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.

Experiental

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

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^{-3}, were prepared by weight dilution of the stock solution (ca. 0.1 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 ±0.01 °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 in [2, 3]. The accuracies of the viscosity and density measurements were 0.05% and $\pm 3 \times 10^{-5}$ g cm^{-3}, respectively.

Density and Viscosity Data

The density (ϱ) and viscosity (η) data for the electrolytes in the molarity range 0.01–0.08 mol dm^{-3} 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]

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

Table 1. Solvent properties of propylene carbonate.

Temp. (°C)	Density (g cm^{-3})	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

Table 2. Concentration, $C/(\text{mol dm}^{-3})$, density, $\varrho/(\text{g cm}^{-3})$ and relative viscosity, η_r, of tetraalkylammonium bromides, LiBF$_4$ and Bu$_4$NBPh$_4$ in propylene carbonate at 25, 35 and 45 °C.

C	ϱ	η_r	C	ϱ	η_r	C	ϱ	η_r	C	ϱ	η_r
Et$_4$NBr	**25 °C**		**Pr$_4$NBr**	**25 °C**		**Hex$_4$NBr**	**35 °C**		**Hep$_4$NBr**	**35 °C**	
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						
Bu$_4$NBr	**25 °C**		**Pen$_4$NBr**	**25 °C**		**LiBF$_4$**	**35 °C**		**Bu$_4$NBPh$_4$**	**35 °C**	
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			
Hex$_4$NBr	**25 °C**		**Hep$_4$NBr**	**25 °C**		**Et$_4$NBr**	**45 °C**		**Pr$_4$NBr**	**45 °C**	
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
LiBF$_4$	**25 °C**		**BuNBPh$_4$**	**25 °C**		**Bu$_4$NBr**	**45 °C**		**Pen$_4$NBr**	**45 °C**	
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
Et$_4$NBr	**35 °C**		**Pr$_4$NBr**	**35 °C**		**Hex$_4$NBr**	**45 °C**		**Hep$_4$NBr**	**45 °C**	
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						
Bu$_4$NBr	**35 °C**		**Pen$_4$NBr**	**35 °C**		**LiBF$_4$**	**45 °C**		**Bu$_4$NBPh$_4$**	**45 °C**	
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			

where η and η_0 are the viscosities of the solution and solvent, respectively, η_r is the relative viscosity and C is the molar concentration.

The plots of $(\eta_r - 1)/\sqrt{C}$ against $\sqrt{C}$ (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]

$$A_{\text{theo}} = \frac{0.2577 \, \Lambda_0}{\eta_0 (\varepsilon T)^{1/2} \, \lambda_0^+ \lambda_0^-} \left[1 - 0.6863 \left(\frac{\lambda_0^+ - \lambda_0^-}{\Lambda_0} \right)^2 \right]. \quad (2)$$

The conductance data required in these calculations were taken from our earlier work [1]. The A_{theo} coeffi-
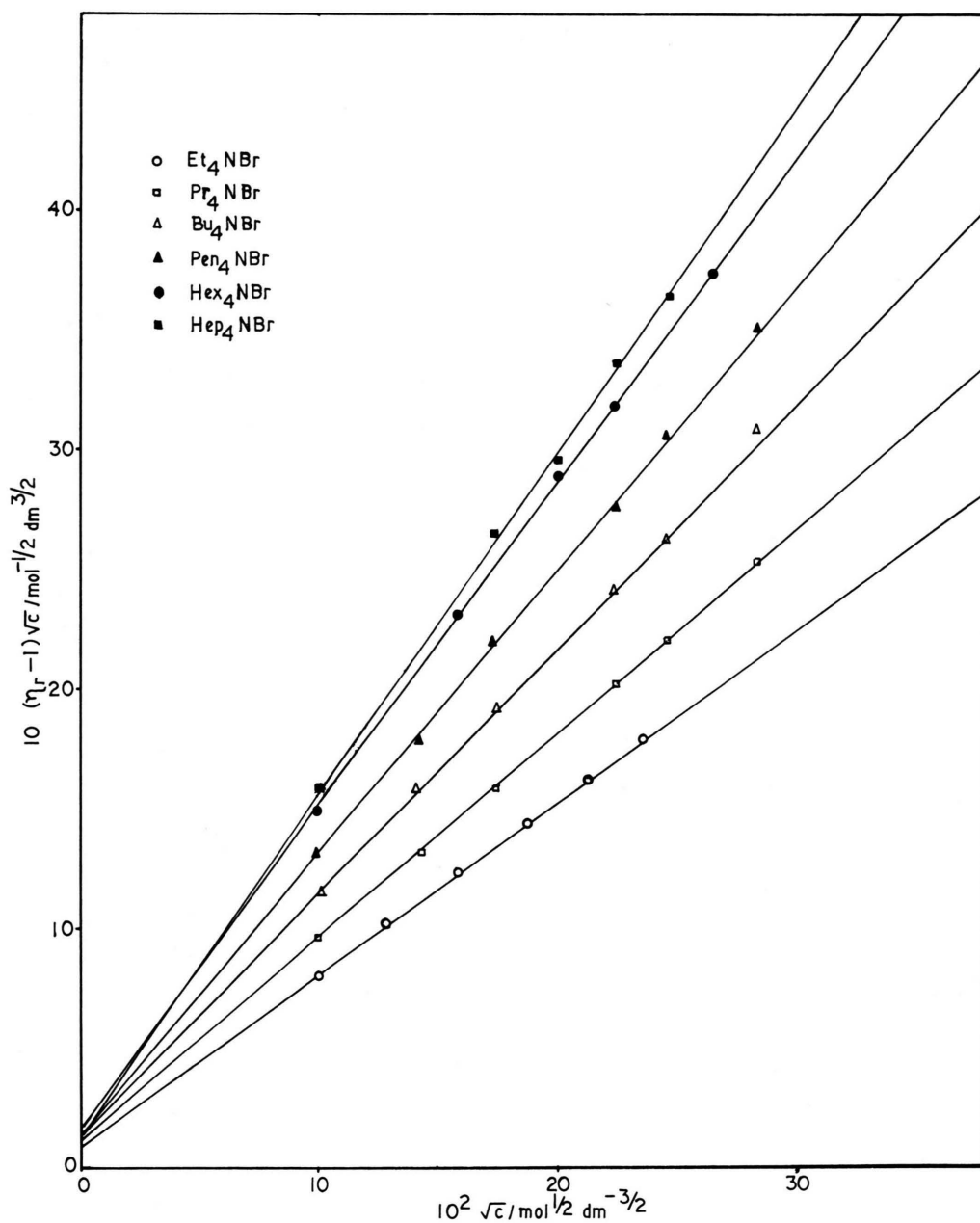
Fig. 1. Representative plot of $(\eta_r - 1)/\sqrt{c}$ against $\sqrt{c}$ for some electrolytes in PC at 25 °C.

cients 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]:

$$B = \frac{\overline{V_1^0} - \overline{V_2^0}}{1000} + \frac{\overline{V_1^0}}{1000} \left(\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT} \right). \quad (3)$$

In the above equation $\overline{V_1^0}$ and $\overline{V_2^0}$ are the partial molar volumes of solvent and solute, respectively. $\Delta\mu_2^{0\neq}$, 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. $\Delta\mu_1^{0\neq}$, the free energy of activation per mole of the pure solvent is given by the equation [7]

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT \ln(\eta_0 \overline{V_1^0}/hN), \quad (4)$$

N = Avogadro's number.

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_4NBr is slightly greater than the B value (0.960)

Table 5. Ionic B coefficients, $B_\pm/(dm^2\ mol^{-1})$ and ionic $\Delta\mu_2^{0\neq}/(kJ\ mol^{-1})$ values in PC at different temperatures.

Ion	25 °C		35 °C		45 °C	
	$B_\pm$	$\Delta\mu_2^{0\neq}$	$B_\pm$	$\Delta\mu_2^{0\neq}$	$B_\pm$	$\Delta\mu_2^{0\neq}$
Et_4N^+	0.258	16.22	0.246	15.57	0.242	15.13
Pr_4N^+	0.397	22.36	0.382	21.97	0.377	21.80
Bu_4N^+	0.585	29.97	0.577	30.60	0.564	30.97
Pen_4N^+	0.736	36.25	0.717	38.75	0.695	40.92
Hex_4N^+	0.927	44.09	0.911	45.69	0.904	47.97
Hep_4N^+	0.996	48.11	0.988	49.44	0.980	50.90
Li^+	0.792	–	–	–	–	–
Br^-	0.458	22.34	0.428	22.29	0.411	22.44
BF_4^-	0.411	–	–	–	–	–
BPh_4^-	0.717	36.71	0.706	37.48	0.692	37.95

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

Salts	A_{theo}	A_{obs}		
		25 °C	35 °C	45 °C
Et_4NBr	0.0102	0.0082	0.0089	0.0066
Pr_4NBr	0.0108	0.0104	0.0080	0.0080
Bu_4NBr	0.0113	0.0093	0.0109	0.0083
Pen_4NBr	0.0130	0.0106	0.0117	0.0138
Hex_4NBr	0.0136	0.0079	0.0125	0.0189
Hep_4NBr	0.0147	0.0115	0.0128	0.0139
$LiBF_4$	0.0114	0.0072	0.0095	0.0152
Bu_4NBPh_4	0.0176	0.0135	0.0198	0.0237

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

Ion	r_c (Å)	r_s (Å)	$R_\pm$ (Å)	n_s
Et_4N^+	4.00	2.82	3.45	−1.94
Pr_4N^+	4.52	3.21	3.98	−2.68
Bu_4N^+	4.94	3.49	4.53	−3.18
Pen_4N^+	5.29	4.81	4.89	−3.82
Hex_4N^+	5.59	5.38	5.28	−4.24
Hep_4N^+	5.88	6.39	5.41	−5.32
Li^+	0.60	3.72	5.01	3.71
Br^-	1.95	1.81	4.17	1.78
BF_4^-	2.01	1.68	4.02	1.53
BPh_4^-	4.20	3.76	4.84	−0.28

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

Salts	25 °C		35 °C		45 °C	
	B	$\Delta\mu_2^{0\neq}$	B	$\Delta\mu_2^{0\neq}$	B	$\Delta\mu_2^{0\neq}$
Et_4NBr	0.716 ± 0.004	38.56	0.674 ± 0.009	37.86	0.653 ± 0.003	37.57
Pr_4NBr	0.855 ± 0.001	44.70	0.810 ± 0.007	44.26	0.788 ± 0.001	44.24
Bu_4NBr	1.043 ± 0.012	52.31	1.005 ± 0.001	52.89	0.975 ± 0.007	53.41
Pen_4NBr	1.194 ± 0.007	58.59	1.145 ± 0.010	61.04	1.106 ± 0.006	63.36
Hex_4NBr	1.385 ± 0.019	66.43	1.339 ± 0.002	67.98	1.315 ± 0.008	70.41
Hep_4NBr	1.454 ± 0.009	70.45	1.416 ± 0.010	71.73	1.391 ± 0.015	73.34
$LiBF_4$	1.203 ± 0.036	49.05	1.105 ± 0.032	47.00	1.021 ± 0.006	44.52
Bu_4NBPh_4	1.302 ± 0.061	66.68	1.283 ± 0.013	68.08	1.256 ± 0.002	68.92

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_4NBr. 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 [11] 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_4NBPh_4 as the "reference electrolyte" [13, 14]:

$$B(Bu_4NBPh_4) = B(Bu_4N^+) + B(BPh_4^-), \quad (5)$$

$$B_{Ph_4B^-}/B_{Bu_4N^+} = (5.35/5.00)^3. \quad (6)$$

The ionic B values along with the ionic $\Delta\mu_2^{0\ne}$ 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^+ at 25 °C was calculated from the reported viscosity B value of LiBr [9] in PC assuming additivity. The observed order of the B_+ coefficients, $Hep_4N^+ > Hex_4N^+ > Pen_4N^+ > Bu_4N^+ > Pr_4N^+ > Et_4N^+$, 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 $BPh_4^- > Br^- > BF_4^-$. The $dB_\pm/dT$ 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 $\Delta\mu_2^{0\ne}$ for tetraalkylammonium ions decrease in the order $Hep_4N^+ > Hex_4N^+ > Pen_4N^+ > Bu_4N^+ > Pr_4N^+ > Et_4N^+$, and for anions $BPh_4^- > Br^-$. 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 of 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_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 [17]

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

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_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, the $R_\pm$ value of Li^+ 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^+ is highly solvated in this medium. Thus, it appears that the large size of the R_4N^+ 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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