.019	41.49	20.463	36.09	20.068	34.97	

Table 3. Conductance parameters of tetraalkylammonium bromides, sodium tetraphenylborate and tetrabutylammonium tetraphenylborate in propylene carbonate (PC) + methanol mixtures at 25°C

Mole fraction of PC	Salt	$\Lambda_{\infty}/S \text{ cm}^2 \text{ mol}^{-1}$	$K_A/\text{dm}^3 \text{ mol}^{-1}$	$\Lambda_{\infty}\eta_{\infty}$	R/\bar{A}	σ
0.10	Me ₄ NBr	112.05 ± 0.04	20.80 ± 0.09	0.702	15.8	0.03
	Et ₄ NBr	105.79 ± 0.05	18.52 ± 0.14	0.663	16.8	0.05
	Pr ₄ NBr	95.50 ± 0.02	21.71 ± 0.06	0.598	16.6	0.02
	Bu ₄ NBr	89.75 ± 0.02	23.55 ± 0.08	0.562	17.1	0.03
	Pen ₄ NBr	86.10 ± 0.03	22.98 ± 0.09	0.539	17.0	0.03
	Hex ₄ NBr	83.87 ± 0.05	23.74 ± 0.19	0.525	17.8	0.06
	Hep ₄ NBr	81.04 ± 0.03	22.86 ± 0.11	0.508	18.0	0.03
	NaBPh ₄	76.01 ± 0.03	24.28 ± 0.13	0.476	18.5	0.04
	Bu ₄ NBPh ₄	73.68 ± 0.04	33.23 ± 0.19	0.462	20.9	0.05

Contd..

Table 3 (Contd..)

	Me ₄ NBr	98.99 ± 0.05	16.30 ± 0.10	0.712	15.3	0.05
	Et ₄ NBr	92.97 ± 0.03	12.75 ± 0.06	0.669	14.8	0.03
	Pr ₄ NBr	83.64 ± 0.03	15.40 ± 0.08	0.602	14.7	0.04
	Bu ₄ NBr	77.38 ± 0.04	16.01 ± 0.11	0.557	15.4	0.05
C.20	Pen ₄ NBr	75.11 ± 0.03	14.30 ± 0.08	0.540	15.3	0.04
	Hex ₄ NBr	73.52 ± 0.03	14.97 ± 0.08	0.529	16.1	0.04
	Hep ₄ NBr	72.21 ± 0.19	15.10 ± 0.54	0.519	12.9	0.03
	NaBPh ₄	66.22 ± 0.02	17.88 ± 0.05	0.476	17.1	0.02
	Bu ₄ NBPh ₄	64.85 ± 0.02	25.25 ± 0.11	0.466	18.9	0.04

Contd..

Table 3 (Contd..)

	Me ₄ NBr	78.15 ± 0.04	10.92 ± 0.07	0.762	14.4	0.05
	Et ₄ NBr	74.17 ± 0.02	10.37 ± 0.03	0.723	14.2	0.03
	Pr ₄ NBr	66.27 ± 0.02	10.13 ± 0.04	0.646	13.8	0.04
	Bu ₄ NBr	62.43 ± 0.01	13.32 ± 0.03	0.609	15.9	0.02
0.40	Pen ₄ NBr	59.59 ± 0.03	13.69 ± 0.07	0.581	14.7	0.05
	Hex ₄ NBr	57.41 ± 0.06	11.99 ± 0.15	0.560	15.3	0.11
	Hep ₄ NBr	55.68 ± 0.03	10.86 ± 0.08	0.543	14.4	0.05
	NaBPh ₄	50.02 ± 0.02	12.14 ± 0.04	0.488	15.7	0.03
	Bu ₄ NBPh ₄	48.84 ± 0.02	18.32 ± 0.10	0.476	19.9	0.05

Contd..

Table 3 (Contd..)

	Me ₄ NBr	60.57 ± 0.02	10.58 ± 0.07	0.786	9.3	0.05
	Et ₄ NBr	58.83 ± 0.03	10.70 ± 0.06	0.763	14.2	0.06
	Pr ₄ NBr	53.39 ± 0.03	12.11 ± 0.08	0.693	15.3	0.08
	Bu ₄ NBr	51.16 ± 0.02	10.88 ± 0.04	0.664	14.6	0.04
0.60	Pen ₄ NBr	47.50 ± 0.02	9.88 ± 0.06	0.616	14.2	0.06
	Hex ₄ NBr	46.76 ± 0.02	11.40 ± 0.07	0.607	15.1	0.06
	Hep ₄ NBr	45.01 ± 0.03	9.88 ± 0.08	0.584	15.0	0.09
	NaBPh ₄	38.96 ± 0.02	12.68 ± 0.09	0.505	17.0	0.06
	Bu ₄ NBPh ₄	37.89 ± 0.02	15.79 ± 0.08	0.492	18.3	0.05

Table 4. Walden products ($\Lambda \cdot \eta_0$) of tetraalkylammonium bromides, NaBPh_4 and Bu_4NBPh_4 in PC + methanol mixtures at 25°C

Salt	Mole fraction of PC					
	0.00	0.10	0.20	0.40	0.60	1.00
Me_4NBr	0.680	0.702	0.712	0.762	0.786	0.768
Et_4NBr	0.636	0.663	0.669	0.723	0.763	0.740
Pr_4NBr	0.558	0.598	0.602	0.646	0.693	0.706
Bu_4NBr	0.519	0.562	0.557	0.609	0.664	0.684
Pen_4NBr	0.497	0.539	0.540	0.581	0.616	0.620
Hex_4NBr	-----	0.525	0.529	0.560	0.607	0.602
Hep_4NBr	0.466	0.508	0.519	0.543	0.584	0.578
NaBPh_4	0.444	0.476	0.476	0.488	0.505	0.484
Bu_4NBPh_4	0.413	0.462	0.466	0.476	0.492	0.452

Table 5. Limiting ionic conductances (λ_0^+ , λ_0^-) in PC + methanol mixtures at 25°C
(λ_0 values are taken from Table 3).

Ion	Mole fraction of PC					
	0.00 ^a	0.10	0.20	0.40	0.60	1.00
Me ₄ N ⁺	68.7	60.39	55.13	43.97	29.00	12.87 ^b
Et ₄ N ⁺	60.5	54.13	49.11	39.99	27.26	11.72 ^b
Pr ₄ N ⁺	46.1	43.84	39.78	32.09	21.82	10.35 ^b
Bu ₄ N ⁺	39.0	38.09	33.52	28.25	19.59	9.46 ^b
Pen ₄ N ⁺	34.8	34.44	31.25	25.41	15.93	6.88 ^b
Hex ₄ N ⁺	---	32.21	29.66	23.23	15.19	6.16 ^b
Hep ₄ N ⁺	29.3	29.38	28.35	21.50	13.44	5.19 ^b
Na ⁺	45.2	40.42	34.89	26.43	20.66	10.74 ^c
Br ⁻	56.4	51.66	43.86	34.18	31.57	18.22 ^b
Ph ₄ B ⁻	36.6	35.59	31.33	23.59	18.30	8.84 ^b

^aData taken from ref. 3, p. 673

^bData taken from Chapter - IV

^cData taken from Chapter - V

Table 6. Stokes radii (r_s) in \AA of the ions in PC + methanol mixtures at 25°C

Ion	$r_c / \text{\AA}$	Mole fraction of PC					
		0.00	0.10	0.20	0.40	0.60	1.00
Me_4N^+	3.47 ^a	2.19	2.16	2.06	1.91	2.18	2.57
Et_4N^+	4.00 ^a	2.49	2.41	2.32	2.10	2.31	2.82
Pr_4N^+	4.52 ^a	3.26	2.98	2.86	2.62	2.89	3.20
Bu_4N^+	4.94 ^a	3.86	3.43	3.39	2.97	3.22	3.50
Pen_4N^+	5.29 ^a	4.32	3.79	3.64	3.30	3.95	4.81
Hex_4N^+	5.59 ^a	---	4.05	3.83	3.61	4.15	5.37
Hep_4N^+	5.88 ^a	5.13	4.44	4.01	3.90	4.70	6.38
Na^+	1.17 ^a	3.33	3.23	3.26	3.18	3.05	3.08
Br^-	1.80 ^b	2.67	2.53	2.59	2.46	2.00	1.82
Ph_4B^-	4.20 ^a	4.11	3.67	3.63	3.56	3.45	3.74

^aR.A. Robinson and H. Stokes, in *Electrolyte Solutions*, 2nd ed., Butterworths, London, 1959.

^bB.S. Gourary and F.J. Adrian, *Solid State Phys.*, 10, 127, 1960.

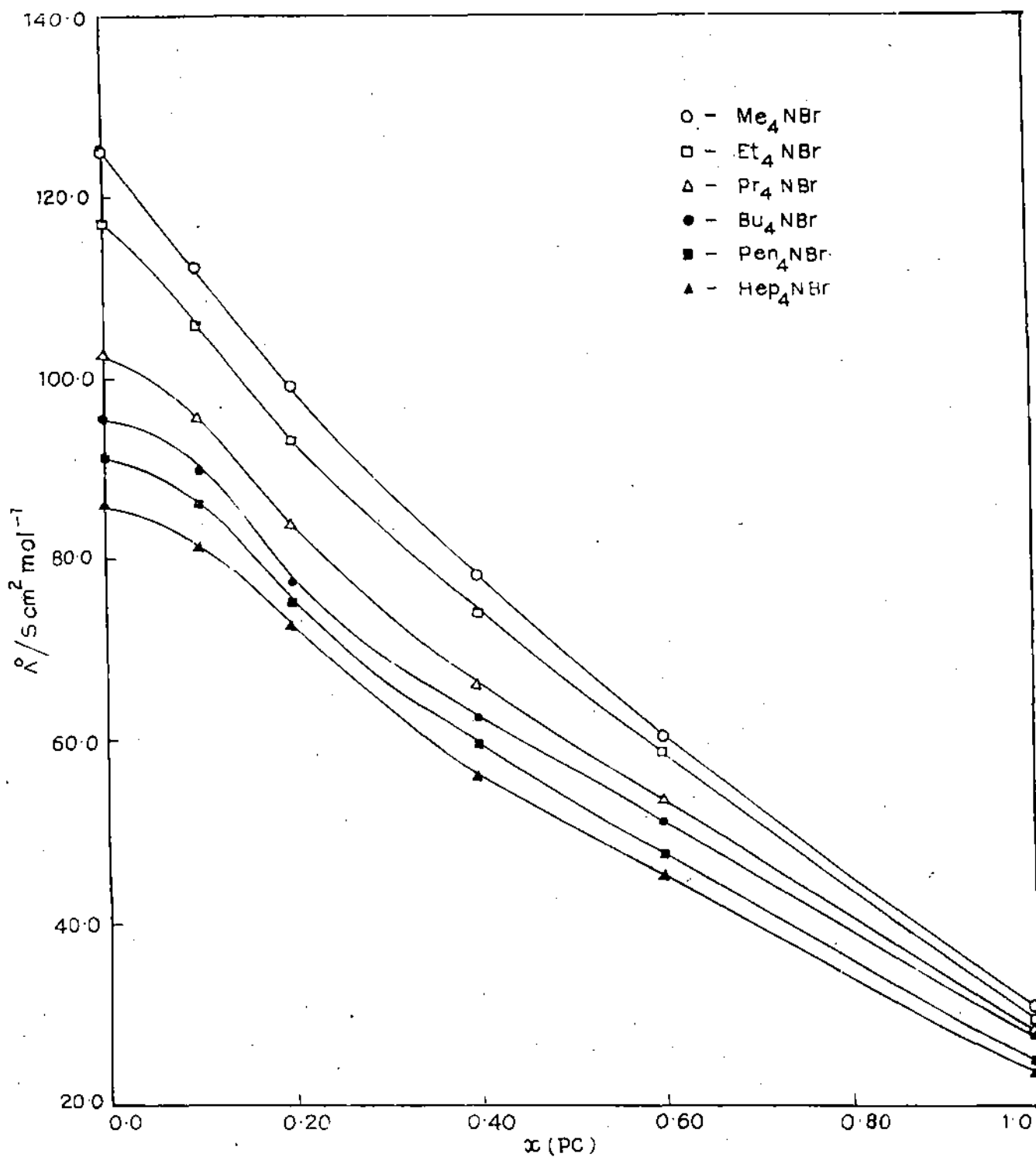


Fig. 1. Variation of limiting equivalent conductance (Λ°) with composition of the solvent mixture.

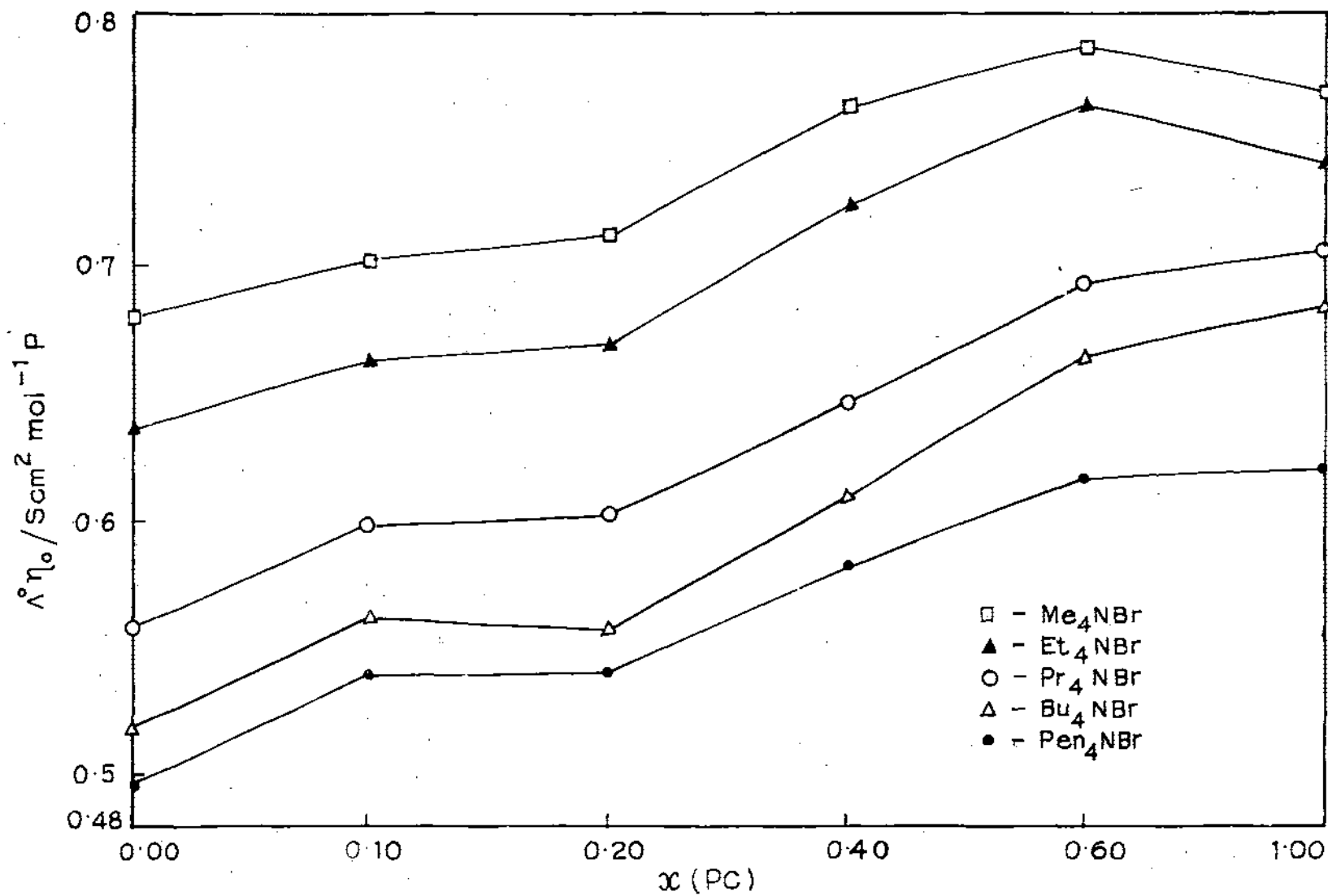


Fig. 2. Variation of Walden product with composition of the solvent mixture.

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