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Apparent and Partial Molar Volumes of Some Symmetrical Tetraalkylammonium Perchlorates in 2-Methoxyethanol at 25, 35, and 45 °C

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The apparent and partial molar volumes (ϕ_v) of six symmetrical tetraalkylammonium perchlorates (Me_4NClO_4 to Hex_4NClO_4) have been determined in 2-methoxyethanol at 25, 35, and 45 °C. The apparent molar volumes were extrapolated to zero concentration to obtain limiting values at infinite dilution. Ionic limiting partial molar volumes have been estimated using the extrapolation method. The analysis of the data shows that the tetraalkylammonium ions are scarcely solvated and that strong ion–ion interaction exists between the oppositely charged ions in this medium. The temperature dependence of the limiting partial molar volumes have been explained on the basis of ion–solvent interactions.

2-Methoxyethanol has drawn much attention in recent years as a solvent medium for various electrochemical studies.[1] It has unique solvating properties associated with its quasi-aprotic character.[2] As it is a monomethyl ether of ethylene glycol, it is very likely to show physicochemical properties midway between protic and aprotic solvents. Hence, it is of much interest to study the behavior of electrolytes in such a solvent medium. Recently, we have investigated the nature of ion–solvent interactions of some 1 : 1 electrolytes in 2-methoxyethanol from the measurements of some thermodynamic and transport properties.[3] The volumetric behavior of electrolytes is also well known to give valuable informations regarding ion–ion, ion–solvent, and solvent–solvent interactions in solution.[4—11] So we have determined in this communication the apparent and partial molar volumes of some tetraalkylammonium perchlorates in 2-methoxyethanol at different temperatures and the results have been analyzed to shed new light on the nature of these interactions in this medium.

Experimental

2-Methoxyethanol (G. R. E. Merck) was distilled twice in an all-glass distillation set before use and the middle fraction collected. The purified solvent had a density of 0.96002 $g\,cm^{-3}$, and a coefficient of viscosity of 1.5414 mPa s at 25 °C and these values compare well with the literature values e.g., 0.96016 $g\,cm^{-3}$ and 1.5430 mPa s respectively.[1,12] Freshly distilled solvent was always used for preparing the experimental solutions. The solvent properties are recorded in Table 1.

Table 1. Solvent Properties

Temp °C	Density $g\,cm^{-3}$	Viscosity×10^3 Pa s
25	0.96002	1.5414
35	0.95356	1.2579
45	0.94715	1.0400

Tetraalkylammonium perchlorates (except tetrapentylammonium perchlorate) were of Fluka purum or puriss grade. Tetrapentylammonium perchlorate (Pen_4NClO_4) was prepared by adding slowly the hot aqueous solution of tetrapentylammonium bromide (Pen_4NBr) 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 perchlorate was recrystallized several times from water–methanol mixtures and dried in vacuo at 150 °C for 96 h.

A stock solution for each salt was prepared by weight and working solutions were obtained by weight dilution. The conversion of the molality into molarity was done by using the density values. The densities were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 25, 35, and 45 °C with doubly distilled water. Measurements were made in an oil bath maintained at ±0.005 °C of the desired temperature by means of a mercury-in-glass thermoregulator and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The precision of the density measurements was greater than $\pm 3\times 10^{-5}$ $g\,cm^{-3}$.

Results and Discussion

The apparent molar volumes (ϕ_v) were calculated from the densities of the solutions using Eq. 1.

$$\phi_v = M/\rho_o - 1000(\rho - \rho_o)/c\rho_o, \qquad (1)$$

where c is the molarity of the electrolyte solution, M is

Table 2. Concentration (c), Density (ρ), Apparent Molar Volume (ϕ_V), and Partial Molar Volume ($\overline{V}^\circ_2$) for Tetraalkylammonium Perchlorates in 2-Methoxyethanol at 25, 35, and 45 °C

c	ρ	ϕ_V	$\overline{V}_2$	c	ρ	ϕ_V	$\overline{V}_2$
mol dm^{-3}	g cm^{-3}	cm^3 mol^{-1}	cm^3 mol^{-1}	mol dm^{-3}	g cm^{-3}	cm^3 mol^{-1}	cm^3 mol^{-1}
25 °C							
	Me_4NClO_4				Et_4NClO_4		
0.00985	0.96073	105.75	106.02	0.00985	0.96066	171.52	171.85
0.01976	0.96144	105.97	106.35	0.02023	0.96133	171.81	172.29
0.02984	0.96216	106.13	106.60	0.02490	0.96163	171.94	172.48
0.03532	0.96255	106.22	106.73	0.03177	0.96207	172.05	172.65
0.04081	0.96294	106.30	106.84	0.04054	0.96263	172.20	172.87
0.04589	0.96330	106.38	106.96	0.04510	0.96292	172.29	173.00
	Pr_4NClO_4				Bu_4NClO_4		
0.01228	0.96070	240.04	240.38	0.01030	0.96049	308.63	309.00
0.02103	0.96118	240.25	240.69	0.02006	0.96093	308.91	309.43
0.02523	0.96141	240.32	240.80	0.02497	0.96115	309.02	309.60
0.03018	0.96168	240.42	240.95	0.02901	0.96133	309.12	309.75
0.03975	0.96220	240.59	241.19	0.03892	0.96177	309.32	310.04
0.04509	0.96249	240.65	241.29	0.04891	0.96221	309.52	310.33
	Pen_4NClO_4				Hex_4NClO_4		
0.00971	0.96037	377.05	377.44	0.00987	0.96028	445.60	446.05
0.01931	0.96071	377.37	377.92	0.02033	0.96054	446.00	446.64
0.02415	0.96088	377.50	378.11	0.02438	0.96065	446.13	446.84
0.02931	0.96106	377.64	378.31	0.02958	0.96078	446.28	447.06
0.03882	0.96139	377.83	378.60	0.03927	0.96102	446.52	447.41
0.04900	0.96174	378.03	378.90	0.04949	0.96127	446.73	447.73
35 °C							
	Me_4NClO_4				Et_4NClO_4		
0.00974	0.95424	108.84	109.14	0.00971	0.95417	175.01	175.37
0.01969	0.95493	109.09	109.52	0.02000	0.95481	175.34	175.85
0.02968	0.95562	109.27	109.79	0.02468	0.95510	175.45	176.01
0.03505	0.95599	109.35	109.92	0.03148	0.95552	175.59	176.23
0.04044	0.95636	109.44	110.05	0.04009	0.95605	175.75	176.47
0.04543	0.95670	109.57	110.22	0.04465	0.95633	175.83	176.59
	Pr_4NClO_4				Bu_4NClO_4		
0.01209	0.95421	243.35	243.73	0.01009	0.95400	312.84	313.25
0.02092	0.95468	243.58	244.08	0.01986	0.95422	313.16	313.73
0.02489	0.95489	243.69	244.23	0.02479	0.95463	313.31	313.95
0.02980	0.95515	243.78	244.37	0.02855	0.95479	313.39	314.08
0.03930	0.95565	243.96	244.64	0.03826	0.95520	313.62	314.41
0.04464	0.95593	244.05	244.77	0.04803	0.95561	313.81	314.69
	Pen_4NClO_4				Hex_4NClO_4		
0.00966	0.95390	380.49	380.91	0.00971	0.95380	450.33	450.79
0.01920	0.95423	380.81	381.39	0.01972	0.95404	450.72	451.38
0.02388	0.95439	380.95	381.60	0.02395	0.95414	450.85	451.57
0.02917	0.95457	381.09	381.81	0.02908	0.95426	451.00	451.79
0.03835	0.95488	381.31	382.13	0.03816	0.95447	451.24	452.14
0.04851	0.95522	381.52	382.44	0.04825	0.95470	451.47	452.48
45 °C							
	Me_4NClO_4				Et_4NClO_4		
0.00970	0.94781	111.45	111.76	0.00965	0.94774	177.97	178.34
0.01962	0.94848	111.72	112.17	0.01990	0.94836	178.32	178.86
0.02959	0.94915	111.92	112.47	0.02454	0.94864	178.41	179.01
0.03496	0.94951	112.01	112.60	0.03138	0.94905	178.59	179.26
0.04035	0.94987	112.11	112.75	0.03990	0.94956	178.75	179.51
0.04529	0.95020	112.18	112.86	0.04443	0.94983	178.83	179.63
	Pr_4NClO_4				Bu_4NClO_4		
0.01194	0.94778	246.05	246.43	0.00999	0.94757	316.61	317.03
0.02075	0.94824	246.30	246.81	0.01964	0.94797	316.92	317.51
0.02479	0.94845	246.39	246.94	0.02475	0.94818	317.06	317.72
0.02961	0.94870	246.49	247.09	0.02842	0.94833	317.16	317.86
0.03910	0.94919	246.67	247.36	0.03801	0.94872	317.39	318.20
0.04435	0.94946	246.77	247.50	0.04769	0.94911	317.61	318.52
	Pen_4NClO_4				Hex_4NClO_4		
0.00940	0.94748	383.16	383.59	0.00964	0.94738	454.28	454.76
0.01898	0.94781	383.52	384.13	0.01960	0.94761	454.69	455.36
0.02367	0.94797	383.65	384.32	0.02355	0.94770	454.81	455.55
0.02898	0.94815	383.80	384.54	0.02844	0.94781	454.97	455.78
0.03819	0.94846	384.01	384.86	0.03742	0.94801	455.21	456.13
0.04843	0.94880	384.26	385.22	0.04745	0.94823	455.44	456.48

the molecular weight of the solute, and ρ and ρ_0 are the densities of the solution and solvent respectively.

The partial molar volumes, $\overline{V}_2$, were computed from ϕ_v data with the help of Eq. 2.

$$\overline{V}_2 = \phi_v + \frac{1000 - c\phi_v}{2000 + c^{3/2}(\partial\phi_v/\partial\sqrt{c})} c^{1/2}(\partial\phi_v/\partial\sqrt{c}). \qquad (2)$$

The molar concentrations, densities, and the apparent and partial molar volumes of the various electrolyte solutions in 2-methoxyethanol at 25, 35, and 45 °C are given in Table 2.

From the ϕ_v data ϕ_v vs. $\sqrt{c}$ curves have been drawn and the plots were found to be linear in all cases with positive slopes. Obviously, the Masson's empirical relation,[13] namely,

$$\phi_v = \phi_v^\circ + S_v^*\sqrt{c} \qquad (3)$$

is applicable within the temperature and concentration ranges studied here. The limiting apparent molar volumes, ϕ_v°, (equal to the partial molar volumes at infinite dilution, $\overline{V}_2^\circ$) are obtained by the least-squares fitting of ϕ_v values to the above equation and these values along with the experimental S_v^* values have been reported in Table 3.

Since our experimental results of apparent molar volumes can be well represented by the Masson's equation i.e., Eq. 3, we have not analyzed these data on the basis of Redlich–Mayer equation,[14]

$$\phi_v = \phi_v^\circ + S_v\sqrt{c} + b_v c, \qquad (4)$$

where S_v is the coefficient given by Debye–Hückel theory and b_v is a fitting constant empirically determined. Moreover, the evaluation of S_v requires the knowledge of the pressure dependence of the dielectric constant of the solvent which is not available in the literature for 2-methoxyethanol.

The experimental S_v^* values (Table 3) for all the salts are found to be positive thereby suggesting that the ion–ion interactions are very strong in this medium. To examine the solute–solvent interactions, however, the ϕ_v° values can be used and from Table 3 we see that the limiting apparent molar volumes (ϕ_v°) are large and positive, and the values increase with increasing size of the cations. This is in agreement with earlier findings in several nonaqueous solvents as well as in water and heavy water.[7] The large ϕ_v° values reveal that the solute–solvent interactions are strong in this medium.

The calculation of the limiting ionic partial molar volumes is a very difficult task. However, several attempts have been made to separate the limiting partial molar volumes into ionic components using various indirect methods.[15—19] From a thorough review of these methods, it has been concluded by Krumgalz[7] that among the various indirect methods, the extrapolation method suggested by Conway and co-workers[15] is the best for the division of the ϕ_v° values. Zana and co-workers,[20—22] on the other hand, have used the ultrasonic vibration potential technique for the determination of the absolute ionic partial molar volumes in some nonaqueous solvents. However, in the absence of ionic ultrasonic vibration potential data in 2-methoxyethanol in the literature, we have used the extrapolation method as suggested by Conway et al.[15] for the division of $\overline{V}_2^\circ$ values into ionic components. Following this procedure the $\overline{V}_2^\circ$ values for the tetraalkylammonium perchlorates in 2-methoxyethanol at 25, 35, and 45 °C were plotted against the formula weight of the corresponding tetraalkylammonium ions. An excellent linear relationship was observed for all the salts. The ionic partial molar volumes ($\overline{V}_{\text{ion}}^\circ$) thus obtained have been presented in Table 4. The $\overline{V}_{\text{ion}}^\circ$ values for the tetraalkylammonium ions are positive and have been found to increase regularly from Me_4N^+ to Hex_4N^+. For comparison purposes, Table 5 summarizes the ionic partial molar volumes of the tetraalkylammonium ions in some nonaqueous solvents. The $\overline{V}_{\text{ion}}^\circ$ values in 2-methoxyethanol are all found to be almost similar to those in other nonaqueous solvents e.g., dimethyl formamide,[6] dimethyl sulfoxide,[6] *N*-methylacetamide,[23] propylene carbonate,[24] formamide[25] etc. This fact indicates that the large tetraalkylammonium ions are scarcely solvated in this solvent medium. The same conclusion has also been reached from conductometric as well as viscometric studies.[3]

It may be noted from Table 3 that for all the salts, ϕ_v°

Table 3. Limiting Apparent Molar Volume (ϕ_v°) and Experimental Slope (S_v^*) of Tetraalkylammonium Perchlorates in 2-Methoxyethanol at 25, 35, and 45 °C

Salt	ϕ_v°			S_v^*		
	$cm^3\ mol^{-1}$			$cm^3\ L^{1/2}\ mol^{-3/2}$		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
Me_4NClO_4	105.21	108.23	110.82	5.41	6.11	6.38
Et_4NClO_4	170.86	174.31	177.25	6.72	7.22	7.63
Pr_4NClO_4	239.36	242.59	245.28	6.09	6.92	7.05
Bu_4NClO_4	307.86	312.01	315.75	7.41	8.19	8.44
Pen_4NClO_4	376.26	379.64	382.30	7.97	8.49	8.85
Hex_4NClO_4	444.69	449.40	453.33	9.19	9.42	9.72

Table 4. Ionic Limiting Partial Molar Volume ($\overline{V}_{\text{ion}}^\circ$) in 2-Methoxyethanol at 25, 35, and 45 °C

Ion	$\overline{V}_{\text{ion}}^\circ/cm^3\ mol^{-1}$		
	25 °C	35 °C	45 °C
Me_4N^+	91.27	91.63	91.90
Et_4N^+	156.92	157.71	158.33
Pr_4N^+	225.42	225.99	226.36
Bu_4N^+	293.92	295.41	296.83
Pen_4N^+	362.32	363.04	363.38
Hex_4N^+	430.75	432.80	434.41
ClO_4^-	13.94	16.60	18.92

Table 5. Limiting Partial Molar Volumes of Tetraalkylammonium Ions in Different Solvents at 35 °C

Solvent	$\overline{V}^{\circ}_{\text{ion}}/\text{cm}^3\ \text{mol}^{-1}$				
	Et_4N^+	Pr_4N^+	Bu_4N^+	Pen_4N^+	Hex_4N^+
Dimethylformamide	160.70	233.40	302.20	372.50	443.70
Dimethylsulfoxide	161.30	230.80	297.80	367.10	—
N-Methylacetamide	161.30	233.40	308.80	377.00	447.10
Propylene carbonate	160.73	229.97	299.21	368.44	437.66
Formamide	158.12	227.53	296.94	366.33	435.73
2-Methoxyethanol	157.71	225.99	295.41	363.04	432.80

values increase with the rise in temperature, although $d\phi^{\circ}_{V}/dT$ decreases as temperature increases. The temperature dependence can be satisfactorily explained from the concept of ion–solvent interactions. On raising the temperature, some solvent molecules may be released from the loose solvation layers of the solutes in solution. This is reflected in the greater solute ϕ°_{V} values at the higher temperature.

Since 2-methoxyethanol is a non-hydrogen bonded solvent, the ion–solvent dipole interaction energy in this medium (in the absence of any appreciable solvent–solvent interaction) would be appreciable and the attachment of the solvent molecules even to the R_4N^+ ions may not be loose and at the same time no structure formation would occur around the ions.[6] Thus, some solvent molecules would be associated with the R_4N^+ ions while outside the ion-sphere the solvent structure would be almost the same as in the pure solvent; so the expansion of the solution on heating would be comparatively less than that of the pure solvent and $d\phi^{\circ}_{V}/dT$ would decrease with the rise in temperature.

The investigation indicates that all the salts studied here exhibit strong ionic interactions, apparently due to the low dielectric constant of the solvent. Moreover, all the tetraalkylammonium ions remain more or less unsolvated in this solvent medium.

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