

## CHAPTER-IV

## PART - A

Electrical Conductances for Some Tetraalkylammonium Bromides, Lithium Tetrafluoroborate, Tetrabutylammonium Tetrabutylborate and Tetrabutylammonium Tetraphenylborate in Propylene Carbonate at 25°C

Propylene carbonate (PC, 4-methyl 1,3-dioxolan-2-one) has drawn much attention in recent years as a solvent medium for various electrochemical studies<sup>1,2</sup> relating to high energy batteries<sup>3,4</sup> and free radical species<sup>5</sup>. It is a stable solvent of moderately high dielectric constant<sup>6</sup> (64.40 at 25°C) and has good solvent properties<sup>7,8</sup> for a variety of organic and inorganic salts. Hence, it is of much interest to study the behaviour of electrolytes in such solvent medium. The conductometric method is also well known<sup>9</sup> to give valuable information regarding the ion-solvent interactions of electrolytes in non-aqueous and mixed solvents.

In this part an attempt has been made by us to understand the nature of ion-solvent interactions of some tetraalkylammonium bromides,  $R_4NBr$  ( $R =$  methyl to heptyl),  $LiBF_4$  and two reference electrolytes, viz.  $Bu_4NBBu_4$  and  $Bu_4NBPh_4$  in PC by using conductometric method. Single ion conductivities have been evaluated by using two reference electrolytes in an effort to provide reliable values of ionic mobilities. Conductance measurements on  $Bu_4NBr$ <sup>10</sup>,  $Bu_4NBBu_4$ <sup>11</sup> and  $Bu_4NBPh_4$ <sup>12</sup> though earlier have been reported by

different authors but these have further been investigated by us in order to maintain the internal consistency amongst the derived values with these electrolytes.

### Experimental

Propylene Carbonate (E. Merck Germany, > 99% pure) was dried over freshly ignited quicklime for several hours<sup>13</sup> and then distilled thrice under reduced pressure in nitrogen gas atmosphere, the middle fraction being taken each time. The purified sample had a density of 1.1988 g cm<sup>-3</sup>, viscosity of 2.471 cP and a specific conductance of ca.  $0.73 \times 10^{-6}$  S cm<sup>-1</sup> at 25°C; these values are in good agreement with the literature values<sup>10,14</sup>.

Tetraalkylammonium bromides were of Fluka's puram or puriss grade and were purified as described in the literature<sup>15,16</sup> and also described earlier in Chapter-II. The salts were purified by recrystallization and the higher homologues were recrystallized twice to ensure maximum purity. The recrystallized salts were dried in vacuo at elevated temperatures for 12 h.

Lithium tetrafluoroborate (Fluka, puriss) was dried under vacuum at high temperature for around 48 hrs immediately prior to use and was used without further purification.

Tetrabutylammonium tetrabutylborate (Alfa Products) was purified as suggested by Lawrence et al.<sup>17</sup>. Tetrabutylammonium tetraphenylborate was prepared by mixing equimolar quantities of  $\text{NaBPh}_4$  and  $\text{Bu}_4\text{NBr}$ . It was purified by recrystallization from 1:3 water-acetone mixture and dried under vacuum at  $40^\circ\text{C}$ .<sup>18</sup>

Conductance measurements were made by a Pye-Unicam PW 9509 conductivity meter at a frequency of 2,000 Hz using a dip-type immersion cell of cell constant  $0.751\text{ cm}^{-1}$  and having an accuracy of  $\pm 0.1\%$ . The cell constant was determined frequently using the standard KCl solutions. Measurements were made in an oil bath maintained at  $25 \pm 0.005^\circ\text{C}$ . The details of experimental procedure have been described in Chapter - II. Several independent solutions were prepared and measurements were made with each of these to ensure the reproducibility of the results. All data were corrected with the specific conductance of the solvent. The corrected values were analysed by means of Fuoss conductance equation<sup>19,20</sup>.

### Results

The measured equivalent conductances and the corresponding concentrations,  $C$ , in molarities are given in Table 1. The data were analyzed with the Fuoss conductance equation<sup>19,20</sup> which can be expressed as,

$$\Lambda = P \left[ \Lambda_0 (1 + R_x) + E_L \right] \quad (1)$$

$$P = [1 - \alpha (1 - \gamma)] \quad (2)$$

$$\gamma = 1 - K_{Ac} \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta c / 2 (1 + cR) \quad (4)$$

$$\beta = \frac{e^2}{\epsilon k_B T} \quad (5)$$

where  $R_X$  and  $E_L$  are relaxation and hydrodynamic terms, respectively, as derived by Fuoss, and the other terms have their usual significance. The parameters  $\Lambda_0$ ,  $K_A$  and  $R$  were obtained by solving the above equations. Initial  $\Lambda_0$  values for the iteration procedure were obtained from Shedlovsky extrapolation of the data.

In practice, calculations were made by finding the values of  $\Lambda_0$  and  $c$  which minimize for a sequence of  $R$ -values, and then plotting  $\sigma\% = 1000\sigma/\Lambda_0$  against  $R$ ; the best fit  $R$  corresponds to

$$\sigma^2 = \sum_j [\Lambda_j(\text{calc}) - \Lambda_j(\text{obs})]^2 / (n-2) \quad (6)$$

a minimum of the  $\sigma\%$  vs  $R$  curve. First approximate runs over a fairly wide range of  $R$  values were made to locate the minimum and

then a fine scan around the minimum was made. Finally, with this minimized value of  $R$ , the corresponding  $\Lambda_0$  and  $\alpha C$  were calculated.

The values of  $\Lambda_0$ ,  $K_A$  and  $R$  obtained by this procedure are recorded in Table 2. The limiting ionic conductances based on the values of  $\text{Bu}_4\text{NBBu}_4$  and  $\text{Bu}_4\text{NBPh}_4$  are given in Table 3. The limiting ion conductance value for  $\text{Li}^+$  ion was taken from the literature<sup>10</sup> to calculate the single ion mobility for  $\text{BF}_4^-$  ion, assuming that the rule of additivity holds too in this case.

### Discussion

Table 2 shows that the limiting equivalent conductances ( $\Lambda_0$ ) of the tetraalkylammonium bromides decrease as the alkyl chain-length increases. This is found to be in absolute agreement with earlier findings for tetraalkylammonium bromides in other aprotic solvents<sup>21</sup>. The size and structure forming effect decrease as the alkyl chain-length increases and consequently the mobility is in the reverse order. The  $\Lambda_0$  value of  $\text{Bu}_4\text{NBr}$  was earlier reported by Jansen and Yeager<sup>10</sup>. A comparison of the limiting equivalent conductance value for  $\text{Bu}_4\text{NBr}$  as obtained by us with that of Jansen and Yeager<sup>10</sup> shows a difference of ca. 0.4%, indicating the closeness of our values with theirs. Also, a comparison of the reported  $\Lambda_0$  value of  $\text{Bu}_4\text{NBBu}_4$  by Takeda et al<sup>11</sup> with ours shows a difference of ca. 1%. While Takeda et al<sup>11</sup> took the  $\Lambda_0$  value directly from the extrapolation of  $\Lambda$  vs.  $\sqrt{C}$  plots, on the other hand we have calculated it by

Fuoss method<sup>20</sup> and hence the observed difference. It is most likely that for similar reasons, our reported  $\Lambda_0$  value for  $\text{Bu}_4\text{NBPh}_4$  is 6.8% larger than the reported value  $(17.14)^{12}$ .

The association constant values in Table 2 show that the salts studied by us are essentially unassociated with the minor exception of  $\text{LiBF}_4$ . Presumably this salt indicates slight ion-pairing though the association constant is much less than that of  $\text{LiCl}^7$  and  $\text{LiBr}^7$ . It may be due to the very large size of tetra-fluoroborate ion which has a lower affinity for the lithium ion than the smaller  $\text{Cl}^-$  and  $\text{Br}^-$  ions. This decrease in the association constant as the anion size increases also agrees with the general contention of the theories of Denison and Ramsey<sup>22</sup>, and Gilkerson<sup>23</sup>. The greater  $\Lambda_0$  value of  $\text{LiBF}_4$  than that of  $\text{LiCl}$  and  $\text{LiBr}$  also corroborates the above view point. However, for  $\text{R}_4\text{N}^+$  ions, the general decrease in the association constant as the cation size increases is in agreement with the charge density values of these ions.

The single ion conductances have been evaluated from the division of  $\Lambda_0$  value of  $\text{Bu}_4\text{NBu}_4$  using the following relationship<sup>17,24</sup>

$$\lambda_0(\text{Bu}_4\text{N}^+) = \lambda_0(\text{Bu}_4\text{B}^-) \quad (7)$$

The reason behind the choice of  $\text{Bu}_4\text{NBu}_4$  as the reference electrolyte is in the fact that the cation and anion in this case are symmetrical

in shape and have almost equal van der Waals volume.

$\text{Bu}_4\text{NBPh}_4$  has also been utilized by various authors<sup>12,25</sup> to calculate limiting ion conductances assuming that  $\lambda_0$  values of its constituent ions viz.  $\text{Bu}_4\text{N}^+$  and  $\text{BPh}_4^-$  are equal. But the validity of this assumption has been questioned in several solvents owing to the unequal size of the cation and anion and also to the unequal electronic environment of the positive charge on the nitrogen atom and the negative charge on the boron atom. Instead of equal division, we have divided the  $\lambda_0$  values using the method similar to that proposed by Krumgalz<sup>26</sup> for division of viscosity B-values

$$\frac{\lambda_0(\text{Bu}_4\text{N}^+)}{\lambda_0(\text{BPh}_4^-)} = \frac{r(\text{BPh}_4^-)}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} = 1.07 \quad (8)$$

The r-values have been taken from the works of Gill et al<sup>24,27</sup>.

The  $\lambda_0$  values obtained by using the above two methods have been presented in Table 3. It can be readily seen that the limiting ionic conductances obtained from the above two methods are in very close agreement with each other. This suggests that either of the two methods can be used to calculate the limiting ionic conductances in organic solvents. Kay and coworkers<sup>8</sup> previously analysed the conductance data of several workers and calculated the best estimate of limiting ion conductances in PC at 25°C. Comparison of our



results with theirs reveals that in the case of  $\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$  and  $\text{Pr}_4\text{N}^+$  ions, the  $\lambda_0$  values obtained by us are 1-11% lower and for  $\text{Bu}_4\text{N}^+$ , the value is 5% higher than the values proposed by Kay <sup>10,11,13,28</sup> et al<sup>8</sup>. This discrepancy is due to the different procedures adopted for the calculation of  $\Lambda_0$  values and also on the choice of the 'reference electrolyte'<sup>8,10</sup>, which was also different for calculating the limiting ion conductances in non-aqueous solvents.

The Walden products ( $\lambda_0^{\pm} \eta_0$ ) and Stokes radii ( $r_s$ ) of the ions are reported in Table 3. The Walden product values are usually employed to discuss the ion-solvent interactions of the ions with the solvent medium. From the table, we see that for large  $\text{R}_4\text{N}^+$  ions,  $\lambda_0^{\pm} \eta_0$  is larger, the smaller is the size of the cation and for the electrolyte taken as a whole, it follows the same sequence (Table 2). It therefore leads to the fact that electrostatic ion-solvent interaction, is very weak in these cases. On the other hand, the alkali metal ions are small enough to possess the high electrostatic charge density on them resulting in strong ion-solvent interactions<sup>10</sup>. From Table 3, we also see that Stokes radii increase with the increasing size of the tetraalkylammonium ions and this is most likely due to less ionic mobilities of these cations. For  $\text{Li}^+$  ion, however, the Stokes radius is much greater than its crystallographic radius ( $0.93 \text{ \AA}$ )<sup>29</sup> indicating it to be substantially solvated in this solvent medium. On the other hand, the higher mobility of  $\text{Br}^-$  ion than the cations relative to its crystallographic size ( $1.80 \text{ \AA}$ )<sup>29</sup> indicates that it is poorly solvated in this medium. The

slight difference in limiting ionic conductance values of  $\text{Br}^-$  and  $\text{BF}_4^-$  ions seem to indicate that the effective sizes of these anions in PC are almost the same and thus very little solvation, if any, is involved in these cases. On the other hand, very low mobility of the tetrabutylboride ion has been attributed to its much larger size. Thus, from the result it appears that the large size of  $\text{R}_4\text{N}^+$  ions, its low charge density and high dielectric constant of PC render these ions to be free, unassociated and almost unsolvated in this medium.

Table 1. Equivalent conductances and corresponding molarities of the tetraalkylammonium bromides, tetrabutylammonium tetrabutylborate, lithium tetrafluoroborate and tetrabutylammonium tetraphenylborate in propylene carbonate at 25°C

$c/10^{-4} \text{ mol dm}^{-3}$	$\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$	$c/10^4 \text{ mol dm}^{-3}$	$\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$
	Me <sub>4</sub> NBr		Et <sub>4</sub> NBr
131.702	27.18	90.445	26.67
100.094	27.67	73.080	27.03
84.861	27.97	62.226	27.26
60.056	28.44	44.137	27.71
50.047	28.73	36.540	27.89
40.037	28.95	29.304	28.12
24.760	29.40	18.089	28.53
10.536	29.99		
	Pr <sub>4</sub> NBr		Bu <sub>4</sub> NBr
444.474	22.85	622.737	20.51
375.533	23.31	498.190	21.34
300.067	23.84	400.628	21.99
226.398	24.54	298.914	22.75
159.916	25.04	201.352	23.54
100.621	25.79	100.261	24.74
75.466	26.10	79.974	25.04
50.059	26.49	60.156	25.35
25.155	27.07	40.164	25.76
		20.052	26.28
	Pen <sub>4</sub> NBr		Hex <sub>4</sub> NBr
519.858	19.30	506.841	18.63
348.875	20.19	349.720	19.54
199.279	21.29	199.357	20.63
100.506	22.11	99.679	21.69
90.109	22.33	89.542	21.85
74.513	22.61	74.337	22.16

Contd..

Table 1 (Contd..)

60.304	22.82	60.097	22.16
45.027	23.10	45.073	22.50
30.152	23.45	30.048	22.80
		10.016	23.36
	Hep <sub>4</sub> NBr		LiBF <sub>4</sub>
523.988	18.12	529.635	19.64
399.977	18.68	398.992	20.73
300.450	19.05	300.127	21.70
200.862	19.73	199.496	23.06
99.558	20.51	100.631	24.66
75.105	20.93	90.038	24.90
60.084	21.00	74.149	25.21
45.063	21.55	60.025	25.59
30.042	21.80	45.019	26.01
		30.013	26.39
		10.004	27.39
	Bu <sub>4</sub> NBBu <sub>4</sub>		Bu <sub>4</sub> NBPh <sub>4</sub>
206.727	15.38	217.489	14.52
149.532	15.85	187.250	14.79
120.591	16.17	158.174	15.10
89.582	16.48	138.402	15.31
74.422	16.64	118.630	15.50
60.364	16.85	98.859	15.73
39.692	17.18	79.087	16.00
24.807	17.54	59.315	16.28
9.923	18.00	39.543	16.65

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Table 2. Conductance parameters of tetraalkylammonium bromides, lithium tetrafluoroborate tetrabutylammonium tetrabutylborate and tetrabutylammonium tetraphenylborate in PC at 25°C

Salts	$\Lambda_w/S \text{ cm}^2 \text{ mol}^{-1}$	$K_A/\text{dm}^3 \text{ mol}^{-1}$	walden product	$R/\overset{\circ}{\text{A}}$	$\sigma$
$\text{Me}_4\text{NBr}$	31.09 ( $\pm 0.02$ )	6.82 ( $\pm 0.11$ )	0.768	14.00	0.06
$\text{Et}_4\text{NBr}$	29.94 ( $\pm 0.01$ )	8.15 ( $\pm 0.10$ )	0.740	17.00	0.03
$\text{Pr}_4\text{NBr}$	28.57 ( $\pm 0.02$ )	4.20 ( $\pm 0.07$ )	0.706	13.30	0.12
$\text{Bu}_4\text{NBr}$	27.68 ( $\pm 0.01$ )	5.00 ( $\pm 0.04$ )	0.684	12.30	0.07
$\text{Pen}_4\text{NBr}$	25.10 ( $\pm 0.03$ )	3.92 ( $\pm 0.12$ )	0.620	8.30	0.20
$\text{Hex}_4\text{NBr}$	24.38 ( $\pm 0.03$ )	4.71 ( $\pm 0.16$ )	0.602	13.00	0.27
$\text{Hep}_4\text{NBr}$	23.41 ( $\pm 0.03$ )	3.65 ( $\pm 0.10$ )	0.578	10.50	0.19
$\text{Bu}_4\text{NBu}_4$	18.88 ( $\pm 0.01$ )	5.79 ( $\pm 0.12$ )	0.467	13.10	0.10
$\text{Bu}_4\text{NPh}_4$	18.30 ( $\pm 0.02$ )	8.16 ( $\pm 0.12$ )	0.452	18.20	0.08
$\text{LiBF}_4$	28.48 ( $\pm 0.02$ )	10.09 ( $\pm 0.11$ )	0.794	13.20	0.15

Table 3. Limiting ionic conductances, Walden products and Stokes radii of the ions in PC at 25°C

Ion	$\lambda_0^\pm$	$\lambda_0^{\pm c}$	$\lambda_0^\pm \eta^a$	$\lambda_0^\pm \eta^c$	$r_s^a$	$r_s^c$
Me <sub>4</sub> N <sup>+</sup>	12.85 <sup>a</sup>	12.87	0.319	0.319	2.56	2.56
Et <sub>4</sub> N <sup>+</sup>	11.70 <sup>a</sup>	11.72	0.290	0.291	2.82	2.81
Pr <sub>4</sub> N <sup>+</sup>	10.33 <sup>a</sup>	10.35	0.255	0.257	3.21	3.18
Bu <sub>4</sub> N <sup>+</sup>	9.44 <sup>a</sup>	9.46	0.234	0.235	3.49	3.48
Pen <sub>4</sub> N <sup>+</sup>	6.86 <sup>a</sup>	6.88	0.170	0.171	4.81	4.78
Hex <sub>4</sub> N <sup>+</sup>	6.14 <sup>a</sup>	6.16	0.152	0.153	5.38	5.35
Hep <sub>4</sub> N <sup>+</sup>	5.17 <sup>a</sup>	5.19	0.128	0.129	6.39	6.34
Li <sup>+</sup>	8.89 <sup>b</sup>	-----	0.220	-----	3.72	-----
Br <sup>-</sup>	18.24 <sup>a</sup>	18.22	0.452	0.450	1.81	1.82
BBu <sub>4</sub> <sup>-</sup>	9.44 <sup>a</sup>	9.42	0.234	0.234	3.49	3.50
BPh <sub>4</sub> <sup>-</sup>	8.86 <sup>a</sup>	8.84	0.219	0.218	3.74	3.75
BF <sub>4</sub> <sup>-</sup>	19.59	-----	0.486	-----	1.68	-----

<sup>a</sup> Calculations based on Bu<sub>4</sub>NBBu<sub>4</sub>

<sup>b</sup>  $\lambda_0^\pm$  of Li<sup>+</sup> ion taken from ref. 10

<sup>c</sup> Calculations based on Bu<sub>4</sub>NBPh<sub>4</sub>

## PART - B

Viscosity B Coefficients of Some Tetraalkylammonium Bromides, Lithium Tetrafluoroborate and Tetrabutylammonium Tetraphenyl borate in Propylene Carbonate at 25, 35 and 45°C

Studies on the transport properties of electrolytes in different solvents are of great importance to obtain information on the behaviour of ions in solutions. Recent years have therefore witnessed increased interest in this topic as are evidenced from numerous publications<sup>9,21,30-33</sup> in this field. One method employed for these investigations is to study solution viscosity. Viscometry is one of the important tools for the determination of ion-solvent interactions which are the controlling forces in dilute solutions where ion-ion interactions are absent<sup>26</sup>. The variations of solvational properties are reflected in the viscosity B-coefficients of ions.

In Part-A of the present chapter, we have studied ion-solvent interactions of some tetraalkylammonium bromides,  $R_4NBr$  and a few other salts in PC at 25°C from conductance measurements. We have now extended this work to study the viscometric behaviour of these electrolytes at different temperatures to obtain more information about specific ion-solvent interactions in this solvent. Ionic B values have been derived on the basis of the reference electrolyte ' $Bu_4NBPh_4$ ' and the transition-state treatment have been applied to analyse the results.

### Experimental

Propylene Carbonate (E. Merck Germany, > 99% pure) was purified according to the procedure described earlier in Chapter-II and also in Part-A of the present chapter. The solvent properties have been recorded in Table 1.

The purification of tetraalkylammonium bromides,  $\text{LiBF}_4$  and  $\text{Bu}_4\text{NBr}$  have been reported earlier in Chapter - II.

The concentrations of the salts generally varied in the range of  $0.01\text{--}0.08 \text{ mol dm}^{-3}$  which were prepared by weight dilution of the stock solution (ca.  $0.1 \text{ mol kg}^{-1}$ ). The conversion of the molality into molarity was done by using the density values. The kinematic viscosities were measured at the desired temperature (accuracy  $\pm 0.01 \text{ }^\circ\text{C}$ ) using a suspended Ubbelohde-type viscometer. The densities were measured using an Ostwald-Sprengel type pycnometer (25 ml) calibrated with distilled water. The details of the experimental procedure have been described previously in Chapter-II. The accuracies of viscosity and density measurements were 0.05% and  $\pm 3 \times 10^{-5} \text{ gcm}^{-3}$  respectively. Viscosity measurement for  $\text{Me}_4\text{NBr}$  in PC could not be performed owing to its poor solubility in this solvent medium.



### Results

The density ( $\rho$ ) and viscosity ( $\eta$ ) data for the electrolytes in the molarity range 0.01-0.08 mol dm<sup>-3</sup> at temperatures 25, 35 and 45°C have been reported in Table 2.

The experimental data have been analysed by the Jones-Dole equation<sup>34</sup>

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B \sqrt{c} \quad (1)$$

where  $\eta$  and  $\eta_0$  are the viscosities of the solution and solvent, respectively,  $c$  is the molar concentration and the other terms have their usual significance.

The plots of  $(\eta/\eta_0 - 1) / \sqrt{c}$  against  $\sqrt{c}$  (Figure 1) for the electrolytes are linear and the experimental A values at 25, 35 and 45°C have been calculated using the least squares method. The A coefficients were also calculated theoretically at 25°C from the physical properties of the solvent and the limiting ionic equivalent conductance by using the Falkenhagen and Vernon equation<sup>35</sup> :

$$A_{\text{theo}} = \frac{0.2577 \Lambda_0}{\eta_0 (\epsilon T)^{1/2} \lambda_+^+ \lambda_-^-} \left[ 1 - 0.6863 \left( \frac{\lambda_+^+ - \lambda_-^-}{\Lambda_0} \right)^2 \right] \quad (2)$$

The conductance data required in the above calculations were taken from Part-A of the present chapter. These A values have been used for analysis of the viscosity data. In view of the weak temperature dependence of the A coefficients, the A values at 25°C have been utilized at the other two temperatures. Theoretical A coefficients obtained from eqn. 2 along with the experimental A values are reported in Table 3.

Viscosity B coefficients obtained at various temperatures using the least squares method have been presented in Table 4.

Viscosity data have also been analysed on the basis of the transition-state treatment of the relative viscosity of electrolyte solutions as suggested by Feakins et al.<sup>36</sup>

$$B = \frac{\bar{V}_1^{\circ} - \bar{V}_2^{\circ}}{1000} + \frac{\bar{V}_1^{\circ}}{1000} \left( \frac{\Delta M_2^{\ddagger} - \Delta M_1^{\ddagger}}{RT} \right) \quad (3)$$

In the above equation  $\bar{V}_1^{\circ}$  and  $\bar{V}_2^{\circ}$  are the partial molar volumes of solvent and solute respectively.  $\Delta M_2^{\ddagger}$ , the contribution per mole of solute to the free-energy of activation for viscous flow of the solution, has been determined from the above relationship and reported in Table 4.  $\Delta M_1^{\ddagger}$ , the free energy of activation per mole of the pure solvent is given by the equation<sup>37</sup> :

$$\Delta \mu_1^{\circ \ddagger} = \Delta G_1^{\circ \ddagger} = RT \ln \left( \frac{\eta_0 \bar{V}_1^{\circ}}{hN} \right) \quad (4)$$

### Discussion

The A coefficients shown in Table 3 are found to be small and positive for all the electrolytes and the experimental results at 25°C agree well with the theoretical ones within 20% for the quarternary ammonium salts. This error in the small A values corresponds to the experimental uncertainty of 0.05% in the viscosity data. Similar results have been found earlier also in other systems<sup>38</sup>.

The viscosity B coefficients (Table 4) are large and positive and the values increase in PC as we go from tetraethylammonium to tetraheptylammonium bromide. Our reported viscosity B coefficient (1.043) at 25°C for Bu<sub>4</sub>NBr is slightly greater than the B value (0.960) reported previously by Boden et al<sup>7</sup> by simply plotting relative viscosity against concentration of Jones-Dole equation. The B value of lithium tetrafluoroborate is found to be approximately equal to that of Pen<sub>4</sub>NBr. The B coefficients show a moderate or weak temperature dependence and the values decrease with increase of temperature as observed earlier in some dipolar aprotic solvents like acetonitrile<sup>38,39</sup>, sulfolane<sup>40</sup> and DMSO<sup>16,41</sup>.

Further, from Table 4 we see that although  $\partial B/\partial T$  is small but it is negative in sign for all the electrolytes, indicating that they behave as structure makers in this solvent medium.

The ionic B values were calculated by eqn. 6 using  $\text{Bu}_4\text{NBPh}_4$  as the 'reference electrolyte'<sup>42,43</sup>.

$$B(\text{Bu}_4\text{NBPh}_4) = B(\text{Bu}_4\text{N}^+) + B(\text{BPh}_4^-) \quad (5)$$

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \left( \frac{5.35}{5.00} \right)^3 \quad (6)$$

The ionic B values along with the ionic  $\Delta \mu_{\pm}^{\text{oz}}$  data obtained from the above relationships have been recorded in Table 5. Table 5 shows that the viscosity B coefficients for cations and anions are all positive and also very high. Ionic B value for  $\text{Li}^+$  at  $25^\circ\text{C}$  was calculated from the reported viscosity B value of  $\text{LiBr}^7$  in PC / with the help of additivity rule. The observed order of  $B_{\pm}$  coefficients,  $\text{HeP}_4\text{N}^+ > \text{Hex}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+$ , shows that the obstruction to solvent viscous flow increases with decrease of ion charge density and with the decrease of the size of hydrodynamic entity by solvation. For anions, the B-value is seen to be in the order  $\text{BPh}_4^- > \text{Br}^- > \text{BF}_4^-$ . The  $\partial B_{\pm}/\partial T$  values of cations and anions are generally found to be negative (structure-making). This

behaviour of tetraalkylammonium ions in PC, arising mainly from the interactions of alkyl groups and solvent molecules is similar to that as observed earlier in sulfolane by Sacco and coworkers<sup>40,44</sup>.

The values of  $\Delta \mu_{\ddagger}^{\ddagger}$  for tetraalkylammonium ions decrease in the order :  $\text{Hep}_4\text{N}^+ > \text{Hex}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+$  and for anions  $\text{BPh}_4^- > \text{Br}^-$ . However, these values are found to be positive and thus the formation of transition-state is less favourable in the presence of these ions.

Ionic  $B_{\ddagger}$  coefficients have also been analysed on the basis of Einstein's equation<sup>45</sup>.

$$B_{\ddagger} = 2.5 \frac{4}{3} \pi \frac{R_{\ddagger}^3 N}{1000} \quad (7)$$

where  $R_{\ddagger}$  is the radius at the ion assumed as the rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The number of solvent molecules ( $n_s$ ) bound to the ion in the primary sphere of solvation can be calculated by combination of the Jones-Dole equation with that of Einstein's<sup>46</sup>.

$$B_{\ddagger} = \frac{2.5}{1000} (V_1 + n_s V_s) \quad (8)$$

where  $V_1$  represents the bare ion molar volume and is related to the crystallographic radius,  $r_c$ , of the ions.  $V_s$  is the solvent molar volume. The values of  $R_{\ddagger}$  and  $n_s$  are shown in Table 6.

The  $R_{\pm}$  values for tetraalkylammonium ions are found to be in reasonable agreement with the Stokes and crystallographic radii. The results indicate that these ions are scarcely solvated in PC and behave as spherical entities. However,  $R_{\pm}$  value of  $\text{Li}^+$  ion is much higher than its crystallographic radius, indicating that it is highly solvated in PC by ion-dipole interactions. Similar results have been obtained by conductometric measurements<sup>33</sup> which shows that  $\text{Li}^+$  is highly solvated in this medium. Thus, it appears that the large size of  $\text{R}_4\text{N}^+$  ions, their low charge density and the high dielectric constant of PC render these ions to be free, unassociated and almost unsolvated in this medium.

Table 1. Solvent properties of propylene carbonate

Temperature (°C)	Density (gcm <sup>-3</sup> )	Viscosity (cP)	Dielectric Constant
25	1.19883	2.4712	64.40 <sup>a</sup>
35	1.18970	2.0476	63.41 <sup>b</sup>
45	1.17796	1.7234	60.92 <sup>c</sup>

<sup>a</sup> from ref. 6

<sup>b</sup> from G. Ritzoulis, *Can. J. Chem.*, **67**, 1105, 1989

<sup>c</sup> from G. Moumouzias, D.K. Panopoulos and G. Ritzoulis, *J. Chem. Eng. Data*, **36**, 20, 1991.

Table 2. Concentration,  $c$ /(mol dm<sup>-3</sup>), density,  $\rho$ /(gcm<sup>-3</sup>) and relative viscosity,  $\eta_r$  of tetraalkylammonium bromides, LiBF<sub>4</sub> and Bu<sub>4</sub>NBPh<sub>4</sub> in PC at 25, 35 and 45°C

$c$	$\rho$	$\eta_r$	$c$	$\rho$	$\eta_r$
	Et <sub>4</sub> NBr	25°C		Pr <sub>4</sub> NBr	25°C
0.01002	1.19000	1.0081	0.00995	1.19870	1.0096
0.01644	1.19910	1.0130	0.02020	1.19856	1.0188
0.02506	1.19925	1.0193	0.03015	1.19843	1.0351
0.03509	1.19941	1.0266	0.05005	1.19816	1.0452
0.04511	1.19957	1.0343	0.06001	1.19803	1.0540
0.05514	1.19973	1.0418	0.08020	1.19776	1.0716
	Bu <sub>4</sub> NBr	25°C		Pen <sub>4</sub> NBr	25°C
0.01015	1.19837	1.0116	0.00990	1.19817	1.0130
0.01999	1.19792	1.0224	0.02011	1.19749	1.0253
0.03076	1.19743	1.0337	0.03001	1.19682	1.0382
0.05014	1.19654	1.0538	0.05011	1.19547	1.0619
0.05998	1.19609	1.0642	0.06002	1.19480	1.0750
0.07997	1.19517	1.0871	0.08012	1.19343	1.0991

Contd...



Table 2. (Contd..)

Hex <sub>4</sub> NBr 25°C			HeP <sub>4</sub> NBr 25°C		
0.00999	1.19779	1.0149	0.01007	1.19750	1.0159
0.02498	1.19621	1.0368	0.03002	1.19485	1.0458
0.03997	1.19464	1.0583	0.04009	1.19351	1.0606
0.04996	1.19359	1.0715	0.04996	1.19219	1.0761
0.06994	1.19149	1.1017	0.06003	1.19084	1.0904
LiBF <sub>4</sub> 25°C			Bu <sub>4</sub> NBPh <sub>4</sub> 25°C		
0.01031	1.19937	1.0134	0.00998	1.19796	1.0149
0.02508	1.20013	1.0311	0.01997	1.19708	1.0293
0.04020	1.20091	1.0503	0.02995	1.19620	1.0418
0.05017	1.20142	1.0623	0.04502	1.19487	1.0513
0.06013	1.20193	1.0784	0.05990	1.19356	1.0844
0.08007	1.20294	1.0975			

Contd..

Table 2. (Contd..)

Et <sub>4</sub> NBr 35°C			Pr <sub>4</sub> NBr 35°C		
0.00995	1.18992	1.0077	0.00988	1.18955	1.0089
0.01632	1.19006	1.0119	0.02004	1.18938	1.0175
0.02487	1.19025	1.0186	0.02992	1.18923	1.0255
0.03483	1.19047	1.0248	0.04967	1.18891	1.0425
0.04478	1.19069	1.0326	0.05954	1.18875	1.0499
0.05473	1.19091	1.0391	0.07958	1.18843	1.0676
Bu <sub>4</sub> NBr 35°C			Pen <sub>4</sub> NBr 35°C		
0.01007	1.18898	1.0113	0.00982	1.18799	1.0125
0.01983	1.18828	1.0215	0.01992	1.18622	1.0244
0.03050	1.18751	1.0325	0.02918	1.18460	1.0361
0.04970	1.18612	1.0523	0.04956	1.18101	1.0587
0.05945	1.18542	1.0625	0.05931	1.17929	1.0716
0.07923	1.18398	1.0828	0.07963	1.17570	1.0949

Contd..

Table 2. (Contd..)

Hex <sub>4</sub> NBr 35°C			Hep <sub>4</sub> NBr 35°C		
0.00991	1.18808	1.0145	0.00999	1.18803	1.0155
0.02475	1.18563	1.0352	0.02976	1.18472	1.0446
0.03958	1.18318	1.0558	0.03974	1.18303	1.0584
0.04945	1.18155	1.0693	0.04951	1.18138	1.0730
0.06917	1.17827	1.0961	0.05947	1.17969	1.0879
LiBF <sub>4</sub> 35°C			Bu <sub>4</sub> NBPh <sub>4</sub> 35°C		
0.01022	1.19025	1.0125	0.00906	1.18873	1.0141
0.02487	1.19104	1.0295	0.01944	1.18762	1.0277
0.03987	1.19184	1.0424	0.02971	1.18651	1.0411
0.04976	1.19237	1.0572	0.04464	1.18490	1.0621
0.05966	1.19290	1.0683	0.05939	1.18331	1.0808
0.07947	1.19396	1.0909			

Contd..

Table 2. (Contd..)

Et <sub>4</sub> NBr 45°C			Pr <sub>4</sub> NBr 45°C		
0.00985	1.17827	1.0071	0.00977	1.17785	1.0077
0.01616	1.17847	1.0117	0.01985	1.17773	1.0161
0.02463	1.17873	1.0174	0.02963	1.17761	1.0241
0.03449	1.17904	1.0243	0.04919	1.17737	1.0401
0.04435	1.17935	1.0310	0.05897	1.17725	1.0401
0.05421	1.17965	1.0374	0.07881	1.17701	1.0480
					1.0640
Bu <sub>4</sub> NBr 45°C			Pen <sub>4</sub> NBr 45°C		
0.00998	1.17707	1.0108	0.00972	1.17541	1.0120
0.01966	1.17621	1.0200	0.01969	1.17279	1.0235
0.03025	1.17526	1.0315	0.02935	1.17026	1.0354
0.04933	1.17355	1.0500	0.04885	1.16514	1.0574
0.05903	1.17267	1.0601	0.05840	1.16263	1.0679
0.07875	1.17089	1.0798	0.07911	1.15719	1.0912

Contd..

Table 2. (Contd..)

Hex <sub>4</sub> NBr 45°C			Hep <sub>4</sub> NBr 45°C		
0.00981	1.17568	1.0147	0.00990	1.17598	1.0151
0.02452	1.17226	1.0347	0.02951	1.17206	1.0435
0.03921	1.16884	1.0546	0.03942	1.17007	1.0585
0.04899	1.16657	1.0678	0.04913	1.16813	1.0711
0.06853	1.16202	1.0940	0.05762	1.16643	1.0836
LiBF <sub>4</sub> 45°C			Bu <sub>4</sub> NBPh <sub>4</sub> 45°C		
0.01012	1.17877	1.0117	0.00980	1.17681	1.0144
0.02463	1.17992	1.0272	0.01926	1.17570	1.0272
0.03951	1.18110	1.0435	0.02943	1.17451	1.0406
0.04932	1.18187	1.0538	0.04423	1.17277	1.0597
0.05915	1.18265	1.0636	0.05886	1.17105	1.0787
0.07882	1.18420	1.0839			

Table 3. Theoretical A values and experimental A Coefficients,  $A_{\text{obs}}/(\text{dm}^{3/2}\text{mol}^{-1/2})$  at 25, 35 and 45°C

Salts	$A_{\text{theo}}$	$A_{\text{obs}}$		
		25°C	35°C	45°C
Et <sub>4</sub> NBr	0.0102	0.0082	0.0089	0.0066
Pr <sub>4</sub> NBr	0.0108	0.0104	0.0080	0.0080
Bu <sub>4</sub> NBr	0.0113	0.0093	0.0109	0.0083
Pen <sub>4</sub> NBr	0.0130	0.0106	0.0117	0.0138
Hex <sub>4</sub> NBr	0.0136	0.0079	0.0125	0.0189
Hep <sub>4</sub> NBr	0.0147	0.0115	0.0128	0.0139
LiBF <sub>4</sub>	0.0114	0.0072	0.0095	0.0152
Bu <sub>4</sub> NBPh <sub>4</sub>	0.0176	0.0135	0.0198	0.0237

Table 4. Viscosity B coefficients,  $B/(\text{cm}^3 \text{mol}^{-1})$  and  $\Delta/\mu_2^{\text{oz}}$  ( $\text{kJ mol}^{-1}$ ) values in propylene carbonate at different temperatures

Salts	25°C		35°C		45°C	
	B	$\Delta/\mu_2^{\text{oz}}$	B	$\Delta/\mu_2^{\text{oz}}$	B	$\Delta/\mu_2^{\text{oz}}$
Et <sub>4</sub> NBr	0.716±0.004	38.56	0.674±0.009	37.86	0.653±0.003	37.57
Pr <sub>4</sub> NBr	0.855±0.001	44.70	0.810±0.007	44.26	0.788±0.001	44.24
Bu <sub>4</sub> NBr	1.043±0.012	52.31	1.005±0.001	52.89	0.975±0.007	53.41
Pen <sub>4</sub> NBr	1.194±0.007	58.59	1.145±0.010	61.04	1.106±0.006	63.36
Hex <sub>4</sub> NBr	1.385±0.019	66.43	1.339±0.002	67.98	1.315±0.008	70.41
Hep <sub>4</sub> NBr	1.454±0.009	70.45	1.416±0.010	71.73	1.391±0.015	73.34
LiBF <sub>4</sub>	1.203±0.036	49.95	1.105±0.032	47.00	1.021±0.006	44.52
Bu <sub>4</sub> NBPh <sub>4</sub>	1.302±0.061	66.68	1.283±0.013	68.08	1.256±0.002	68.92

Table 5. Ionic B coefficients,  $B_{\pm}/(\text{dm}^3 \text{mol}^{-1})$  and ionic  $\Delta/M_2^{\ddagger}/(\text{kJ mol}^{-1})$  values in PC at different temperatures

Ion	25°C		35°C		45°C	
	$B_{\pm}$	$\Delta/M_2^{\ddagger}$	$B_{\pm}$	$\Delta/M_2^{\ddagger}$	$B_{\pm}$	$\Delta/M_2^{\ddagger}$
Et <sub>4</sub> N <sup>+</sup>	0.258	16.22	0.246	15.57	0.242	15.13
Pr <sub>4</sub> N <sup>+</sup>	0.397	22.36	0.382	21.97	0.377	21.80
Bu <sub>4</sub> N <sup>+</sup>	0.585	29.97	0.577	30.60	0.564	30.97
Pen <sub>4</sub> N <sup>+</sup>	0.736	36.25	0.717	38.75	0.695	40.92
Hex <sub>4</sub> N <sup>+</sup>	0.927	44.09	0.911	45.69	0.904	47.97
Hep <sub>4</sub> N <sup>+</sup>	0.996	48.11	0.988	49.44	0.980	50.90
Li <sup>+</sup>	0.792	-----	-----	-----	-----	-----
Br <sup>-</sup>	0.458	22.34	0.428	22.29	0.411	22.44
BF <sub>4</sub> <sup>-</sup>	0.411	-----	-----	-----	-----	-----
BPh <sub>4</sub> <sup>-</sup>	0.717	36.71	0.706	37.48	0.692	37.95



Table 6. Ionic radii,  $R_{\pm}^{\circ}$  (Å) and solvation number,  $n_s$ , of ions in PC at 25°C

Ion	$r_c$ (Å)	$r_s$ (Å)	$R_{\pm}^{\circ}$ (Å)	$n_s$
Et <sub>4</sub> N <sup>+</sup>	4.00	2.82	3.45	-1.94
Pr <sub>4</sub> N <sup>+</sup>	4.52	3.21	3.98	-2.68
Bu <sub>4</sub> N <sup>+</sup>	4.94	3.49	4.53	-3.18
Pen <sub>4</sub> N <sup>+</sup>	5.29	4.81	4.89	-3.82
Hex <sub>4</sub> N <sup>+</sup>	5.59	5.38	5.28	-4.24
Hep <sub>4</sub> N <sup>+</sup>	5.88	6.39	5.41	-5.32
Li <sup>+</sup>	0.60	3.72	5.01	3.71
Br <sup>-</sup>	1.95	1.81	4.17	1.78
BF <sub>4</sub> <sup>-</sup>	2.01	1.68	4.02	1.53
BPh <sub>4</sub> <sup>-</sup>	4.20	3.76	4.84	-0.28

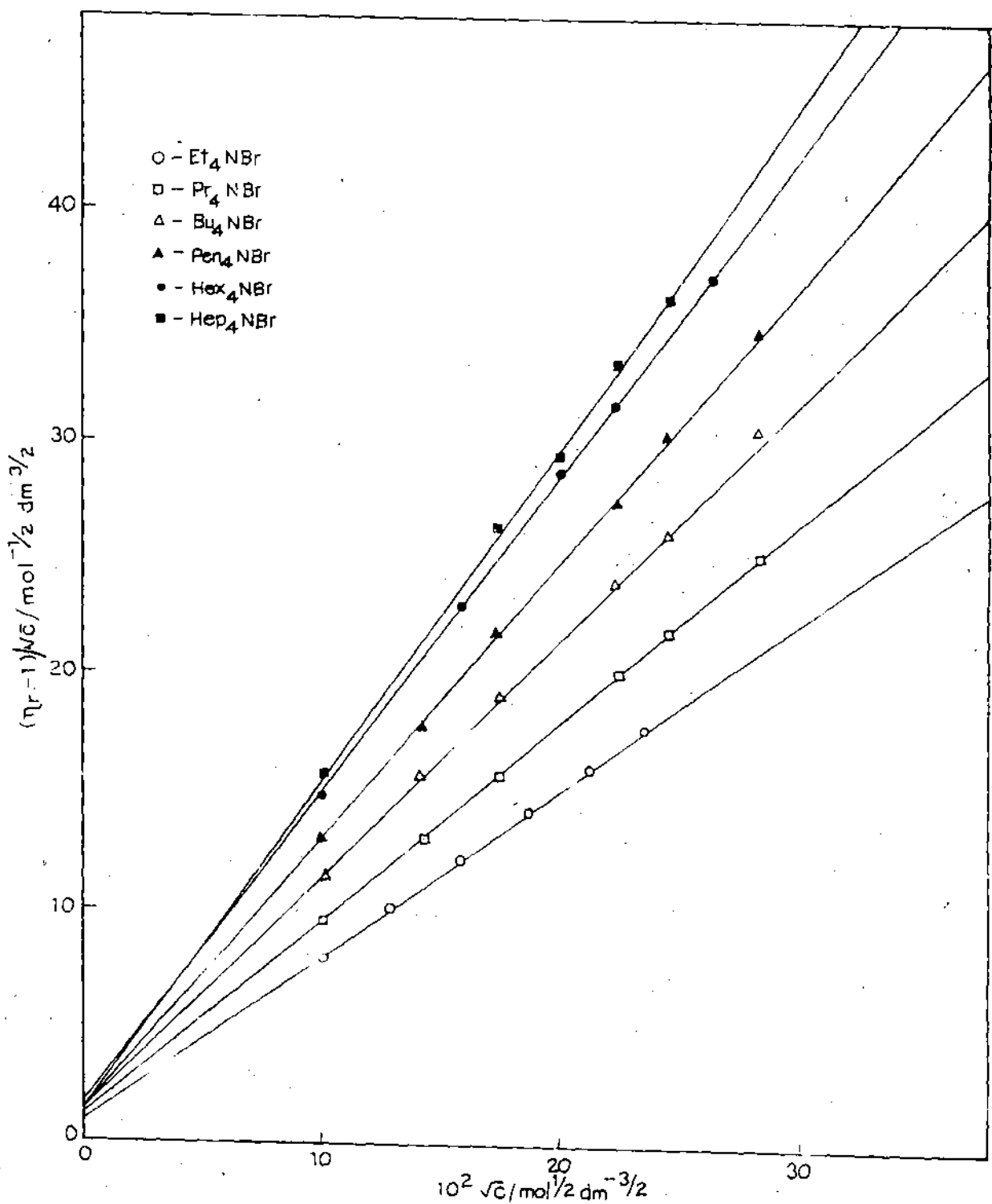


Fig. 1. Representative plot of  $(\eta_r - 1)/\sqrt{c}$  against  $\sqrt{c}$  for some electrolytes in PC at 25°C

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