

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

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Conductance measurements are reported for several symmetrical tetraalkylammonium bromides, lithium tetrafluoroborate ( $\text{LiBF}_4$ ) and tetrabutylammonium tetrabutylborate ( $\text{Bu}_4\text{NBBu}_4$ ) in propylene carbonate (PC) at 25 °C. The data have been analysed by the 1978 Fuoss conductance equation in terms of the limiting molar conductivity,  $\Lambda^\circ$ , the association constant,  $K_A$ , and the association distance  $R$ . The single-ion conductances have been determined from the  $\Lambda^\circ$  value of  $\text{Bu}_4\text{NBBu}_4$  using it as a 'reference electrolyte'. The results indicate that with the exception of  $\text{LiBF}_4$  to some extent, other salts are almost unassociated in this solvent medium. The evaluation of Stokes radii of the ions indicate that  $\text{Li}^+$  is extensively solvated while the other ions remain almost unsolvated. The results have been discussed in terms of the ion-solvating ability of PC and also compared with the previous values in this system.

Propylene carbonate (PC) has drawn much attention in recent years as a solvent medium for electrochemical studies<sup>1</sup> relating to high-energy batteries<sup>2,3</sup> and free-radical species.<sup>4</sup> It is a stable solvent of moderately high relative permittivity<sup>5</sup> (64.40 at 25 °C) and has good solvent properties<sup>6,7</sup> for a variety of organic and inorganic salts. Hence, it is of much interest to study the behaviour of electrolytes in such a solvent medium. The conductometric method is well known<sup>8</sup> to give valuable information regarding ion-solvent interactions of electrolytes in non-aqueous and mixed solvents. Although conductance measurements on alkali-metal iodides<sup>9-11</sup> and quaternary ammonium perchlorates<sup>6,11</sup> have been reported in PC, no such experimental data for tetraalkylammonium bromides (except tetrabutylammonium bromide) and lithium tetrafluoroborate are available in the literature. Conductance measurements on tetrabutylammonium tetrabutylborate have been reported by Takeda and co-workers,<sup>12</sup> but this compound has been further investigated by us in order to maintain an internal consistency amongst the derived values with these electrolytes.

We have therefore repeated a few of the earlier measurements and have also measured the electrical conductances of several additional tetraalkylammonium bromides,  $\text{R}_4\text{NBr}$  ( $\text{R}$  = methyl to heptyl),  $\text{LiBF}_4$  and  $\text{Bu}_4\text{NBBu}_4$  in PC at 25 °C. Single-ion conductances have been derived using  $\text{Bu}_4\text{NBBu}_4$  as the 'reference electrolyte' in an effort to provide reliable values of the ionic mobilities for these ions in this medium.

## Experimental

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

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described in the literature.<sup>15,16</sup> 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 ca. 48 h immediately prior to use and was used without further purification.

Tetrabutylammonium tetrabutylborate (Alfa Products) was purified as suggested in ref. 17.

Conductance measurements were made using a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 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 checked frequently using standard KCl solutions. Measurements were made in an oil bath maintained at  $25 \pm 0.005$  °C. Details of the experimental procedure have been described previously.<sup>18</sup> 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 the 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 analysed with the Fuoss conductance equation<sup>19,20</sup> which can be expressed as

$$\Lambda = P[(\Lambda^\circ(1 + R_x) + E_L)] \quad (1)$$

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

$$\bar{\gamma} = 1 - K_A c \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta k/2(1 + kR) \quad (4)$$

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

where  $R_x$  and  $E_L$  are relaxation and hydrodynamic terms, respectively, and the other terms have their usual meanings. The parameters  $\Lambda^\circ$ ,  $K_A$  and  $R$  were obtained by solving the above equations. Initial  $\Lambda^\circ$  values for the iteration procedure were obtained from Shedlovsky extrapolation of the data.

In practice, calculations were made by finding the minimum values of  $\Lambda^\circ$  and  $\alpha$  for a sequence of  $R$  values and then plotting

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

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

$C/10^{-4}$ mol dm <sup>-3</sup>	$\Lambda/S$ cm <sup>2</sup> mol <sup>-1</sup>	$C/10^3$ mol dm <sup>-3</sup>	$\Lambda/S$ cm <sup>2</sup> mol <sup>-1</sup>
<b>Me<sub>4</sub>NBr</b>		<b>Et<sub>4</sub>NBr</b>	
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		
<b>Pr<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NBr</b>	
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	79.874	25.04
50.059	26.49	60.156	25.35
25.155	27.07	40.104	25.76
		20.052	26.28
<b>Pen<sub>4</sub>NBr</b>		<b>Hex<sub>4</sub>NBr</b>	
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
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
<b>Hep<sub>4</sub>NBr</b>		<b>LiBF<sub>4</sub></b>	
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
<b>Bu<sub>4</sub>NBBu<sub>4</sub></b>			
206.727	15.38		
149.532	15.85		
120.591	16.17		
89.582	16.48		
74.422	16.64		
60.364	16.85		
39.692	17.18		
24.807	17.54		
9.923	18.00		

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

ion	$\lambda_0^\pm/S$ cm <sup>2</sup> mol <sup>-1</sup>	$\lambda_0^\pm \eta_0/S$ cm <sup>2</sup> mol <sup>-1</sup> P <sup>1</sup>	$r_s/\text{nm}$
Me <sub>4</sub> N <sup>+</sup>	12.85	0.319	0.26
Et <sub>4</sub> N <sup>+</sup>	11.70	0.290	0.28
Pr <sub>4</sub> N <sup>+</sup>	10.33	0.255	0.32
Bu <sub>4</sub> N <sup>+</sup>	9.44	0.234	0.35
Pen <sub>4</sub> N <sup>+</sup>	6.86	0.170	0.48
Hex <sub>4</sub> N <sup>+</sup>	6.14	0.152	0.54
Hep <sub>4</sub> N <sup>+</sup>	5.17	0.128	0.64
Li <sup>+</sup>	8.89	0.220	0.37
Br <sup>-</sup>	18.24	0.452	0.18
BBu <sub>4</sub> <sup>-</sup>	9.44	0.234	0.35
BF <sub>4</sub> <sup>-</sup>	19.59	0.486	0.17

$\sigma(\%) = 100\sigma/\Lambda^0$  against  $R$ ; the best-fit  $R$  corresponds to 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  $\alpha$  were calculated.

The values of  $\Lambda^0$ ,  $K_A$  and  $R$  obtained by this procedure are recorded in Table 2. The limiting ionic conductances ( $\lambda_0^\pm$ ) based on the value of Bu<sub>4</sub>NBBu<sub>4</sub> are given in Table 3. The  $\lambda_0^\pm$  value for the Li<sup>+</sup> ion was taken from ref. 11 to calculate the single-ion mobility for BF<sub>4</sub><sup>-</sup> ion, assuming that the rule of additivity holds 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 in 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.  $\Lambda^0$  for Bu<sub>4</sub>NBr was reported by Jansen and Yeager.<sup>11</sup> A comparison of the limiting equivalent conductance for Bu<sub>4</sub>NBr as obtained by us with that of ref. 11 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 Bu<sub>4</sub>NBBu<sub>4</sub> by Takeda and co-workers<sup>12</sup> with ours shows a difference of ca. 1%. Takeda and co-workers<sup>12</sup> reported the  $\Lambda^0$  value directly from the extrapolation of  $\Lambda$  vs.  $\sqrt{C}$  plots, while our value was determined by the Fuoss method,<sup>20</sup> hence the observed difference.

The association constants in Table 2 show that these salts are essentially unassociated with the minor exception of LiBF<sub>4</sub>. Presumably this salt shows slight ion-pairing though the association constant is much less than that of LiCl<sup>6</sup> and LiBr.<sup>6</sup> This may be due to the very large size of the tetrafluoroborate ion which has a lower affinity for the lithium ion

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

salts	$\Lambda^0/S$ cm <sup>2</sup> mol <sup>-1</sup>	$K_A/\text{dm}^3$ mol <sup>-1</sup>	Walden product	$R/\text{nm}$	$\sigma$
Me <sub>4</sub> NBr	31.09 ± 0.02	6.82 ± 0.11	0.768	1.40	0.06
Et <sub>4</sub> NBr	29.94 ± 0.01	8.15 ± 0.10	0.740	1.70	0.03
Pr <sub>4</sub> NBr	28.57 ± 0.02	4.20 ± 0.07	0.706	1.33	0.12
Bu <sub>4</sub> NBr	27.68 ± 0.01	5.00 ± 0.04	0.684	1.23	0.07
Pen <sub>4</sub> NBr	25.10 ± 0.03	3.92 ± 0.12	0.620	0.83	0.20
Hex <sub>4</sub> NBr	24.38 ± 0.03	4.71 ± 0.16	0.602	1.30	0.27
Hep <sub>4</sub> NBr	23.41 ± 0.03	3.65 ± 0.10	0.578	1.05	0.19
Bu <sub>4</sub> NBBu <sub>4</sub>	18.88 ± 0.01	5.79 ± 0.12	0.467	1.31	0.10
LiBF <sub>4</sub>	28.48 ± 0.02	10.09 ± 0.11	0.704	1.32	0.15

than the smaller  $\text{Cl}^-$  and  $\text{Br}^-$  ions. The decrease in the association constant with increasing anion size agrees with the theories of Denison and Ramsey,<sup>22</sup> and Gilkerson.<sup>23</sup> The higher  $\Lambda^0$  value of  $\text{LiBF}_4$  than that of  $\text{LiCl}$  and  $\text{LiBr}$  also corroborates the above viewpoint. However, for  $\text{R}_4\text{N}^+$  ions, the general decrease in the association constant with increasing cation size is in agreement with the charge density values of these ions.

The single-ion conductances were evaluated from the division of  $\Lambda^0$  value of  $\text{Bu}_4\text{NBBu}_4$  using the 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  $\text{Bu}_4\text{NBBu}_4$  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 volumes.

The  $\lambda_0$  values of the ions thus obtained are presented in Table 3. Kay and co-workers<sup>7</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 and co-workers. This discrepancy is due to the different procedures adopted<sup>10–13</sup> for the calculation of  $\Lambda^0$  values and also on the choice of the 'reference electrolyte',<sup>7,11</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. Walden products are usually employed to discuss the interactions of the ions with the solvent medium. From Table 3, we see that for large  $\text{R}_4\text{N}^+$  ions,  $\lambda_0^\pm \eta_0$  increases from the tetraheptylammonium ion to the tetramethylammonium ion and for the electrolyte taken as a whole it follows the same sequence (Table 2). This 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 high charge density, resulting in strong ion-solvent interactions.<sup>11</sup> From Table 3, it can be seen that the Stokes radii increase with increasing size of the tetraalkylammonium ions and this is most likely due to the lower ionic mobilities of these cations. For  $\text{Li}^+$ , however, the Stokes radius was much greater than its crystallographic radius (0.93 Å),<sup>25</sup> indicating that it was substantially solvated in this solvent medium. On the other hand the higher mobility of the  $\text{Br}^-$  ion than the cations relative to its crystallographic size (1.80 Å)<sup>25</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 seems to indicate that the effective sizes of these anions in PC are almost the same and

thus very little solvation, if any, is involved. On the other hand, the very low mobility of the tetrabutylborate ion has been attributed to its very much larger size. Thus, it appears that the large sizes of  $\text{R}_4\text{N}^+$  ions, their low charge densities and the high relative permittivity of PC render these ions to be free, unassociated and almost unsolvated in this medium.

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## Viscosity *B* Coefficients of Some Tetraalkylammonium Bromides, Lithium Tetrafluoroborate and Tetrabutylammonium Tetraphenyl borate in Propylene Carbonate

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The viscosities of solutions of tetraalkylammonium bromides,  $R_4NBr$  ( $R = -C_2H_5$  to  $-C_7H_{15}$ ), lithium tetrafluoroborate ( $LiBF_4$ ) and tetrabutylammonium tetraphenylborate ( $Bu_4NBPh_4$ ) in propylene carbonate (PC) have been measured at 25, 35 and 45 °C. The relative viscosities have been analyzed using the Jones-Dole equation in the form of unassociated electrolytes, and the viscosity *B*-coefficients have been evaluated. The thermodynamic parameters have been calculated using the transition-state treatment and the measured temperature dependencies. Ionic *B* values have also been derived and discussed in terms of Einstein's equation. The analysis shows that  $Li^+$  is highly solvated compared to other cations and anions in this medium.

### Introduction

Recently we have reported [1] the results of conductance measurements on  $LiBF_4$  and tetraalkylammonium bromides in propylene carbonate (PC) at 25 °C. These salts have been found to be almost unassociated in this solvent of a moderately high dielectric constant (64.40 at 25 °C). Single ion mobilities were also derived and discussed in terms of the ion solvating ability of PC.

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 has been applied to analyse the results.

### Experimental

Propylene carbonate (E. Merck, Germany, >99% pure) was purified according to the procedure described previously [1]. The solvent properties have been recorded in Table I.

The purification of tetraalkylammonium bromides,  $LiBF_4$  and  $Bu_4NBPh_4$  have been reported earlier [1].

The concentrations of the salts, generally varying in the range of 0.01–0.08 mol dm<sup>-3</sup>, were prepared by

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weight dilution of the stock solution (ca. 0.1 mol kg<sup>-1</sup>). The conversion of the molality into molarity was done by using the density values. The kinematic viscosities were measured at the desired temperature (accuracy ±0.01 °C) using a suspended Ubbelohde-type viscometer. The densities were measured using a Ostwald-Sprengel type pycnometer (25 ml) calibrated with distilled water. The details of the experimental procedure have been described in [2, 3]. The accuracies of the viscosity and density measurements were 0.05% and ±3 × 10<sup>-3</sup> g cm<sup>-3</sup>, respectively.

### Density and Viscosity Data

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 are reported in Table 2.

### Viscosity *A* and *B* Coefficients

The experimental data have been analysed with the Jones-Dole equation [4]

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

Table 1. Solvent properties of propylene carbonate.

Temp. (°C)	Density (g cm <sup>-3</sup> )	Viscosity (cP)	Dielectric constant
25	1.19883	2.4712	64.40
35	1.18970	2.0476	63.41
45	1.17796	1.7234	60.92

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Table 2. Concentration, *C* (mol dm<sup>-3</sup>), density, *ρ* (g cm<sup>-3</sup>) and relative viscosity, *η<sub>r</sub>*, of tetraalkylammonium bromides, LiBF<sub>4</sub> and Bu<sub>4</sub>NBPh<sub>4</sub> in propylene carbonate at 25, 35 and 45 °C.

<i>C</i>	<i>ρ</i>	<i>η<sub>r</sub></i>	<i>C</i>	<i>ρ</i>	<i>η<sub>r</sub></i>	<i>C</i>	<i>ρ</i>	<i>η<sub>r</sub></i>	<i>C</i>	<i>ρ</i>	<i>η<sub>r</sub></i>
<b>Et<sub>4</sub>NBr 25 °C</b>			<b>Pr<sub>4</sub>NBr 25 °C</b>			<b>Hex<sub>4</sub>NBr 35 °C</b>			<b>Hep<sub>4</sub>NBr 35 °C</b>		
0.01002	1.19000	1.0081	0.00995	1.19870	1.0096	0.00991	1.18808	1.0145	0.00999	1.18803	1.0155
0.01644	1.19910	1.0130	0.02020	1.19856	1.0188	0.02475	1.18563	1.0352	0.02976	1.18472	1.0446
0.02506	1.19925	1.0193	0.03015	1.19843	1.0351	0.03958	1.18318	1.0558	0.03974	1.18303	1.0584
0.03509	1.19941	1.0266	0.05005	1.19816	1.0452	0.04945	1.18155	1.0693	0.04951	1.18138	1.0730
0.04511	1.19957	1.0343	0.06001	1.19803	1.0540	0.06917	1.17827	1.0961	0.05947	1.17969	1.0879
0.05514	1.19973	1.0418	0.08020	1.19776	1.0716						
<b>Bu<sub>4</sub>NBr 25 °C</b>			<b>Pen<sub>4</sub>NBr 25 °C</b>			<b>LiBF<sub>4</sub> 35 °C</b>			<b>Bu<sub>4</sub>NBPh<sub>4</sub> 35 °C</b>		
0.01015	1.19837	1.0116	0.00990	1.19817	1.0130	0.01022	1.19025	1.0125	0.00906	1.18873	1.0141
0.01999	1.19792	1.0224	0.02011	1.19749	1.0253	0.02487	1.19104	1.0295	0.01944	1.18762	1.0277
0.03076	1.19743	1.0337	0.03001	1.19682	1.0382	0.03987	1.19184	1.0424	0.02971	1.18651	1.0411
0.05014	1.19654	1.0538	0.05011	1.19547	1.0619	0.04976	1.19237	1.0572	0.04464	1.18490	1.0621
0.05998	1.19609	1.0642	0.06002	1.19480	1.0750	0.05966	1.19290	1.0683	0.05939	1.18331	1.0808
0.07997	1.19517	1.0871	0.08012	1.19343	1.0991	0.07947	1.19396	1.0909			
<b>Hex<sub>4</sub>NBr 25 °C</b>			<b>Hep<sub>4</sub>NBr 25 °C</b>			<b>Et<sub>4</sub>NBr 45 °C</b>			<b>Pr<sub>4</sub>NBr 45 °C</b>		
0.00999	1.19779	1.0149	0.01007	1.19750	1.0159	0.00985	1.17827	1.0071	0.00977	1.17785	1.0077
0.02498	1.19621	1.0368	0.03002	1.19485	1.0458	0.01616	1.17847	1.0117	0.01985	1.17773	1.0161
0.03997	1.19464	1.0583	0.04009	1.19351	1.0606	0.02463	1.17873	1.0174	0.02963	1.17761	1.0241
0.04996	1.19359	1.0715	0.04996	1.19219	1.0761	0.03449	1.17904	1.0243	0.04919	1.17737	1.0401
0.06994	1.19149	1.1017	0.06003	1.19084	1.0904	0.04435	1.17935	1.0310	0.05897	1.17725	1.0480
						0.05421	1.17965	1.0374	0.07881	1.17701	1.0640
<b>LiBF<sub>4</sub> 25 °C</b>			<b>Bu<sub>4</sub>NBPh<sub>4</sub> 25 °C</b>			<b>Bu<sub>4</sub>NBr 45 °C</b>			<b>Pen<sub>4</sub>NBr 45 °C</b>		
0.01031	1.19937	1.0134	0.00998	1.19796	1.0149	0.00998	1.17707	1.0108	0.00972	1.17541	1.0120
0.02508	1.20013	1.0311	0.01997	1.19708	1.0293	0.01966	1.17621	1.0200	0.01969	1.17279	1.0235
0.04020	1.20091	1.0503	0.02995	1.19620	1.0418	0.03025	1.17526	1.0315	0.02935	1.17026	1.0354
0.05017	1.20142	1.0623	0.04502	1.19487	1.0513	0.04933	1.17355	1.0500	0.04885	1.16514	1.0574
0.06013	1.20193	1.0784	0.05990	1.19356	1.0844	0.05903	1.17267	1.0601	0.05840	1.16263	1.0679
0.08007	1.20294	1.0975				0.07875	1.17089	1.0798	0.0911	1.15719	1.0912
<b>Et<sub>4</sub>NBr 35 °C</b>			<b>Pr<sub>4</sub>NBr 35 °C</b>			<b>Hex<sub>4</sub>NBr 45 °C</b>			<b>Hep<sub>4</sub>NBr 45 °C</b>		
0.00995	1.18992	1.0077	0.00988	1.18955	1.0089	0.00981	1.17568	1.0147	0.00990	1.17598	1.0151
0.01632	1.19006	1.0119	0.02004	1.18938	1.0175	0.02452	1.17226	1.0347	0.02951	1.17206	1.0435
0.02487	1.19025	1.0186	0.02992	1.18923	1.0255	0.03921	1.16884	1.0546	0.03942	1.17007	1.0585
0.03483	1.19047	1.0248	0.04967	1.18891	1.0425	0.04899	1.16657	1.0678	0.04913	1.16813	1.0711
0.04478	1.19069	1.0326	0.05954	1.18875	1.0499	0.06853	1.16202	1.0940	0.05762	1.16643	1.0836
0.05473	1.19091	1.0391	0.07958	1.18843	1.0676						
<b>Bu<sub>4</sub>NBr 35 °C</b>			<b>Pen<sub>4</sub>NBr 35 °C</b>			<b>LiBF<sub>4</sub> 45 °C</b>			<b>Bu<sub>4</sub>NBPh<sub>4</sub> 45 °C</b>		
0.01007	1.18898	1.0113	0.00982	1.18799	1.0125	0.01012	1.17877	1.0117	0.00980	1.17681	1.0144
0.01983	1.18828	1.0215	0.01992	1.18622	1.0244	0.02463	1.17992	1.0272	0.01926	1.17570	1.0272
0.03050	1.18751	1.0325	0.02918	1.18460	1.0361	0.03951	1.18110	1.0435	0.02943	1.17451	1.0406
0.04970	1.18612	1.0523	0.04956	1.18101	1.0587	0.04932	1.18187	1.0538	0.04423	1.17277	1.0597
0.05945	1.18542	1.0625	0.05931	1.17929	1.0716	0.05915	1.18265	1.0636	0.05886	1.17105	1.0787
0.07923	1.18398	1.0828	0.07968	1.17570	1.0949	0.07882	1.18420	1.0839			

1.0784

1.172

where *η* and *η<sub>0</sub>* are the viscosities of the solution and solvent, respectively, *η<sub>r</sub>* is the relative viscosity and *C* is the molar concentration.

The plots of (*η<sub>r</sub>* - 1)/√*C* against √*C* (Fig. 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 at 25 °C from the physical properties of the

solvent and the limiting ionic equivalent conductance by using the Falkenhagen and Vernon equation [5]

$$A_{theo} = \frac{0.2577 A_0}{\eta_0 (\epsilon T)^{1/2} \lambda_0^+ \lambda_0^-} \left[ 1 - 0.6863 \left( \frac{\lambda_0^+ - \lambda_0^-}{A_0} \right)^2 \right] \quad (2)$$

The conductance data required in these calculations were taken from our earlier work [1]. The *A<sub>theo</sub>* coeffi-

coefficients obtained from (2) along with the experimental *A* values are reported in Table 3.

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

*Activation Parameters for the Viscous Flow*

The 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. [6]:

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000} \left( \frac{\Delta\mu_2^{0*} - \Delta\mu_1^{0*}}{RT} \right) \quad (3)$$

In the above equation  $\bar{V}_1^0$  and  $\bar{V}_2^0$  are the partial molar volumes of solvent and solute, respectively.  $\Delta\mu_2^{0*}$ , 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 as reported in Table 4.  $\Delta\mu_1^{0*}$ , the free energy of activation per mole of the pure solvent is given by the equation [7]

$$\Delta\mu_1^{0*} = \Delta G_1^{0*} = RT \ln \left( \frac{\eta_0 \bar{V}_1^0}{hN} \right) \quad (4)$$

*N* = Avogadro's number.

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

Salts	<i>A</i> <sub>theo</sub>	<i>A</i> <sub>obs</sub>		
		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

**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 one within 20% for the quarternary ammonium salts. This error in the small *A* values corresponds to the experimental uncertainty of 0.05% of the viscosity data. Similar results have been found in other systems [8].

The viscosity *B* coefficients (Table 4) are large, positive and 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. [9] by simply plotting the relative viscosity against the concentration in the 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 moderate temperature dependence and the values decrease with increase of temperature as observed earlier in some dipolar aprotic solvents like acetonitrile [8, 10], sulfolane [1] and DMSO [2, 12]. Further, from Table 4 we see that, although *dB/dT* is small, 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 using Bu<sub>4</sub>NBPh<sub>4</sub> as the "reference electrolyte" [13, 14]:

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

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

The ionic *B* values along with the ionic  $\Delta\mu_2^{0*}$  data obtained from the above relationships are given in Table 5. Table 5 shows that the viscosity *B* coefficients for cations and anions are all positive and also very high. The ionic *B* value for Li<sup>+</sup> at 25 °C was calculated

Table 4. Viscosity *B* coefficients, *B* (dm<sup>3</sup> mol<sup>-1</sup>) and  $\Delta\mu_2^{0*}/(\text{kJ mol}^{-1})$  values in propylene carbonate at different temperatures.

Salts	25 °C		35 °C		45 °C	
	<i>B</i>	$\Delta\mu_2^{0*}$	<i>B</i>	$\Delta\mu_2^{0*}$	<i>B</i>	$\Delta\mu_2^{0*}$
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	49.05	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

[11]

7

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

Ion	25 °C		35 °C		45 °C	
	$B_{\pm}$	$\Delta\mu_{\pm}^{\circ}$	$B_{\pm}$	$\Delta\mu_{\pm}^{\circ}$	$B_{\pm}$	$\Delta\mu_{\pm}^{\circ}$
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,  $R_{\pm}/(\text{Å})$  and solvation number,  $n_{\pm}$ , of ions in PC at 25 °C.

Ion	$r_c$ (Å)	$r_s$ (Å)	$R_{\pm}$ (Å)	$n_{\pm}$
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

from the reported viscosity *B* value of LiBr [9] in PC assuming additivity. The observed order of the  $B_{\pm}$  coefficients, Hep<sub>4</sub>N<sup>+</sup> > Hex<sub>4</sub>N<sup>+</sup> > Pen<sub>4</sub>N<sup>+</sup> > Bu<sub>4</sub>N<sup>+</sup> > Pr<sub>4</sub>N<sup>+</sup> > Et<sub>4</sub>N<sup>+</sup>, shows that the obstruction of the solvent viscous flow increases with decrease of the ion charge density and with decrease of the size of the hydrodynamic entity by solvation. For anions, the *B*-values are seen to be in the order BPh<sub>4</sub><sup>-</sup> > Br<sup>-</sup> > BF<sub>4</sub><sup>-</sup>. The  $\text{d}B_{\pm}/\text{d}T$  values of the 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 observed in sulfolane by Sacco and coworkers [11, 15].

The values of  $\Delta\mu_{\pm}^{\circ}$  for tetraalkylammonium ions decrease in the order Hep<sub>4</sub>N<sup>+</sup> > Hex<sub>4</sub>N<sup>+</sup> > Pen<sub>4</sub>N<sup>+</sup> > Bu<sub>4</sub>N<sup>+</sup> > Pr<sub>4</sub>N<sup>+</sup> > Et<sub>4</sub>N<sup>+</sup>, and for anions BPh<sub>4</sub><sup>-</sup> > Br<sup>-</sup>. However, these values are found to be positive, and thus the formation of the transition-state is less favourable in the presence of these ions.

Ionic  $B_{\pm}$  coefficients have also been analysed on the basis of Einstein's equation [16]

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

where  $R_{\pm}$  (in Å) is the radius at the ion assumed to be a rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The number of solvent molecules ( $n_{\pm}$ ) bound to the ion in the primary sphere of solvation can be calculated by combination of the Jones-Dole equation with that of Einstein [17]

$$B_{\pm} = \frac{2.5}{1000} (V_i + n_{\pm} V_s), \quad (8)$$

where  $V_i$  represents the bare ion molar volume and is related to the crystallographic radius ( $r_c$ ) of the ion.  $V_s$  is the solvent molar volume. The values of  $R_{\pm}$  and  $n_{\pm}$  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, the  $R_{\pm}$  value of Li<sup>+</sup> 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 [1], which shows that Li<sup>+</sup> is highly solvated in this medium. Thus, it appears that the large size of the R<sub>4</sub>N<sup>+</sup> 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.

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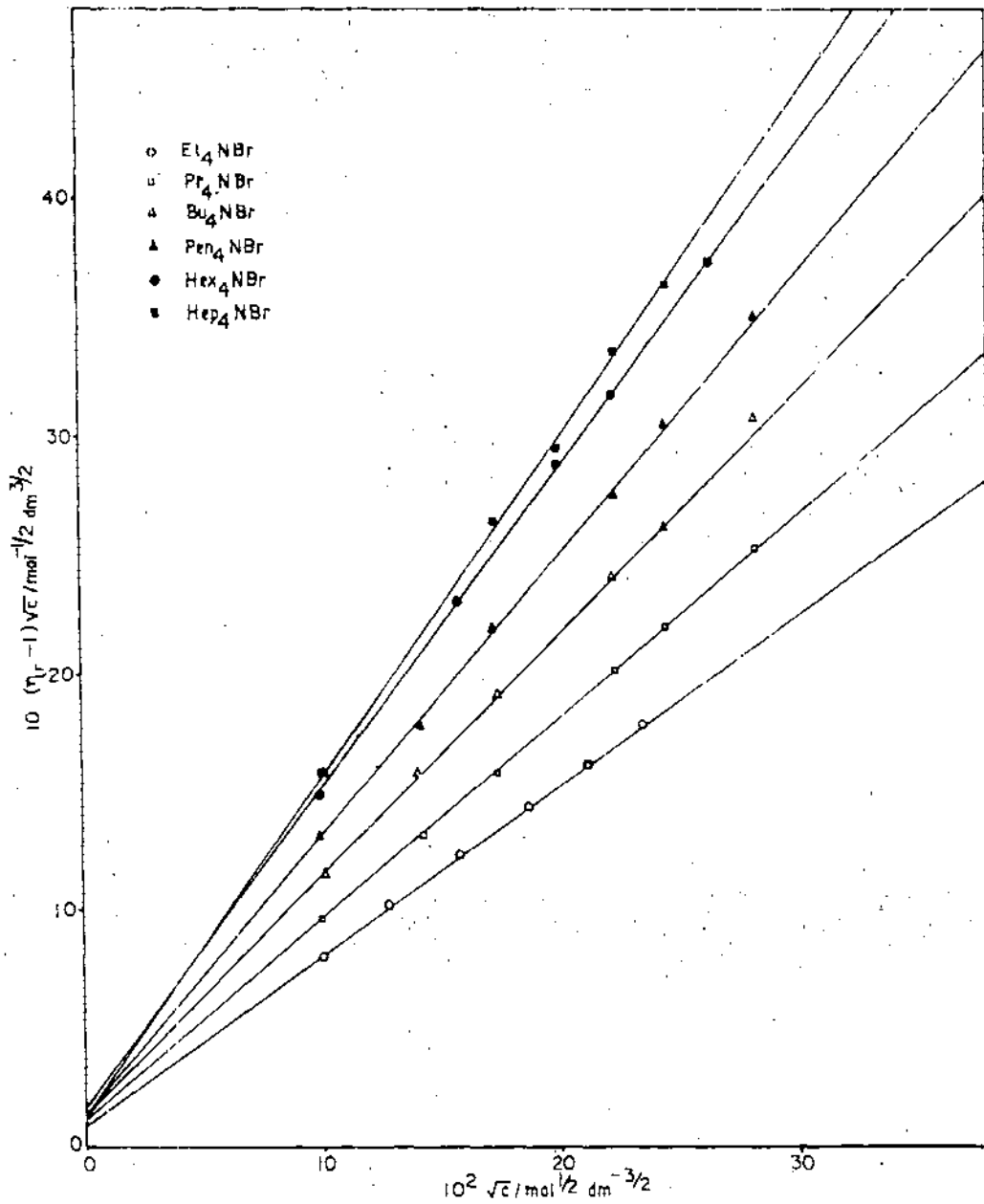


Fig. 1 Representative plot of  $(\eta_r - 1) / \sqrt{c}$  against  $\sqrt{c}$  for some electrolytes in PC at 25°C

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# Solubilities of Some Alkali-Metal Salts, Tetraphenylarsonium Chloride, and Tetraphenylphosphonium Bromide in Propylene Carbonate at 25 °C Using the Ion-Selective Electrode Technique

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The solubilities of 15 alkali-metal salts, MX ( $M^+ = \text{Li, Na, K, Rb, and Cs}$ ;  $X^- = \text{Cl, Br, and ClO}_4$ ), tetraphenylarsonium chloride, and tetraphenylphosphonium bromide are reported in propylene carbonate (PC) at 25 °C, and the free energies of solution for these electrolytes in this solvent have been determined. Combination of these values with solubility results in water yields the free energies of transfer of the electrolytes from water to propylene carbonate. Transfer activity coefficients for the electrolytes have also been computed from their solubility products in water and in the nonaqueous solvent. The results indicate that the perchlorates are more soluble in propylene carbonate compared to the corresponding chloride or bromide salts.

## Introduction

Propylene carbonate (4-methyl-1,3-dioxolan-2-one, PC), a dipolar aprotic solvent with high dielectric constant (64.40 at 25 °C) and dipole moment (4.94 D) has been assumed to be an "ideal structureless dielectric" solvent for studies of electrolytes (1, 2). The chemical properties of this solvent have given it an important place in the development of high-energy batteries (3), and thus there has been a growing interest to study various electrochemical reactions in this medium (4, 5). Solubility offers one of the most obvious ways of studying ionic solvation, but in PC these values in general are not available, except of a very few alkali-metal halides (2, 6). It is therefore desirable to obtain the useful solubility data particularly for the salts containing  $\text{Ph}_4\text{As}^+$  or  $\text{Ph}_4\text{P}^+$  ions and thus to have an idea of solute-solvent interactions in this nonaqueous medium.

Hence, we have measured the solubilities of a number of 1:1 electrolytes in PC at 25 °C using the ion-selective electrode technique, and from these the solubility products and free energies of solution for the salts have been determined. The free energies of transfer of the electrolytes from water to PC or the corresponding transfer activity coefficients,  $m\gamma$ 's, have been evaluated and compared with the previous values obtained mainly from emf measurements (7).

## Experimental Section

**Materials.** Propylene carbonate (E. Merck, Germany; >99% pure) was purified as reported earlier (8); the viscosity and density were 2.4711 mPa s and 1.1988 g cm<sup>-3</sup> at 25 °C, respectively. Solutions were always prepared with the freshly distilled solvent.

All salts were of Fluka's either purum or puriss grade.

The alkali-metal chlorides and bromides were dried in vacuo for a long time immediately prior to use and were used without further purification.

Lithium perchlorate was recrystallized three times from distilled water and then heated under vacuum for several days (2). Sodium perchlorate was heated under vacuum over silica gel and calcium chloride for 5-7 days. These were tested with silver nitrate solution to detect any chloride before use. Other alkali-metal perchlorates were prepared by mixing equimolar solutions of the corresponding alkali-metal chloride and sodium perchlorate (9), washed with a 1:1 methanol-water mixture, recrystallized three times from water, and dried in vacuum over calcium chloride and silica gel for several days.

Tetraphenylarsonium chloride (Fluka) was recrystallized from absolute ethanol solution by dry ether and dried in vacuum (10). Tetraphenylphosphonium bromide (Fluka, puriss grade) was dissolved in absolute ethanol, reprecipitated by the addition of dry ether, and vacuum dried at 100 °C (10).

**Solubility Measurements.** Saturated solutions were prepared by shaking the solid with the solvent in a glass-stoppered bottle at 27 °C for 24 h. The bottle was then placed in a thermostatic bath maintained at  $25 \pm 0.01$  °C for 2 days. Finally, the solution was transferred to a Campbell solubility apparatus (11) fitted with a sintered disk and fine tube and allowed to equilibrate at 25 °C. At regular intervals, the solution was filtered by inverting the apparatus (while keeping it within the thermostat) and appropriately diluted with the solvent (if necessary), and then the concentration was measured by using an Orion ion analyzer (model EA 920) having an accuracy of  $\pm 0.01\%$ . A solution was considered saturated when two successive analyses at 2-3-day intervals indicated no change in concentration. Thus, the concentrations of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{ClO}_4^-$  ions were determined by using specific Orion ion-selective electrodes. A double junction reference electrode was used with each of the  $\text{Cl}^-$  and  $\text{ClO}_4^-$  ion electrodes. However, for measuring  $\text{ClO}_4^-$  ion concentrations, the outer chamber of the reference electrode was filled with  $(\text{NH}_4)_2\text{SO}_4$  solution as suggested in the brochure. A single junction reference electrode was used in conjunction with the  $\text{Br}^-$  ion electrode. Each ion-selective electrode was tested for a Nernstian response. In order to check the correctness of the data, a known concentration of the sample solution was measured by using the specific ion-selective electrode and the results were compared. At least two trials were given for all the solutions which were under study.

## Results and Discussion

Solubility data for the electrolytes in PC at 25 °C (molar scale) are reported in Table I along with their standard deviations.

The standard free energy of solution for a solute on the molar scale is usually given by the relation

$$\Delta G^\circ_{\text{soln}} = -RT \ln K \quad (1)$$

where  $K$  is the equilibrium constant for the reaction  $\text{MX} = \text{M}^+ + \text{X}^-$ . Upon introduction of the Debye-Hückel expression

**Table I. Solubilities  $S$ , Standard Free Energies of Solution  $\Delta G^\circ_{\text{soln}}$ , and Standard Free Energies of Formation  $\Delta G^\circ_f$ , and Solvation  $\Delta G^\circ_{\text{solv}}$  of the Electrolytes in Propylene Carbonate at 25 °C**

salt	$S$ (mol L <sup>-1</sup> )	$\Delta G^\circ_{\text{soln}}$ (kJ mol <sup>-1</sup> )	$-\Delta G^\circ_f$ (kJ mol <sup>-1</sup> )	$-\Delta G^\circ_{\text{solv}}$ (kJ mol <sup>-1</sup> )
LiCl	0.019 ± 0.002	19.12	364.55	824.79
NaCl	0.00017 ± 0.00002	42.97	341.08	726.47
KCl	0.00058 ± 0.00004	36.82	371.50	667.35
RbCl	0.0033 ± 0.0006	28.07	376.94	653.08
CsCl	0.0076 ± 0.0007	23.85	380.33	633.88
Ph <sub>4</sub> AsCl	0.50 ± 0.02	1.51		
LiBr	1.10 ± 0.008	-2.97	342.71	802.11
NaBr	0.0036 ± 0.0010	27.66	320.03	706.64
KBr	0.0030 ± 0.0006	28.58	350.62	643.79
RbBr	0.0099 ± 0.0005	22.51	355.84	634.80
CsBr	0.0098 ± 0.0007	22.55	360.70	610.07
Ph <sub>4</sub> PBr	0.120 ± 0.003	9.37		
LiClO <sub>4</sub>	1.40 ± 0.03	-4.35		
NaClO <sub>4</sub>	2.50 ± 0.08	-7.70	264.60	
KClO <sub>4</sub>	0.017 ± 0.001	19.71	284.47	
RbClO <sub>4</sub>	0.025 ± 0.002	17.70	288.53	
CsClO <sub>4</sub>	0.052 ± 0.003	13.85	292.75	

**Table II. Free Energies of Transfer,  $\Delta G^\circ_t$ , and Transfer Activity Coefficients,  $\log m\gamma_t$ , of the Electrolytes from Water to Propylene Carbonate at 25 °C**

salt	$\Delta G^\circ_{\text{soln}}(\text{H}_2\text{O})$ (kJ mol <sup>-1</sup> )	$\Delta G^\circ_t$ (kJ mol <sup>-1</sup> )	$\log m\gamma_t$
LiCl	-41.42	60.54	10.61
NaCl	-8.79	51.76	9.07
KCl	-5.02	41.84	7.33
RbCl	-8.37	36.44	6.39
CsCl	-9.20	33.05	5.79
Ph <sub>4</sub> AsCl	-0.59	2.09	0.37
LiBr	-56.90	53.93	9.45
NaBr	-17.15	44.81	7.85
KBr	-5.86	34.43	6.04
RbBr	-6.69	29.20	5.12
CsBr	-1.67	24.23	4.25
Ph <sub>4</sub> PBr	14.64	-5.27	-0.92
LiClO <sub>4</sub>	very soluble		
NaClO <sub>4</sub>	very soluble		
KClO <sub>4</sub>	11.30	8.41	0.52
RbClO <sub>4</sub>	14.23	3.47	0.61
CsClO <sub>4</sub>	13.81	0.04	0.007

for the mean activity coefficient, one obtains (12)

$$\Delta G^\circ_{\text{soln}} = 2.303RT[-\nu \log m - \log(\nu_+ \nu_- \nu_{\pm} + \nu \delta_0 d_0^{1/2} m^{1/2})] \quad (2)$$

In eq 2,  $d_0$  is the density of PC,  $\delta$  is the Debye-Hückel limiting slope,  $\nu$  is the total number of ions, and the other symbols have their usual significance.

We have applied eq 2 to obtain the standard free energies of solution; further, these were combined with the free energies of formation of the respective crystalline salts (13) to obtain the corresponding standard free energies of formation for the alkali-metal salts. Results of these calculations have been listed in Tables I and II.

The transfer activity coefficients were calculated from the solubility products by using the relationship

$$\log m\gamma_t = \log m\gamma_{\pm}^2 = \log_w K_s - \log_a K_s \quad (3)$$

where  $m\gamma_t$  is the transfer activity coefficient (medium effect) and subscripts  $w$  and  $a$  denote aqueous and nonaqueous solvents, respectively. The values have been given in Table II. The standard free energies of solution in water,  $\Delta G^\circ_{\text{soln}}(\text{H}_2\text{O})$ , except for the tetraphenyl salts, have been taken from the literature (7, 14). We have measured the solubilities of Ph<sub>4</sub>AsCl and Ph<sub>4</sub>PBr in water at 25 °C (0.81 and 0.047 M for Ph<sub>4</sub>AsCl and Ph<sub>4</sub>PBr, respectively). Abraham et al. (15) have reported the free energies of solution for the tetraphenyl salts

**Table III. Crystallographic Radii,  $r_c$ , Free Energies of Transfer,  $\Delta G^\circ_t$ , Transfer Activity Coefficients,  $\log m\gamma_t$ , and Free Energies of Solvation,  $\Delta G^\circ_{\text{solv}}$ , of Single Ions in Propylene Carbonate at 25 °C**

ion	$r_c/\text{Å}$	$\Delta G^\circ_t$ (kJ mol <sup>-1</sup> )	$\log m\gamma_t$	$-\Delta G^\circ_{\text{solv}}$ (kJ mol <sup>-1</sup> )
Li <sup>+</sup>	0.60	22.47	3.94	471.58
Na <sup>+</sup>	0.95	13.68	2.40	379.87
K <sup>+</sup>	1.33	3.77	0.66	313.63
Rb <sup>+</sup>	1.48	-1.63	-0.29	293.47
Cs <sup>+</sup>	1.69	-5.02	-0.88	269.20
Ph <sub>4</sub> As <sup>+</sup>	6.40	-35.98	-6.31	94.31
Ph <sub>4</sub> P <sup>+</sup>	6.30	-35.98	-6.31	95.65
Cl <sup>-</sup>	1.81	38.07	6.67	243.34
Br <sup>-</sup>	1.95	30.71	5.38	231.79
ClO <sub>4</sub> <sup>-</sup>	2.16	5.06	0.89	216.40

<sup>a</sup> Calculated by using the relation  $\Delta G^\circ_t(\text{ClO}_4^-) = \Delta G^\circ_t(\text{CsClO}_4) - \Delta G^\circ_t(\text{Cs}^+)$ .

(3.48 and 4.38 for Ph<sub>4</sub>AsCl and Ph<sub>4</sub>PBr, respectively) on the basis of the osmotic pressure and activity coefficient data of Kalfoglou and Bowen (10), which on comparison with the values reported in Table II would seem to be in error.

Single ion free energies of transfer from water to PC based on Ph<sub>4</sub>AsBPh<sub>4</sub> convention have been reported in Table III. The  $\Delta G^\circ_t$  values for Ph<sub>4</sub>As<sup>+</sup> and Ph<sub>4</sub>P<sup>+</sup> ions from water to PC have been taken from the literature (7). Ionic transfer free energy values together with ionic transfer activity coefficients have been reported in Table III. Following Latimer, Pitzer, and Slansky (16), we have also calculated the single ion free energies of solvation by the modified Born equation:

$$\Delta G^\circ_{\text{solv}} = -\frac{Nz^2e^2}{2} [1 - 1/\epsilon] / (r_i + \delta) \quad (4)$$

taking  $\delta_c = 0.85 \text{ Å}$  and  $\delta_a = 1.00 \text{ Å}$  as taken by Criss et al. in DMF medium (12). The values thus obtained have been reported in Table III.

An examination of the solubilities of the alkali-metal salts (Table I) shows that most electrolytes are much less soluble in propylene carbonate than in water (7) and also in some other dipolar aprotic solvents like DMSO (6) and DMF (6, 12). Lithium salts are found to be more soluble in PC compared to other alkali-metal salts, a notable exception being NaClO<sub>4</sub>, which is more soluble in PC than LiClO<sub>4</sub>. Also with the exception of lithium, other alkali-metal halides appear to be sparingly soluble and the solubilities are usually in the order Cl<sup>-</sup> < Br<sup>-</sup> < ClO<sub>4</sub><sup>-</sup> as in water and other dipolar aprotic solvents. The poor solubility of these salts in such a high dielectric medium may be due to the dipolar aprotic nature of this solvent medium. The perchlorates, we see, have a much higher solubility than the halides. This indicates that ClO<sub>4</sub><sup>-</sup> ion tends to increase the PC liquid structure more so than does Cl<sup>-</sup> or Br<sup>-</sup> ion. Further, salts having large polarizable groups, viz., Ph<sub>4</sub>AsCl and Ph<sub>4</sub>PBr, are found to be reasonably soluble in this medium. However, Ph<sub>4</sub>AsCl is found to be much more soluble than Ph<sub>4</sub>PBr. This shows that Ph<sub>4</sub>As<sup>+</sup> is more polarizable than Ph<sub>4</sub>P<sup>+</sup> and is preferentially solvated, most probably through a combination of dispersion and ion-dipole interactions.

From Table II we see that, in general, the standard free energies of transfer,  $\Delta G^\circ_t$ , of the electrolytes from water to PC are positive and so the transfer process is not favorable. A notable exception is Ph<sub>4</sub>PBr. The negative sign reflects the fact that the distribution of its ions favors the nonaqueous phase, compared to the positive medium effects for most electrolytes. Cox and his co-workers (7) have presented  $\Delta G^\circ_t$  values of some common salts from water to PC by taking the basic data from the literature. Our reported  $\Delta G^\circ_t$  values for the alkali-metal halides are found to be in good agreement

with theirs. This avoids the uncertainties in the solubility method due to ion pairing and activity coefficient measurements. Solomon (17) has also reported  $\Delta G^\circ$  values of LiCl and LiBr from water to PC as 14.74 and 12.98 kcal/mol<sup>-1</sup> from a potentiometric study, whereas we have found them to be 14.47 and 12.89 kcal mol<sup>-1</sup>, respectively, from direct solubility measurements.

Ionic  $\Delta G^\circ$  values have been calculated taking Ph<sub>4</sub>AsBPh<sub>4</sub> as the "reference electrolyte" (7). An attempt was made to calculate the  $\Delta G^\circ$  value of Ph<sub>4</sub>AsBPh<sub>4</sub> from water to PC by measuring the solubilities of Ph<sub>4</sub>AsCl, NaCl, and NaBPh<sub>4</sub> in PC. But NaBPh<sub>4</sub> was found to be highly soluble in PC, and to avoid the experimental error we discarded the idea. From the table we see that among the cations, Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> have a positive value of transfer free energy, whereas Rb<sup>+</sup>, Cs<sup>+</sup>, Ph<sub>4</sub>As<sup>+</sup>, and Ph<sub>4</sub>P<sup>+</sup> have negative  $\Delta G^\circ$  values. The positive values of  $\Delta G^\circ$ , and log  $m\gamma$ , indicate that these ions are more favorably solvated by the reference medium (water) than by the nonaqueous medium (PC) to which it is transferred. For negative values of  $\Delta G^\circ$ , it is just the reverse.

Solvation of small cations is generally determined by the relative basicity of the solvents, i.e., by their donor ability. PC has weakly basic oxygen, and so cations are poorly solvated in this medium, resulting in positive  $\Delta G^\circ$  values (Table III). However, for Rb<sup>+</sup> and Cs<sup>+</sup> ions, the  $\Delta G^\circ$  values are negative in PC. From this evidence we may come to the conclusion that the transfer of Rb<sup>+</sup> and Cs<sup>+</sup> ions from water to PC is more favorable compared to other alkali-metal cations.

### Conclusion

The solubilities of alkali-metal salts are comparable, although smaller than the corresponding solubilities in water as well as in other dipolar aprotic solvents. The perchlorates,

however, are more soluble than the halides. The higher solubility of NaClO<sub>4</sub> compared to LiClO<sub>4</sub>, somehow, tends to indicate its more compactness with the solvent dipoles than the latter. The single ion free energies of transfer from water to PC correlate well with the free energies of transfer of the ions derived by other methods.

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