Bull. Chem. Soc. Jpn., 62, 1246—1249 (1989) [Vol. 62, No. 4

Viscosity *B*-Coefficients of Tetraalkylammonium Bromides in 2-Methoxyethanol at 25 °C

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(Received April 18, 1988)

The relative viscosities of solutions of tetraalkylammonium bromides, R_4NBr, ($R=C_2H_5$ to C_7H_{15}) have been measured in 2-methoxyethanol (ME) at 25 °C. The data have been analyzed in the form of associated electrolytes and the *B*-coefficients have been evaluated. The ionic *B*-values have been determined using the "reference electrolytes" viz. Bu_4NBBu_4 and Bu_4NBPh_4. The results have been discussed on the basis of Einstein's equation and in terms of a transition state treatment.

The potentiality of 2-methoxyethanol (ME) as a solvent for use in nonaqueous batteries and its application in synthesis[1] and electrochemical[2] studies have been widely stressed. These necessitate the study of the transport properties of various ions in this 'quasi-aprotic' medium[3] both conductometrically and viscometrically. The viscometric method is known to give valuable information regarding ion–solvent interactions which are the controlling forces in dilute solutions where ion–ion interactions are absent.[4] The variations of the solvational properties are reflected in the viscosity *B*-coefficients of ions. Although a number of extensive viscometric studies[5,6] have been made in various solvents with different electrolytes, but literature provides no information regarding the viscometric studies of tetraalkylammonium halides in 2-methoxyethanol. This led us to undertake the title investigation and the results are reported in this article.

Experimental

2-Methoxyethanol (G.R.E. Merck) was distilled twice in an all-glass distillation set before use. The properties at 25 °C obtained for the purified sample were 0.96002 $\mathrm{g\,cm^{-3}}$ for the density and 1.5414 cP (1 P=0.1 Pa s) for the viscosity (η_0) and these values are in good agreement with the literature values.[7]

Tetraalkylammonium bromides were of Fluka's purum or puriss grade and purified in the manner as given in the literature[8] and also described by us earlier.[9] The salts were purified by recrystallization and the higher homologues were recrystallized twice to ensure highest purity. The recrystallized salts were dried in vacuum at elevated temperatures for 12 h.

Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) was prepared by mixing equimolar quantities of $NaBPh_4$ and Bu_4NBr as described in the literature.[10] Tetrabutylammonium tetrabutylborate (Bu_4NBBu_4) (Alfa product) was purified as suggested by Lawrence et al.[11]

The concentration of the salts was generally varied from 0.009 M to 0.05 M (1M=1 $\mathrm{mol\,dm^{-3}}$) which was prepared by weight dilution of the stock solution (ca. 0.1 M). The conversion of the molality into molarity was done using the density values. The kinetic viscosities were measured at the desired temperature (accuracy ±0.01 °C) using a suspended Ubbelohde-type viscometer. The densities were measured using an Ostwald-Sprengal type pycknometer. The details of the experimental procedure employed have been described previously.[9] The accuracies of the density and viscosity measurements were $\pm 3\times10^{-5}\ \mathrm{g\,cm^{-3}}$ and 0.01% respectively. The electrical conductivities were measured with a Pye-Unicam conductivity meter (PW 9509) within an accuracy of ±0.1%.

The dielectric constant of ME ($\varepsilon=16.93$) was taken from the literature.[12]

Results and Discussion

The relative viscosities of the electrolytes in solution are generally analyzed by the well-known Jones-Dole equation,[13]

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

where η and η_0 are the viscosities of the solution and the solvent respectively and c is the molar concentration.

As these electrolytes have been found to be strongly associated in this solvent from conductivity measurements,[14] so the viscosity data have been analyzed by Eq. 2 as recently done by Feakins et al.[15] instead of Eq. 1,

$$\eta_r=1+A\sqrt{\alpha c}+B_i(\alpha c)+B_p(1-\alpha)c, \tag{2}$$

where, A, B_i, B_p are the characteristic constants and α is the degree of dissociation of the ion pair. The values of ion-pair dissociation constants for the electrolytes were calculated from the conductivity data[14] using the set of equations as described in the literature.[15]

Equation 2 was rearranged to give

$$(\eta_r-1-A\sqrt{\alpha c}\,)/\alpha c=B_i+B_p\left(\frac{1-\alpha}{\alpha}\right). \tag{3}$$

The $(\eta_r-1-A\sqrt{\alpha c})/\alpha c$, concentration c, density ρ, and $(1-\alpha)/\alpha$ values of the solutions of different electrolytes at 25 °C are reported in Table 1.

The A-values were calculated theoretically from the physical properties of the solvent and the limiting ionic equivalent conductances[14] using the Falkenhagen and Vernon equation,[16]

$$A_{\mathrm{Theo}}=\frac{0.2577\,\Lambda^\circ}{\eta_0(\varepsilon T)^{1/2}\lambda^\circ_+\lambda^\circ_-}\left[1-0.6863\left(\frac{\lambda^\circ_+-\lambda^\circ_-}{\Lambda^\circ}\right)^2\right] \tag{4}$$

Table 1. Density (ρ), Concentration (c), Relative Viscosity (η_r), $(1-\alpha)/\alpha$ and $(\eta_r-1-A\sqrt{\alpha c})/\alpha c$ of Tetraalkylammonium Bromides and the Two Reference Electrolytes viz. Bu_4NBBu_4 and Bu_4NBPh_4 in 2-Methoxyethanol at 25 °C

Salt	$(\eta_r-1-A\sqrt{\alpha c})/\alpha c$	η_r	c / mol dm^{-3}	$(1-\alpha)/\alpha$	ρ / g cm^{-3}
Tetraethylammonium bromide	0.700	1.005	0.00963	0.970	0.96064
	1.299	1.012	0.02417	2.209	0.96158
	1.478	1.014	0.02904	2.581	0.96188
	1.667	1.019	0.03883	2.971	0.96250
	1.816	1.024	0.04867	3.281	0.96312
Tetrapropylammonium bromide	0.801	1.007	0.00963	0.498	0.96057
	1.010	1.014	0.01933	0.721	0.96112
	1.100	1.018	0.02419	0.811	0.96139
	1.180	1.022	0.02908	0.891	0.96167
	1.301	1.029	0.03890	1.028	0.96221
	1.421	1.037	0.04878	1.149	0.96275
Tetrabutylammonium bromide	1.350	1.009	0.00964	0.776	0.96042
	1.651	1.019	0.01934	1.029	0.96082
	1.900	1.024	0.02422	1.235	0.96102
	2.350	1.030	0.02912	1.614	0.96121
	2.475	1.049	0.04889	1.720	0.96208
Tetrapentylammonium bromide	1.347	1.010	0.00964	0.750	0.96038
	1.660	1.019	0.01936	1.071	0.96075
	1.781	1.023	0.02425	1.197	0.96093
	1.880	1.028	0.02916	1.308	0.96111
	2.082	1.037	0.03905	1.500	0.96146
	2.281	1.046	0.04902	1.672	0.96182
Tetrahexylammonium bromide	1.600	1.013	0.00964	0.551	0.96026
	2.001	1.025	0.01937	0.802	0.96049
	2.175	1.032	0.02428	0.900	0.96061
	2.325	1.039	0.02920	0.992	0.96073
	2.575	1.052	0.03912	1.152	0.96095
	2.850	1.066	0.04913	1.321	0.96118
Tetraheptylammonium bromide	2.001	1.006	0.00965	0.624	0.96023
	2.505	1.028	0.01939	1.050	0.96043
	2.550	1.040	0.02925	1.107	0.96064
	2.775	1.053	0.03920	1.278	0.96084
	2.950	1.066	0.04926	1.426	0.96104
Tetrabutylammonium tetrabutylborate	1.350	1.013	0.00964	0.368	0.95939
	1.700	1.026	0.01986	0.543	0.95878
	1.851	1.033	0.02425	0.616	0.95847
	1.950	1.039	0.02917	0.679	0.95816
	2.200	1.067	0.03906	0.793	0.95757
	2.400	1.069	0.04903	0.890	0.95696
Tetrabutylammonium tetraphenylborate	1.661	1.002	0.00964	0.993	0.96024
	2.027	1.034	0.01979	1.540	0.96045
	2.441	1.041	0.02418	1.742	0.96075
	2.628	1.047	0.02951	1.923	0.96087
	2.803	1.077	0.04922	2.096	0.96095

The A-coefficient values thus obtained have been recorded in Table 2. These A-values have been used for analysis of the data.

The plots of $(\eta_r-1-A\sqrt{\alpha c})/\alpha c$ against $(1-\alpha)/\alpha$ were linear in all cases. The intercept at $(1-\alpha)/\alpha=0$ were taken as the required value of B_i. The B-coefficients (B_i-values) reported in Table 2 for the electrolytes were obtained using the least square method.

Viscosity data have also been analyzed on the basis of the transition state treatment of the relative viscosity of electrolytic solutions as suggested by Feakins et al.[17] The B-coefficient is expressed by

$$B = \frac{\bar{V}_1^\circ - \bar{V}_2^\circ}{1000} + \frac{\bar{V}_1^\circ}{1000}\left(\frac{\Delta\mu_2^{\circ\neq} - \Delta\mu_1^{\circ\neq}}{RT}\right), \tag{5}$$

where $\bar{V}_1^\circ$ and $\bar{V}_2^\circ$ are the partial molar volumes of the solvent and the solute respectively. $\Delta\mu_2^{\circ\neq}$, 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. $\Delta\mu_1^{\circ\neq}$, the free energy of activation per mole of the pure solvent, is given by

Table 2. A-Coefficients (Theoretical), B-Coefficients and $\Delta\mu_2^{0\neq}$ Values for the Electrolytes in 2-Methoxyethanol at 25 °C

Salt	A	B-Coefficient	$\Delta\mu_2^{0\neq}$
	$\mathrm{dm^{3/2}\,mol^{-1/2}}$	$\mathrm{dm^3\,mol^{-1}}$	$\mathrm{kJ\,mol^{-1}}$
Et_4NBr	0.0215	0.231	23.69
Pr_4NBr	0.0244	0.327	28.76
Bu_4NBr	0.0260	0.425	34.09
$(C_5H_{11})_4NBr$	0.0281	0.607	41.76
$(C_6H_{13})_4NBr$	0.0308	0.703	47.01
$(C_7H_{15})_4NBr$	0.0345	1.258	66.26
Bu_4NBBu_4	0.0326	0.609	48.41
Bu_4NBPh_4	0.0201	0.678	50.36

The maximum uncertainty of the B-coefficient is ±0.005. Errors in $\Delta\mu_2^{0\neq}$ values are generally ±0.1 or less.

Table 3. $B_\pm$-Coefficients and Ionic $\Delta\mu_2^{0\neq}$ Values in 2-Methoxyethanol at 25 °C

Ion	$B_\pm$-Coefficient/$\mathrm{dm^3\,mol^{-1}}$ a)	b)	$\Delta\mu_2^{0\neq}$/kJ mol^{-1}
Et_4N^+	0.112	0.111	13.81
Pr_4N^+	0.207	0.206	18.88
Bu_4N^+	0.305	0.304	24.21
$(C_5H_{11})_4N^+$	0.488	0.487	31.88
$(C_6H_{13})_4N^+$	0.583	0.583	37.13
$(C_7H_{15})_4N^+$	1.138	1.138	56.38
Br^-	0.119	—	9.88
BPh_4^-	—	0.373	27.72

a) Calculations based on Bu_4NBBu_4. b) Calculations based on Bu_4NBPh_4.

Table 4. Ionic Radii ($R_\pm$) and Solvation Number (n_s) of Ions in 2-Methoxyethanol at 25 °C

Ion	r_c a)	$R_\pm$ b)	r_s c)	n_s
Et_4N^+	4.00	2.61	2.48	−1.47
Pr_4N^+	4.52	3.20	3.22	−1.89
Bu_4N^+	4.94	3.64	3.69	−2.29
$(C_5H_{11})_4N^+$	5.29	4.26	4.35	−2.24
$(C_6H_{13})_4N^+$	5.60	4.52	5.37	−2.64
$(C_7H_{15})_4N^+$	5.88	5.65	5.89	−0.725
Br^-	1.95	2.67	2.38	0.369
BPh_4^-	4.20	3.89	4.02	−0.473

a) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butlerworths, London (1959). b) From viscometric data. c) From Ref. 14.

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT \ln\left(\frac{\eta_0 \bar{V}_1^0}{hN}\right), \tag{6}$$

and the value for 2-methoxyethanol at 25°C is 14.18 kJ mol^{-1}. The activation parameters for viscous flow for the electrolytes are given in Table 2.

The viscosity B-coefficients (Table 2) are larger and positive and increase as we go from Et_4NBr to $(C_7H_{15})_4NBr$. This is a common feature in most nonaqueous solvents.[18] The B-coefficients for tetraalkylammonium halides in almost in all dipolar aprotic solvents show a weak temperature dependence[18] whereas those in ME show a strong temperature dependence as observed in water.[18] This may be due to the 'quasi-aprotic' nature of ME. The changes in the $\Delta\mu_2^{0\neq}$ follows the same pattern as the B-values.

In order to distinguish the effect each single has in 2-methoxyethanol, the ionic B-values were calculated using Bu_4NBBu_4[18–21] and Bu_4NBPh_4[14,22,23] as reference electrolytes by

$$B_{Bu_4N^+} = B_{Bu_4B^-} = \frac{1}{2}\,B_{Bu_4NBBu_4} \tag{7}$$

and

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left(\frac{5.35}{5.00}\right)^3. \tag{8}$$

The average B_{ion}-values of tetraalkylammonium ions are recorded in Table 3. The ionic $\Delta\mu_2^{0\neq}$ values have also been recorded in Table 3.

The ionic B-coefficients for the tetraalkylammonium ions have been found to increase continuously from Et_4N^+ to $(C_7H_{15})_4N^+$ in ME. An analysis of B-coefficients can be made on the basis of Einstein's equation,[24]

$$B_\pm = 2.5 \times \frac{4}{3}\pi\frac{R_\pm^3 N}{1000}, \tag{9}$$

where $R_\pm$ is the radius of the ion assumed as a rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The number (n_s) of solvent molecules bound to the ion in the primary sphere of solvation can be calculated by combining the Jones-Dole equation with Einstein's[25]

$$B_\pm = \frac{2.5}{1000}\,(V_i + n_s v_s), \tag{10}$$

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 4. The values may be compared with the corrected Stokes' radii obtained from conductance studies. For cations R_+ values are much less than r_c values, showing that these ions are scarcely solvated in this medium. On the other hand the comparatively high n_s as well as R value for Br^- ion indicate this ion's capacity for interactions in the solvent as already found in other aprotic solvents.[6]

From Table 3 we find that the change in ionic $\Delta\mu_2^{0\neq}$ values is much more in case of larger ions than the smaller ones. If the solvent offers no appreciate structure resistance to the coordination of the solvent molecules in the ground state, steric inhibition will now limit the coordination of ions and this will effect the smaller ion more than the larger. With a bond breaking mechanism the effects on $\Delta\mu_2^{0\neq}$ will be complex, but the relief of steric hindrance in the transition state would be one factor tending to decrease $\Delta\mu_2^{0\neq}$ for the smaller relative to the larger ions. Moreover, $\Delta\mu_2^{0\neq}$ for all the ions is positive, thus, the formation of the transition state is less favorable by these ions. $\Delta\mu_2^{0\neq}$ for the Br^- ion is lower than the cations and this suggests that cations interact with ME more strongly than the anion.

One of the authors (D.D) thanks the CSIR, New Delhi, for the award of a Junior Research Fellowship.

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