Studies on the Viscosities, Conductances, and Adiabatic Compressibilities of Some Tetraalkylammonium Perchlorates in 2-Methoxyethanol

Bijan DAS and Dilip K. HAZRA*
Department of Chemistry, North Bengal University-734430, Darjeeling, India
(Received May 30, 1992)

Electrical conductances, relative viscosities, and apparent molal adiabatic compressibilities of solutions of some symmetrical tetraalkylammonium perchlorates in 2-methoxyethanol (ME) have been reported. The conductance data have been analyzed by the 1978 Fuoss conductance equation and the viscosity data by the Jones–Dole equation for associated electrolytes. The ionic contribution to the limiting equivalent conductance, viscosity *B* coefficient and other thermodynamic parameters have been determined using the "reference electrolyte" method. The viscosity data show that the tetraalkylammonium ions are poorly solvated and behave as structure-breakers in 2-methoxyethanol. Analysis of the conductance as well as the compressibility data reveals the existence of strong ion–ion interactions in this solvent medium. The compressibility data also indicate the electrostriction of solvent molecules around the tetraethylammonium ion, while for the larger tetraalkylammonium ions they are accommodated inside the space between the coiled alkyl chains attached to the nitrogen atom.

Studies on the thermodynamic and transport properties of electrolytes in different solvents are of great importance to obtain information on the behavior of ions in solutions. Recent years have therefore witnessed increased interests on this topic as are evidenced from numerous publications in this field.[1—10] In the present work, an attempt has been made to provide an unequivocal interpretation of solute–solvent interactions for some symmetrical tetraalkylammomium perchlorates in 2-methoxyethanol (ME) through the measurements of their conductances, viscosities, and adiabatic compressibilities. The solvent 2-methoxyethanol is "quasi-aprotic" in nature[11] with low dielectric constant ($\varepsilon_{25\,°C}$=16.93).[12] The importance of this solvent lies in the fact that it has found its applications in many industrial processes and also as a solvent medium for various electrochemical investigations.[13—15]

Experimental

2-Methoxyethanol (G.R.E. Merck) was distilled twice immediately before use and the middle fraction collected. The purified solvent had a density of 0.96002 g cm^{-3}, a coefficient of viscosity of 1.5414×10^{-3} Pa s, and a specific conductance of ca. 1.01×10^{-6} S cm^{-1} at 25 °C. These values are in good agreement with the literature values.[16] The solvent properties are recorded in Table 1.

Tetraalkylammonium perchlorates (except tetrapentylammonium perchlorate) were or purum or puriss grade (Fluka). Tetrapentylammonium perchlorate (Pen_4ClO_4) was prepared by adding slowly a hot aqueous solution of tetrapentylammonium bromide (Pen_4Br) to a hot aqueous solution of sodium perchlorate ($NaClO_4$). All the salts were recrystallized twice from conductivity water and dried in vacuo at 70 °C for 24 h. Sodium tetraphenylborate ($NaBPh_4$) (Fluka, puriss) was recrystallized three times from acetone and then deried in vacuo at 80 °C for 72 h. Sodium perchlorate was recrystallized several times from water+methanol mixtures and dried in vacuo at 150 °C for 96 h.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 0.751 cm^{-1} and having an accuracy of ±0.1%. Measurements were made in an oil bath maintained at 25±0.005 °C. The details of the experimental procedure have been described earlier.[5] Due correction was made for the solvent contribution to the conductance values of all the salt solutions.

The kinematic viscosities were measured at the desired temperature (accuracy ±0.01 °C) using a suspended Ubbelohde-type viscometer. The densities were measured with an Ostwald-Sprengal type pycnometer of about 25 cm^3 capacity. The precisions of the density and viscosity measurements were ±3×10^{-5} g cm^{-3} and 0.05%, respectively. The kinematic viscosities were converted into the absolute viscosities by multiplying the former with density.

Sound velocities were determined using a single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 5 MHz which was calibrated with water, methanol, and benzene at 25 °C. The maximum uncertainty of the sound velocity measurements in all cases was ±0.03%.

The dielectric constants of 2-methoxyethanol at 25, 35, and 45 °C were taken from the literature.[12]

Table 1. Solvent Properties

Temperature °C	Density g cm^{-3}	Dielectric constant	Viscosity×10^3 Pa s
25	0.96002	16.93	1.5414
35	0.95356	16.15	1.2579
45	0.94715	15.39	1.0400

Data Treatment

Conductance. The experimental equivalent conductances at various concentrations are given in Table 2. The data have been analyzed by the Fuoss conductance equation,[17,18] which can be expressed as

$$\Lambda = p\,[\Lambda^{\circ}(1+R_{X})+E_{L}] \tag{1}$$

$$p=[1-\alpha(1-\gamma)] \tag{2}$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \tag{3}$$

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

$$\beta = e^2 / \varepsilon k_B T \tag{5}$$

Table 2. Equivalent Conductances (Λ) of Tetraalkylammonium Perchlorates and $NaClO_4$ in 2-Methoxyethanol at 25 °C

10^4c mol dm^{-3}	Λ S cm^2 mol^{-1}	10^4c mol dm^{-3}	Λ S cm^2 mol^{-1}
Me_4ClO_4		Et_4NClO_4	
10.510	39.20	16.000	34.88
9.108	39.85	14.001	35.71
8.408	40.20	11.998	36.60
7.006	41.00	8.995	38.08
6.306	41.45	5.995	39.84
4.905	42.35	5.498	40.18
3.503	43.45	4.004	41.28
2.803	44.05	2.996	42.14
2.102	44.72	2.001	43.15
Pr_4NClO_4		Bu_4NClO_4	
14.340	33.56	8.310	31.83
9.306	34.06	6.648	32.82
8.272	34.57	5.817	33.38
7.238	34.95	4.986	33.93
6.204	35.62	4.155	34.45
5.170	36.17	3.324	35.23
4.136	37.11	2.493	36.03
3.102	37.72		
Pen_4NClO_4		Hex_4NClO_4	
15.999	26.85	16.001	24.99
12.225	28.31	13.962	25.72
10.064	29.25	10.115	27.26
8.498	30.00	9.022	27.75
7.105	30.72	8.006	28.20
6.001	31.35	6.132	29.21
4.014	32.64	5.026	29.86
2.998	33.43	3.003	31.27
2.003	34.34	1.998	32.16
$NaClO_4$			
16.021	27.28		
13.998	27.95		
12.002	28.67		
9.998	29.44		
8.001	30.29		
5.080	31.76		
4.119	32.34		
2.995	33.11		
2.001	33.92		

$$K_A = K_R/(1-\alpha) = K_R(1+K_S) \tag{6}$$

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

In practice, calculations were made by finding the values of Λ° and α which minimize

$$\sigma^2 = \sum_j [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2/(n-2) \tag{7}$$

for a sequence of R-values and then plotting $\sigma\% = 100\,\sigma/\Lambda^\circ$ against R; the best-fit R corresponds to the minimum in the $\sigma\%$ vs. R curve. However, since a rough scan using unit increment of R values from 4 to 20 gave no significant minima in the $\sigma\%$–R curves for all the salts studied, the R value is assumed to be $R=a+d$ where a is the sum of the crystallographic radii and d is given by[18]

$$d = 1.183\,(M/\rho_o)^{1/3}\ \text{Å} \tag{8}$$

where M is the molecular weight of the solvent and ρ_o its density.

The values of Λ°, K_A, and R are reported in Table 3. The limiting ionic conductances were estimated by using $\lambda^\circ_{Bu_4N^+} = 14.29$ from our previous work.[5] The $\lambda^\circ_\pm$-values thus obtained are presented in Table 4. The salt $NaClO_4$ has also been studied because of the requirement of its conductance data in the analysis of its

Table 4. Limiting Ionic Conductances, Walden Products and Stokes Radii of Tetraalkylammonium, Sodium and Perchlorate Ions in 2-Methoxyethanol at 25 °C

Ion	$\lambda^\circ_\pm$ S cm^2 mol^{-1}	$\lambda^\circ_\pm \eta \times 10^3$ S cm^2 mol^{-1} Pa s	r_S nm
Me_4N^+	22.58	0.348	0.236
Et_4N^+	21.30	0.328	0.250
Pr_4N^+	16.34	0.252	0.325
Bu_4N^+	14.29	0.220	0.373
Pen_4N^+	12.09	0.186	0.441
Hex_4N^+	9.78	0.151	0.543
Na^+	11.25	0.173	0.473
ClO_4^-	26.51	0.409	0.200

Table 3. Conductance Parameters of Tetraalkylammonium Perchlorates and $NaClO_4$ in 2-Methoxyethanol at 25 °C

Salt	Λ° S cm^2 mol^{-1}	K_A dm^3 mol^{-1}	$\Lambda^\circ \eta \times 10^3$ S cm^2 mol^{-1} Pa s	R nm	σ
Me_4NClO_4	49.09±0.07	255± 5	0.757	1.09	0.06
Et_4NClO_4	47.81±0.16	326±12	0.737	1.15	0.15
Pr_4NClO_4	42.85±0.16	304±13	0.660	1.20	0.09
Bu_4NClO_4	40.80±0.11	389±12	0.629	1.24	0.06
Pen_4NClO_4	38.60±0.20	409±19	0.595	1.28	0.16
Hex_4NClO_4	36.29±0.20	428±20	0.559	1.31	0.16
$NaClO_4$	37.76±0.14	300±13	0.582	0.86	0.13

Table 5. Concentration (c), Density (ρ), and Relative Viscosity (η_r) of Tetraalkylammonium Perchlorates, $NaClO_4$ and $NaBPh_4$ in 2-Methoxyethanol at 25, 35, and 45 °C

c / mol dm^{-3}	ρ / g cm^{-3}	η_r	c / mol dm^{-3}	ρ / g cm^{-3}	η_r	c / mol dm^{-3}	ρ / g cm^{-3}	η_r	c / mol dm^{-3}	ρ / g cm^{-3}	η_r
Me_4NClO_4 25 °C			Bu_4NClO_4 25 °C			Pen_4NClO_4 35 °C			$NaBPh_4$ 35 °C		
0.00985	0.96073	1.0035	0.01030	0.96049	1.0097	0.00966	0.95390	1.0152	0.01004	0.95430	1.0163
0.01976	0.96144	1.0063	0.02006	0.96093	1.0193	0.01920	0.95423	1.0300	0.01974	0.95501	1.0342
0.02984	0.96216	1.0090	0.02497	0.96115	1.0243	0.02388	0.95439	1.0374	0.02448	0.95536	1.0439
0.03532	0.96255	1.0105	0.02901	0.96133	1.0284	0.02917	0.95457	1.0457	0.03100	0.95584	1.0579
0.04081	0.96294	1.0120	0.03892	0.96177	1.0385	0.03835	0.95488	1.0603	0.03539	0.95616	1.0679
0.04589	0.96330	1.0134	0.04891	0.96221	1.0491	0.04851	0.95522	1.0766	0.04089	0.95658	1.0811
Et_4NClO_4 25 °C			Pen_4NClO_4 25 °C			Hex_4NClO_4 35 °C			Me_4NClO_4 45 °C		
0.00985	0.96066	1.0048	0.00971	0.96037	1.0111	0.00971	0.95380	1.0177	0.00970	0.94781	1.0061
0.02023	0.96133	1.0094	0.01931	0.96071	1.0222	0.01972	0.95404	1.0359	0.01962	0.94848	1.0116
0.02490	0.96163	1.0115	0.02415	0.96088	1.0280	0.02395	0.95414	1.0436	0.02959	0.94915	1.0171
0.03177	0.96207	1.0146	0.02931	0.96106	1.0342	0.02908	0.95426	1.0531	0.03496	0.94951	1.0201
0.04054	0.96263	1.0187	0.03882	0.96139	1.0458	0.03816	0.95447	1.0699	0.04035	0.94978	1.0231
0.04510	0.96292	1.0208	0.04900	0.96174	1.0583	0.04825	0.95470	1.0885	0.04529	0.95020	1.0263
Pr_4NClO_4 25 °C			Hex_4NClO_4 25 °C			$NaClO_4$ 35 °C			Et_4NClO_4 45 °C		
0.01228	0.96070	1.0092	0.00987	0.96208	1.0139	0.00999	0.95471	1.0090	0.00965	0.94774	1.0072
0.02103	0.96118	1.0159	0.02003	0.96054	1.0288	0.01964	0.95583	1.0180	0.01990	0.94836	1.0142
0.02523	0.96141	1.0192	0.02438	0.96065	1.0354	0.02477	0.95643	1.0230	0.02454	0.94864	1.0173
0.03018	0.96168	1.0231	0.02958	0.96078	1.0433	0.02999	0.95723	1.0282	0.03138	0.94905	1.0219
0.03975	0.96220	1.0310	0.03927	0.96102	1.0584	0.04084	0.95835	1.0391	0.03990	0.94956	1.0276
0.04509	0.96249	1.0354	0.04949	0.96127	1.0745	0.05026	0.95938	1.0487	0.04443	0.94983	1.0305
$NaClO_4$ 25 °C			Et_4NClO_4 35 °C			Pr_4NClO_4 45 °C			Hex_4NClO_4 45 °C		
0.01006	0.96121	1.0085	0.00971	0.95417	1.0060	0.01194	0.94778	1.0144	0.00964	0.94738	1.0216
0.01978	0.96234	1.0164	0.02000	0.95481	1.0117	0.02075	0.94828	1.0250	0.01960	0.94761	1.0431
0.02494	0.96298	1.0207	0.02468	0.95510	1.0143	0.02474	0.94845	1.0300	0.02355	0.94770	1.0516
0.03019	0.96360	1.0251	0.03148	0.95552	1.0181	0.02961	0.94870	1.0359	0.02844	0.94781	1.0621
0.04112	0.96491	1.0345	0.04009	0.95605	1.0229	0.03910	0.94919	1.0470	0.03742	0.94801	1.0815
0.05061	0.96603	1.0427	0.04465	0.95633	1.0256	0.04435	0.94946	1.0544	0.04745	0.94823	1.1029
$NaBPh_4$ 25 °C			Pr_4NClO_4 35 °C			Bu_4NClO_4 45 °C			$NaClO_4$ 45 °C		
0.01011	0.96079	1.0131	0.01209	0.95421	1.0124	0.00999	0.94757	1.0153	0.00994	0.94827	1.0092
0.01988	0.96154	1.0269	0.02092	0.95468	1.0217	0.01964	0.94797	1.0300	0.01952	0.94935	1.0188
0.02465	0.96190	1.0343	0.02489	0.95489	1.0260	0.02475	0.94818	1.0379	0.02461	0.94995	1.0241
0.03121	0.96240	1.0450	0.02980	0.95515	1.0313	0.02842	0.94833	1.0436	0.02981	0.95082	1.0297
0.03563	0.96274	1.0526	0.03930	0.95565	1.0418	0.03801	0.94872	1.0585	0.04056	0.95173	1.0415
0.04126	0.96317	1.0626	0.04464	0.95593	1.0479	0.04769	0.94911	1.0738	0.04992	0.95279	1.0521
Me_4NClO_4 35 °C			Bu_4NClO_4 35 °C			Pen_4NClO_4 45 °C			$NaBPh_4$ 45 °C		
0.00974	0.95424	1.0048	0.01009	0.95400	1.0129	0.00940	0.94748	1.0182	0.00997	0.94738	1.0193
0.01969	0.95493	1.0090	0.01986	0.95442	1.0257	0.01898	0.94781	1.0359	0.01961	0.94848	1.0421
0.02968	0.95562	1.0131	0.02479	0.95463	1.0323	0.02367	0.94797	1.0446	0.02431	0.94880	1.0542
0.03505	0.95599	1.0153	0.02855	0.95479	1.0374	0.02898	0.94815	1.0544	0.03078	0.94924	1.0720
0.04044	0.95636	1.0176	0.03826	0.95520	1.0506	0.03819	0.94846	1.0715	0.03514	0.94953	1.0846
0.04543	0.95670	1.0197	0.04803	0.95561	1.0640	0.04843	0.94880	1.0906	0.04069	0.94991	1.1014

viscosity data.

Viscosity. The relative viscosities are generally analyzed by the Jones–Dole equation[19]

$$\eta_r = 1 + Ac^{1/2} + Bc \tag{9}$$

where η_r is the relative viscosity of the solution and c is the molar concentration.

As these electrolytes have been found to be strongly associated in ME from conductivity measurements, the viscosity data have been analyzed by Eq. 10 as recently done by Feakins and co-workers[20] instead of Eq. 9,

$$\eta_r = 1 + A(\alpha c)^{1/2} + B_i \alpha c + B_p(1-\alpha)c \tag{10}$$

Here A, B_i, and B_p are the characteristic constants and α is the degree of dissociation of the ion pair. The values of α were calculated from the conductance data (for $NaBPh_4$, these were obtained from our earlier work[7]) using the equations as described in the literature.[20]

Equation 10 can be rearranged to give

$$[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c = B_i + B_p\left(\frac{1-\alpha}{\alpha}\right) \tag{11}$$

The concentration (c), density (ρ), and the relative viscosity (η_r) of the solutions of different electrolytes at 25, 35, and 45 °C are presented in Table 5. The A values were calculated theoretically from the physical properties of the solvent and the limiting ionic equivalent conductances using Falkenhagen and Vernon equation[21]

$$A_{\text{theo}} = \frac{0.2577\,\Lambda^{\circ}}{\eta_0(\varepsilon T)^{1/2}\lambda_+^{\circ}\lambda_-^{\circ}}\left[1 - 0.6863\left(\frac{\lambda_+^{\circ} - \lambda_-^{\circ}}{\Lambda^{\circ}}\right)^2\right] \tag{12}$$

The values of the A coefficients thus obtained have been recorded in Table 6. These A values have been used for the analysis of the data. In view of the weak temperature dependence of the A coefficients, the A values at 25 °C were utilized at the other temperatures.

The plots of $[\eta_r-1-A(\alpha c)^{1/2}]/\alpha c$ against $(1-\alpha)/\alpha$ were linear in all cases. A representative plot for Me_4NClO_4, Pr_4NClO_4, Bu_4NClO_4, and Hex_4NClO_4 in ME at 25 °C is shown in Fig. 1. The intercept at $(1-\alpha)/\alpha=0$ was taken as the required value of B_i. The B coefficients, i.e., B_i reported in Table 6 for the electrolytes were obtained from these plots using the least-squares method.

The ionic B values (Table 7) were calculated using Bu_4NBPh_4[22,23] as the reference electrolyte by Eq. 13.

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}}=\frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}}=\left(\frac{5.35}{5.00}\right)^3 \tag{13}$$

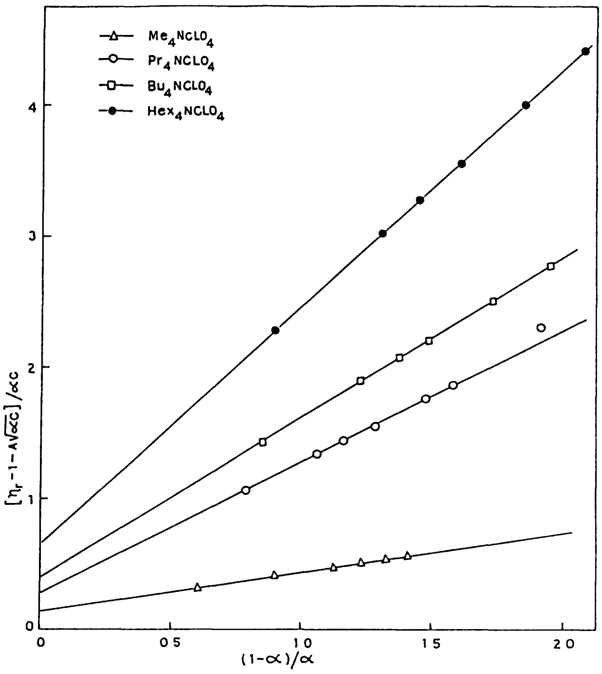

Fig. 1. Representative plot of $[\eta_r-1-A(\alpha c)^{1/2}]/\alpha c$ against $(1-\alpha)/\alpha$ for some electrolytes in ME at 25 °C.

Table 6. Theoretical A-Coefficients at 25 °C and Viscosity B-Coefficients for the Electrolytes in 2-Methoxyethanol at 25, 35, and 45 °C

Salt	A	B/dm³ mol⁻¹		
	dm$^{3/2}$ mol$^{1/2}$	25 °C	35 °C	45 °C
Me_4NClO_4	0.0192	0.149	0.276	0.392
Et_4NClO_4	0.0198	0.191	0.360	0.523
Pr_4NClO_4	0.0224	0.286	0.541	0.785
Bu_4NClO_4	0.0238	0.383	0.731	1.070
Pen_4NClO_4	0.0256	0.567	1.093	1.604
Hex_4NClO_4	0.0281	0.664	1.284	1.892
$NaClO_4$	0.0264	0.394	0.322	0.256
$NaBPh_4$	0.0341	0.687	0.920	1.156

Because Bu_4NBPh_4 is scarcely soluble in ME, its B coefficient was obtained from the following relationship:

$$B_{Bu_4NClO_4}+B_{NaBPh_4}-B_{NaClO_4}=B_{Bu_4NBPh_4} \tag{14}$$

On applying transition state treatment to the relative viscosity of electrolytic solutions[24] an equation can be obtained from which it is possible to calculate the molar free energy of activation of the solution for viscous flow, $\Delta\mu_2{}^{\theta\neq}$:

$$B=\frac{\bar{V}_2{}^\circ-\bar{V}_1{}^\circ}{1000}+\frac{\bar{V}_1{}^\circ}{1000}\left(\frac{\Delta\mu_2{}^{\theta\neq}-\Delta\mu_1{}^{\theta\neq}}{RT}\right) \tag{15}$$

where $\Delta\mu_1{}^{\theta\neq}$ is the molar free energy of activation of solvent[25] and the other symbols have usual significance. The activation parameters for viscous flow are given in

Table 7. Ionic B Values in 2-Methoxyethanol at 25, 35, and 45 °C

Ion	$B_\pm$/dm³ mol⁻¹		
	25 °C	35 °C	45 °C
Me_4N^+	0.070	0.142	0.207
Et_4N^+	0.112	0.226	0.338
Pr_4N^+	0.207	0.407	0.600
Bu_4N^+	0.304	0.597	0.885
Pen_4N^+	0.488	0.959	1.419
Hex_4N^+	0.585	1.150	1.707
Na^+	0.315	0.188	0.071
ClO_4^-	0.079	0.134	0.185
BPh_4^-	0.372	0.732	1.085

Table 8. $\Delta\mu_2^{\theta\neq}$/kJ mol⁻¹ Values of Electrolytes in 2-Methoxyethanol at 25, 35, and 45 °C

Salt	25 °C	35 °C	45 °C
Me_4NClO_4	19.68	23.97	28.05
Et_4NClO_4	23.06	28.79	34.55
Pr_4NClO_4	28.16	36.79	45.41
Bu_4NClO_4	33.35	45.12	57.12
Pen_4NClO_4	41.24	58.91	76.88
Hex_4NClO_4	46.43	67.28	88.70
$NaClO_4$	24.14	22.15	20.21
$NaBPh_4$	41.83	50.16	59.03

Table 9. Ionic $\Delta\mu_2^{\theta\neq}$ Values in 2-Methoxyethanol at 25, 35, and 45 °C

Ion	$\Delta\mu_2^{\theta\neq}$/kJ mol⁻¹		
	25 °C	35 °C	45 °C
Me_4N^+	9.27	11.72	14.05
Et_4N^+	12.65	16.54	20.55
Pr_4N^+	17.75	24.54	31.41
Bu_4N^+	22.94	32.87	43.12
Pen_4N^+	30.83	46.66	62.88
Hex_4N^+	36.02	55.03	74.70
Na^+	13.73	9.90	6.21
ClO_4^-	10.41	12.25	14.00
BPh_4^-	28.10	40.26	52.82

Table 10. Concentration (c), Density (ρ), Adiabatic Compressibility (β), and Apparent Molal Adiabatic Compressibility (ϕ_K) of Tetraalkylammonium Perchlorates in 2-Methoxyethanol at 25 °C

Salt	c	ρ	$\beta \times 10^{13}$	$\phi_K \times 10^{15}$
	mol dm^{-3}	g cm^{-3}	Pa^{-1}	m^3 mol^{-1} Pa^{-1}
Et_4NClO_4	0.05014	0.96324	57.560	10.05
	0.10011	0.96639	57.153	14.65
	0.15071	0.96954	56.771	18.35
	0.20005	0.97258	56.420	21.33
	0.24883	0.97556	56.095	24.06
	0.30197	0.97878	55.761	26.75
Pr_4NClO_4	0.03514	0.96195	57.542	6.05
	0.06994	0.96383	57.098	9.25
	0.10494	0.96570	56.667	11.92
	0.14500	0.96782	56.188	14.48
	0.18006	0.96966	55.780	16.45
	0.21594	0.97153	55.373	18.33
Bu_4NClO_4	0.02497	0.96115	57.576	5.06
	0.05116	0.96231	57.139	9.12
	0.07520	0.96336	56.749	11.95
	0.10252	0.96454	56.318	14.83
	0.12520	0.96551	55.968	16.93
	0.15066	0.96659	55.583	19.11
Pen_4NClO_4	0.01931	0.96071	57.592	1.93
	0.03882	0.96139	57.183	5.89
	0.05719	0.96202	56.806	8.68
	0.07610	0.96266	56.425	11.14
	0.09493	0.96329	56.052	13.33
	0.11519	0.96396	55.656	15.40
Hex_4NClO_4	0.01454	0.96040	57.630	−3.41
	0.02958	0.96078	57.248	0.95
	0.04377	0.96113	56.895	4.12
	0.05821	0.96148	56.542	6.90
	0.07291	0.96183	56.188	9.38
	0.08740	0.96217	55.884	11.61

Table 11. Limiting Apparent Molal Adiabatic Compressibilities (ϕ_K°) and Experimental Slopes (S_K) of Tetraalkylammonium Perchlorates in 2-Methoxyethanol at 25 °C

Salt	$\phi_K^\circ \times 10^{15}$	$S_K \times 10^{15}$
	m^3 mol^{-1} Pa^{-1}	m^3 mol$^{-3/2}$ Pa^{-1} kg$^{1/2}$
Et_4NClO_4	−0.72	47.63
Pr_4NClO_4	−2.31	42.40
Bu_4NClO_4	−4.29	57.59
Pen_4NClO_4	−7.04	63.55
Hex_4NClO_4	−13.46	81.52

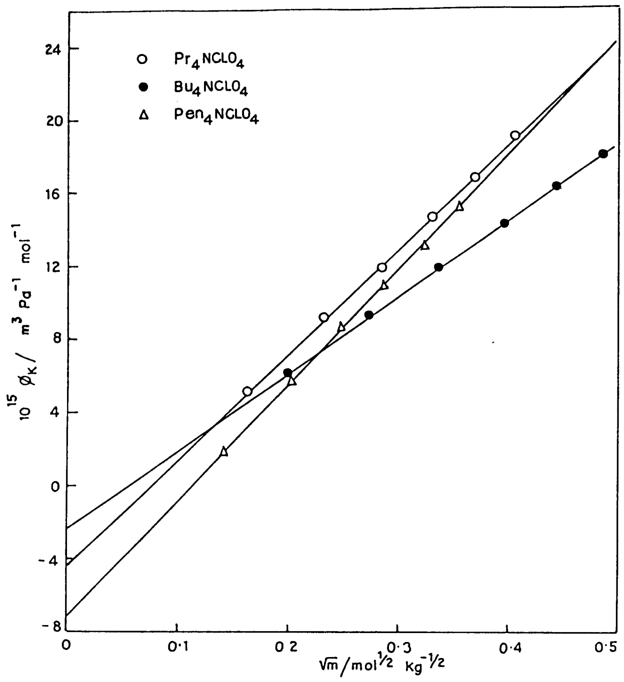

Fig. 2. Representative plot of ϕ_K against $m^{1/2}$ for some electrolytes in ME at 25 °C.

Table 8. The ionic free energies of activation for viscous flow based on the division of Bu_4NBPh_4 have been presented in Table 9.

Appparent Molal Adiabatic Compressibility. Adiabatic compressibility coefficients, β, were derived from the relation

$$\beta = 1/u^2\rho \tag{16}$$

where ρ is the solution density and u is the sound velocity in the solution. The apparent molal adiabatic compressibility (ϕ_K) of liquid solutions was calculated from the relation

$$\phi_K = \frac{1000}{m\rho\rho_\circ}(\beta\rho_\circ - \beta_\circ\rho) + \beta\frac{M}{\rho_\circ} \tag{17}$$

where m is the molality of the solution and the other symbols have their usual significance. The molar concentration (c), density (ρ), adiabatic compressibility coefficient (β), and the apparent molal adiabatic compressibility (ϕ_K) of the solutions of different electrolytes at 25 °C are given in Table 10.

The limiting apparent molal compressibilities (ϕ_K°) were obtained[8,26] by extrapolating the plots of ϕ_K versus the square root of molal concentration of the solute to zero concentration:

$$\phi_K = \phi_K^\circ + S_K\, m^{1/2} \tag{18}$$

Here S_K is the experimental slope. A representative plot for Pr_4NClO_4, Bu_4NClO_4, and Pen_4NClO_4 in ME at 25 °C is shown in Fig. 2. The values of ϕ_K° and S_K have been reported in Table 11.

Results and Discussion

Table 3 shows that the limiting equivalent conductances of the tetraalkylammonium perchlorates decrease with increasing length of the alkyl chain. This is found to be in agreement with earlier findings in several pure and mixed solvents.[2]

The association constants (K_A) in Table 3 indicate that all the salts are highly associated in this solvent medium. This is quite expected owing to the low dielectric constant of the solvent. The most outstanding feature is that the electrolytes containing larger ions show considerable amount of association. Furthermore, the process of ionic association of these electrolytes does not exhibit the simple dependence upon ionic size predicted by electrostatic theory. Here K_A increases as the size of the cation increases with the exception of Pr_4NClO_4. This trend in association constants has also been observed for tetraalkylammonium salts in other solvents.[27a] A comparision of the K_A values for R_4NClO_4 salts with those for R_4NBr salts[5] in ME shows that R_4NClO_4 salts are, in general, more associated than their corresponding bromide homologues (Pr_4NClO_4 being an exception). The same pattern has also been manifested by the tetraalkylammonium salts in methanol,[28] ethanol,[27a] 1-propanol,[27a] 1-butanol,[27b] and 1-pentanol.[27b] This can be accounted for by the assumption that solvation of the anion increases in the order $ClO_4^- < Br^-$ and that the solvation of the cations is relatively independent of their sizes.

The $\lambda°$-values of the R_4N^+ ions obtained from the $\Lambda°$-values of tetraalkylammonium perchlorates are in excellent agreement with those obtained earlier from tetraalkylammonium bromides.[5] The order of the anionic conductance in ME is $ClO_4^- > Br^-$, which is the same as that observed in 1-propanol,[27a] 2-propanol,[29] and 1-butanol.[27b]

The viscosity B-coefficients shown in Table 6 are large and positive and increase as we go from Me_4NClO_4 to Hex_4NClO_4. These values show a strong temperature dependence in ME as observed in water.[30] On the other hand, the B-coefficients in almost all dipolar aprotic solvents exhibit a weak temperature dependence.[30] The observed strong temperature dependence in ME may be attributed to the "quasi-aprotic" nature of the solvent. From Table 8, we see that the changes in the $\Delta\mu_2^{\theta\neq}$ values follow the same pattern as the B values.

The sign of $\mathrm{d}B/\mathrm{d}T$ values gives important information regarding the structure-breaking and structure-making roles of the solute in the solvent media.[31] The ionic B values increase with the rise of temperature except Na^+ ion in which case a gradual decrease in this value with increasing temperature is noticed, i.e., $\mathrm{d}B_{\text{ion}}/\mathrm{d}T$ values are positive (structure-breaking) for all the cations with the exception of Na^+ ion.

An analysis of $B_\pm$ coefficients can be made on the basis of the Einstein's equation[32]

$$B_\pm = 2.5\frac{4}{3}\pi\frac{R_\pm^3 N}{1000} \tag{19}$$

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 of solvent molecules bound to the ion in its primary sphere of solvation (n_s) can be calculated by combining the Jones–Dole equation with that of Einstein[33]

$$B_\pm = \frac{2.5}{1000}(V_i + n_s V_s) \tag{20}$$

Table 12. Ionic Radii ($R_\pm$) and Solvation Numbers (n_S) of Ions in 2-Methoxyethanol at 25 °C

Ion	r_c[a)]/nm	$R_\pm$/nm	n_S
Me_4N^+	0.35	0.22	−0.98
Et_4N^+	0.40	0.26	−1.47
Pr_4N^+	0.45	0.32	−1.89
Bu_4N^+	0.49	0.36	−2.29
Pen_4N^+	0.53	0.43	−2.24
Hex_4N^+	0.56	0.45	−2.64
Na^+	0.12	0.37	1.50
ClO_4^-	0.24	0.23	−0.01
BPh_4^-	0.42	0.39	−0.46

a) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London (1959).

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 12. The $R_\pm$ values are found to be in good agreement with the corrected Stokes' radii obtained from conductance studies (Table 4). For tetraalkylammonium, perchlorate, and tetraphenylborate ions, $R_\pm$ values are less than their corresponding crystallographic radii indicating that these ions are scarcely solvated in ME. On the other hand, for Na^+ ion R_+ value is much higher than its crystallographic radius suggesting that this ion is somewhat solvated in this solvent medium. The negative values of the solvation numbers (n_s) listed in Table 12 are physically unacceptable. They seem to indicate that the determination of solvation numbers on the basis of Eq. 20 does not appear to be correct. This probably arises from the fact that the electrolytic solutions are different from the model which underlies Eq. 20.

It is interesting to note that for all ions except Na^+ ion, $\Delta H_2^{\theta\neq}$ and $T\Delta S_2^{\theta\neq}$ are negative, indicating that the formation of the transition state is associated with bond making and an increase in order. In the case of Na^+ ion, positive entropy of activation suggests that the attainment of transition state for viscous flow is accompanied by bond breaking and a concomitant decrease in order.

It is seen from Table 11 that all the salts studied here (Me_4NClO_4 has been omitted due to its low solubility) have negative limiting apparent molal adiabatic compressibilities ($\phi_K°$) which become more negative with increase in chain length of the tetraalkylammonium ion. Negative $\phi_K°$ values of the salts are interpreted in terms of the loss of compressibility of ME due to the electrostrictive forces in the vicinity of the ions. The extent of electrostriction is maximum in the case of Et_4N^+ ion, but it will gradually decrease with increasing chain length. Therefore, although the negative $\phi_K°$ value of Et_4NClO_4 may be due to the electrostriction of the solvent molecules around the Et_4N^+ ion, those for the higher homologues (with lower surface charge density on the R_4N^+ ion) have a different origin. One effect that is possible in the case of larger R_4N^+ ions is the penetration of the solvent molecules into the space between the coiled alkyl chains attached to the nitrogen atom. This so happens mainly due to the directing influence of the positively charged nitrogen atom of the tetraalkylammonium ion. This, obviously, causes constriction in the solution volumes. The initiation of the phenomenon of penetration from Pr_4N^+ ion has also been manifested by the abrupt decrease in the mobility of Pr_4N^+ ion (Table 4). The greater the number of $-CH_2-$ groups in the cation, the lower is the limiting apparent molal adiabatic compressibility. The increased size of the tetraalkylammonium ions increases the extent of penetration resulting in a decrease in the compressibility of the solution.

The high values of the limiting slopes (S_K) (Table 4) indicate the existence of strong ion–ion interactions in ME. The possible explanation for the positive slopes in ME may be that the ionic association would become quite appreciable in this medium as the concentration of the electrolyte is increased and thereby weakening the ion–solvent interaction. As a consequence, contraction of the solvent would be gradually lowered with increasing concentration of the electrolyte resulting in a net positive volume change per mole of the added solute. The S_K values (and hence the ion–ion interactions) increase as the size of the cation increases with the exception of Pr_4NClO_4 (Table 11). Exactly the same conclusion regarding the ion-association behavior of these electrolytes in ME have been drawn from conductometric studies (Table 3).

References

1) "Water and Aqueous Solutions," ed by R. A. Horne, Wiley-Interscience, New York (1972), Chap. 4, pp. 13—15.

2) R. Fernandez-Prini, "Physical Chemistry of Organic Solvent Systems," ed by A. K. Covington and T. Dickinson, Plenum Press, London–New York (1973).

3) O. Popovych and R. P. T. Tomkins, "Non Aqueous Solution Chemistry," Wiley-Interscience, New York (1981).

4) B. S. Krumgalz, *J. Chem. Soc., Faraday Trans. 1,* **76**, 1887 (1980).

5) D. Dasgupta, S. Das, and D. K. Hazra, *J. Chem. Soc., Faraday Trans. 1,* **84**, 1057 (1988).

6) S. Taniewska-Osińska and M. Jóźwiak, *J. Chem. Soc., Faraday Trans. 1,* **85**, 2141 (1989).

7) D. Nandi and D. K. Hazra, *J. Chem. Soc., Faraday Trans. 1,* **85**, 4227 (1989).

8) M. Iqbal and R. E. Verral, *Can. J. Chem.,* **67**, 727 (1989).

9) K. Ibuki and M. Nakahara, *J. Phys. Chem.,* **94**, 8370 (1990).

10) B. Das and D. K. Hazra, *J. Chem. Eng. Data,* **36**, 403 (1991).

11) F. Farnks and D. J. G. Ives, *Q. Rev. Chem. Soc.,* **20**, 1 (1966).

12) G. Franchini, E. Ori, C. Preti, L. Tassi, and G. Tosi, *Can. J. Chem.,* **65**, 722 (1987).

13) J. F. Grast, "Solute-Solvent Interactions," ed by J. F. Grast and C. D. Ritchie, Marcel Dekkar, New York (1969), Chap. 8.

14) A. G. Schwartz and J. B. Barkar, *Talanta,* **22**, 773 (1975).

15) G. Roux, G. Perron, and J. E. Desnoyers, *J. Solution Chem.,* **7**, 639 (1978).

16) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, "Techniques of Chemistry, Vol II," ed by A. Weissberger, Wiley, New York (1970).

17) R. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.,* **75**, 16 (1978).

18) R. M. Fuoss, *J. Phys. Chem.,* **82**, 2427 (1978).

19) G. Jones and M. Dole, *J. Am. Chem. Soc.,* **51**, 2950 (1929).

20) J. Crudden, G. M. Delaney, D. Feakins, P. J. O'Reilly, W. E. Waghorne, and K. G. Lawrence, *J. Chem. Soc., Faraday Trans. 1,* **82**, 2195 (1986).

21) H. Falkenhagen and E. L. Vernon, *Phys. Z.,* **33**, 140 (1932).

22) D. F. Tuan and R. M. Fuoss, *J. Phys. Chem.,* **67**, 1343 (1963).

23) D. S. Gill and M. B. Sekhri, *J. Chem. Soc., Faraday Trans. 1,* **78**, 475 (1982).

24) D. Feakins, D. J. Freemantle, and K. G. Lawrence, *J. Chem. Soc., Faraday Trans. 1,* **70**, 795 (1974).

25) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York (1941), p. 477.

26) S. Bhowmik, A. K. Das, and R. K. Mohanty, *Indian J. Chem., Sect. A,* **24**, 1018 (1985).

27) a) D. F. Evans and P. Gardam, *J. Phys. Chem.,* **72**, 3281 (1968); b) D. F. Evans and P. Gardam, *J. Phys. Chem.,* **73**, 158 (1969).

28) R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.,* **69**, 4208 (1965).

29) S. M. A. Matesich, J. A. Nadas, and D. F. Evans, *J. Phys. Chem.,* **74**, 4568 (1970).

30) A. N. Sharma and D. S. Gill, *J. Chem. Soc., Faraday Trans. 1,* **78**, (1982), and references therein.

31) M. Kaminsky, *Discuss. Faraday Soc.,* **24**, 171 (1957).

32) A. Einstein, *Ann. Phys.,* **19**, 289 (1906).

33) D. Feakins and K. G. Lawrence, *J. Chem. Soc. A,* **1966**, 212.