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Apparent and Partial Molal Volumes of Selected Symmetrical Tetraalkylammonium Bromides in 2-Methoxy-1-ethanol at 25 °C

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The apparent and partial molal volumes of six symmetrical tetraalkylammonium bromides, R_4NBr (R = C_2H_5 to C_7H_{15}) in 2-methoxy-1-ethanol (ME) have been determined at 25 °C. The limiting apparent molal volumes (ϕ°_v) and the experimental slopes (S^*_v) have been interpreted in terms of ion-solvent and ion-ion interactions, respectively. Use has been made of the nonthermodynamic, so-called extrapolation method to split the limiting apparent molal volumes into ionic contributions. The $\bar{V}^\circ_{R_4NX}$ values in 2-methoxy-1-ethanol are found to be almost similar to those in other organic solvents examined and differ greatly from the values in water and heavy water solutions. The ion-solvent interaction effect, as estimated by the combination of the viscosity B_{ion} values with $\bar{V}^\circ_{ion}$ values, indicates that these ions may be classified as "structure breakers" in this solvent medium.

Introduction

The volumetric behavior of solutes has proved to be very useful in elucidating the various interactions occurring in aqueous and nonaqueous solutions (*1*). Studies on the apparent and partial molal volumes of electrolytes have been used to examine the ion-ion, ion-solvent, and solvent-solvent interactions (*2*). The apparent and partial molal volumes of tetraalkylammonium salts have been investigated rather extensively in aqueous (*3-5*) and nonaqueous solutions (*6*, *7*). Such measurements have also been reported for water-organic solvent binary systems (*8*). However, no work has been reported on the apparent and partial molal volumes of tetraalkylammonium bromides, R_4NBr (R = C_2H_5 to C_7H_{15}) in 2-methoxy-1-ethanol at 25 °C. 2-Methoxy-1-ethanol is a "quasi-aprotic" solvent (*9*) of low dielectric constant ($\epsilon_{25\,°C}$ = 16.93). In recent years much attention has been given to this solvent, since it is of particular interest in the field of various industrial processes, synthesis, and electrochemical studies (*10*, *11*).

Experimental Section

2-Methoxy-1-ethanol (G.R.E. Merck) was distilled twice in an all-glass distillation set immediately before use. The purified solvent had a density of 0.960 02 g cm^{-3}, a coefficient of viscosity of 1.5414 cP, and a specific conductance of ca. 1.01 × 10^{-6} Ω^{-1} cm^{-1} at 25 °C. These values are in good agreement with the literature values (*12*), 0.960 24 g cm^{-3}, 1.60 cP, and 1.09 × 10^{-6} Ω^{-1} cm^{-1} (at 20 °C), respectively.

Tetraalkylammonium bromides were of Fluka purum or puriss grade; these were purified as described in the literature (*13*) and also described earlier by us (*14*). The salts were purified by recrystallization, and the higher homologues were recrystallized twice to ensure highest purity. The recrystallized salts were dried under vacuum at elevated temperatures for 12 h. The salts were stored in a vacuum desiccator and dried for 3-4 h at 100 °C prior to use.

A stock solution for each salt was prepared by weight, and working solutions in the concentration range $0.01 < c/(\text{mol dm}^{-3}) < 0.12$ 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-Sprengal 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 °C with doubly distilled water. Measurements were made in an oil bath maintained at 25 ± 0.005 °C 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 ±3 × 10^{-5} g cm^{-3}.

Results and Discussion

The apparent molal volumes, ϕ_v, of the solutes were calculated from the densities of the solutions by using the equation

$$\phi_v = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \quad (1)$$

where M is the molecular weight of the solute, ρ_0 and ρ are the densities of the solvent and the solution, respectively, and c is the concentration in molarity.

The partial molal volumes, $\bar{V}_2$, were computed from ϕ_v with the equation

$$\bar{V}_2 = \phi_v + \frac{1000 - c\phi_v}{2000 + c^{3/2}(\partial\phi_v/\partial c^{1/2})} c^{1/2}(\partial\phi_v/\partial c^{1/2}) \quad (2)$$

The molar concentrations, densities, and apparent and partial molal volumes of the solutions of various tetraalkylammonium bromides in 2-methoxy-1-ethanol at 25 °C are reported in Table I. The limiting apparent molal volumes, ϕ°_v (equal to the partial molal volumes at infinite dilution, $\bar{V}^\circ_2$), were obtained by least-squares fitting of ϕ_v values to the equation

$$\phi_v = \phi^\circ_v + S^*_v c^{1/2} \quad (3)$$

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Table I. Concentrations (c), Densities (ρ), Apparent Molal Volumes (ϕ_v), and Partial Molal Volumes ($\bar{V}_2$) for Various Tetraalkylammonium Bromides in 2-Methoxy-1-ethanol at 25 °C

c, mol dm^{-3}	ρ, g cm^{-3}	ϕ_v, cm^3 mol^{-1}	$\bar{V}_2$, cm^3 mol^{-1}
		Et_4NBr	
0.011 04	0.960 74	150.98	151.63
0.020 35	0.961 33	151.06	152.74
0.031 21	0.962 02	152.16	153.25
0.040 96	0.962 63	152.54	153.79
0.051 34	0.963 28	152.77	154.17
0.062 05	0.963 95	152.94	154.48
0.080 19	0.965 06	153.44	155.18
0.091 19	0.965 73	153.69	155.54
0.112 50	0.967 03	154.01	156.06
		Pr_4NBr	
0.009 63	0.960 57	217.87	218.12
0.021 11	0.961 22	218.12	218.49
0.029 97	0.961 72	218.27	218.71
0.040 46	0.962 31	218.40	218.91
0.050 11	0.962 85	218.53	219.09
0.061 01	0.963 46	218.63	219.25
0.070 92	0.964 01	218.75	219.42
0.083 12	0.964 69	218.83	219.55
		Bu_4NBr	
0.010 36	0.960 49	288.54	288.92
0.021 08	0.960 97	288.86	289.40
0.030 78	0.961 40	289.10	289.75
0.041 89	0.961 89	289.30	290.05
0.053 33	0.962 39	289.51	290.36
0.065 07	0.962 90	289.70	290.63
0.070 12	0.963 12	289.75	290.72
0.081 52	0.963 61	289.93	290.97
0.091 23	0.964 03	290.02	291.12
		$Pent_4NBr$	
0.009 55	0.960 38	354.97	355.30
0.020 59	0.960 79	355.29	355.78
0.031 48	0.961 19	355.53	356.13
0.042 72	0.961 60	355.72	356.42
0.050 16	0.961 87	355.82	356.57
0.061 29	0.962 27	356.00	356.83
0.072 49	0.962 67	356.16	357.06
0.085 41	0.963 13	356.31	357.28
0.095 00	0.963 47	356.41	357.43
		Hex_4NBr	
0.011 00	0.960 32	424.27	424.55
0.031 99	0.960 88	424.68	425.16
0.041 10	0.961 12	424.80	425.34
0.055 30	0.961 49	424.99	425.62
0.070 01	0.961 87	425.15	425.85
0.081 35	0.962 16	425.28	426.03
0.089 15	0.962 36	425.34	426.12
0.095 32	0.962 52	425.36	426.17
0.121 50	0.963 18	425.59	426.49
		$Hept_4NBr$	
0.009 79	0.960 23	488.78	489.06
0.021 71	0.960 48	489.05	489.47
0.030 45	0.960 66	489.23	489.73
0.041 16	0.960 88	489.36	489.92
0.045 13	0.960 96	489.43	490.03
0.050 06	0.961 06	489.48	490.11
0.061 07	0.961 28	489.63	490.32
0.070 19	0.961 46	489.75	490.49
0.080 31	0.961 66	489.85	490.64

where S^*_v is the experimental slope. The plots of ϕ_v against $c^{1/2}$ were linear in all cases, and from the intercept and the slope one can obtain the values of ϕ°_v ($= \bar{V}^\circ_2$) and S^*_v, respectively. The values of ϕ°_v and S^*_v along with their standard errors are given in Table II. A representative plot for Pr_4NBr, Bu_4NBr, and $Pent_4NBr$ in 2-methoxy-1-ethanol at 25 °C are shown in Figure 1. The experimental slope S^*_v depends on ion–ion interactions while ϕ°_v values can be used to examine

Table II. Limiting Apparent Molal Volumes (ϕ°_v) and Experimental Slopes (S^*_v) of Tetraalkylammonium Bromides in 2-Methoxy-1-ethanol at 25 °C

electrolyte	ϕ°_v, cm^3 mol^{-1}	S^*_v, cm^3 L$^{1/2}$ mol$^{-3/2}$
Et_4NBr	149.91 (±0.01)	12.47 (±0.06)
Pr_4NBr	217.38 (±0.01)	5.09 (±0.07)
Bu_4NBr	287.78 (±0.01)	7.47 (±0.06)
$Pent_4NBr$	354.30 (±0.01)	6.85 (±0.05)
Hex_4NBr	423.71 (±0.02)	5.47 (±0.07)
$Hept_4NBr$	488.20 (±0.02)	5.80 (±0.08)

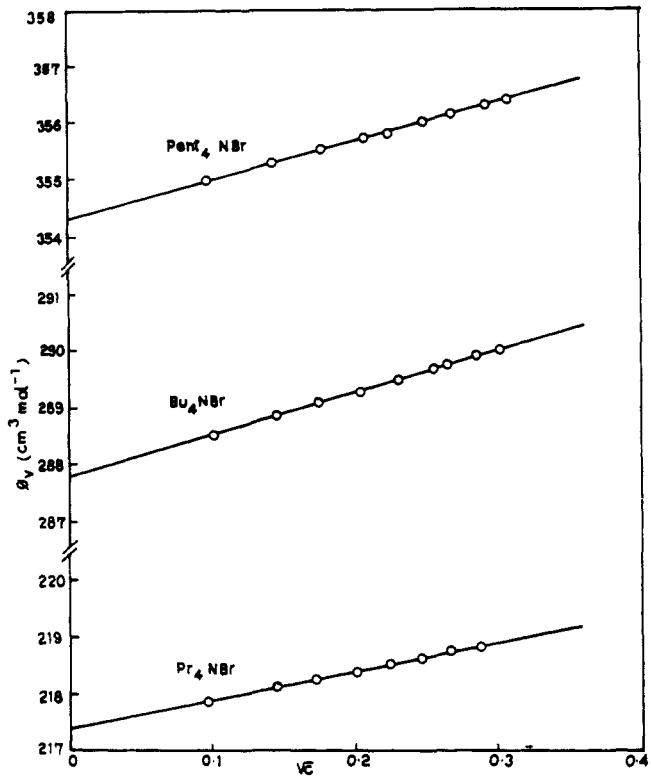

Figure 1. Representative plot of ϕ_v versus $c^{1/2}$ for some tetraalkylammonium bromides in 2-methoxy-1-ethanol at 25 °C.

the solute–solvent interactions since at infinite dilution the apparent molal volumes are, by definition, independent of ion–ion interactions.

The S^*_v values shown in Table II are positive for all tetraalkylammonium bromides in 2-methoxy-1-ethanol, indicating strong ion–ion interactions in this solvent medium. This type of behavior of tetraalkylammonium halides has also been observed in solvents of medium dielectric contents, e.g., methanol, *N*,*N*-dimethylformamide, dimethyl sulfoxide, etc. (*6*, *15*). The possible explanation for the positive slopes in 2-methoxy-1-ethanol may be that the ionic association would become quite appreciable in this medium as the concentration of the electrolyte is increased, 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^*_v values (and hence the ion–ion interactions) decrease as the size of the cation increases, with the exception of Pr_4NBr and Hex_4NBr (Table II). Exactly the same conclusion regarding the ion-association behavior of these electrolytes in 2-methoxy-1-ethanol has been drawn from conductometric studies (*16*).

The limiting apparent molal volumes ϕ°_v shown in Table II are large and positive, and the values increase regularly as the size of tetraalkylammonium ions increases. This is in agreement with the earlier findings in several nonaqueous solvents, as well as in water and heavy water (*17*). The large ϕ°_v values

Table III. Ionic Limiting Partial Molal Volumes ($\bar{V}°_{ion}$), Ionic B Coefficients, and Δ Values in 2-Methoxy-1-ethanol at 25 °C

ions	$\bar{V}°_{ion}$, cm^3 mol^{-1}	B_{ion}, dm^3 mol^{-1}	Δ, dm^3 mol^{-1}
Et_4N^+	157.15	0.112	−0.281
Pr_4N^+	224.62	0.206	−0.356
Bu_4N^+	295.02	0.304	−0.433
$Pent_4N^+$	361.54	0.487	−0.417
Hex_4N^+	430.95	0.583	−0.494
$Hept_4N^+$	495.44	1.138	−0.101
Br^-	−7.24	0.119	0.137

reveal that the solute–solvent interactions are strong in this solvent.

The calculations of the ionic limiting partial molal volumes have been done following the method suggested by Conway et al. (*3*). Uosaki et al. (*18*) have used this method for the separation of some literature values and of their own $\bar{V}°_{R_4NX}$ values into ionic contributions in organic electrolyte solutions. Krumgalz (*17*) applied the same method to a large number of partial molal volume data for nonaqueous electrolyte solutions in a wide temperature range.

The $\bar{V}°_2$ values for the tetraalkylammonium bromides in 2-methoxy-1-ethanol at 25 °C were plotted against the formula weight of the corresponding tetraalkylammonium ions. An excellent linear relationship was observed for all the salts examined. The $\bar{V}°_{ion}$ values of tetraalkylammonium and bromide ions are presented in Table III. The $\bar{V}°_{ion}$ values for the tetraalkylammonium ions are positive and have been found to increase continuously from Et_4N^+ to $Hept_4N^+$. The $\bar{V}°_{R_4N^+}$ values in 2-methoxy-1-ethanol are found to be almost similar to those in other organic solvents, e.g., methanol, ethylene carbonate, propylene carbonate, formamide, *N*,*N*-dimethylformamide, *N*-methylacetamide, etc. (*17*). This fact indicates that the large tetraalkylammonium cations are scarcely solvated in this solvent medium. The same conclusion has also been reached both conductometrically (*16*) and viscometrically (*19*). The positive $\bar{V}°_{R_4N^+}$ values indicate that the solvent molecules form a less compact structure around the incorporated ion, thus giving rise to a positive change in volume. This fact provides additional support in favor of the unsolvation of these cations.

That the tetraalkylammonium ions act as "structure breakers" in 2-methoxy-1-ethanol can be shown by the combination of the ionic viscosity B coefficients with the limiting ionic partial molal volumes. Desnoyers and Perron (*20*) showed that the quantity $B - 0.0025\bar{V}°_2$ is a measure of the solute–solvent interaction (here B is expressed in dm^3 mol^{-1}). Similarly, the ion–solvent interaction effect, Δ, for organic ions can be derived by the equation given below:

$$\Delta = B_{ion} - 0.0025\bar{V}°_{ion} \quad (4)$$

According to these authors, the structure-breaking ions would exhibit negative values of Δ. It may be pointed out that the Δ values are of a semiquantitative nature, because the absolute values of Δ depend on the two conventions adopted for separating the B values and the $\bar{V}°_2$ values into respective ionic contributions. As is indicated in Table III, the Δ values for the tetraalkylammonium ions are negative; the corresponding B_{ion} values were taken from the literature (*19*). Therefore, it may be concluded that each of the R_4N^+ ions acts as a structure breaker in 2-methoxy-1-ethanol.

These investigations thus indicate 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 are more or less unsolvated and behave as structure breakers in this solvent medium.

Registry No. Tetraethylammonium bromide, 71-91-0; tetrapropylammonium bromide, 1941-30-6; tetrabutylammonium bromide, 1643-19-2; tetrapentylammonium bromide, 866-97-7; tetrahexylammonium bromide, 4328-13-6; tetraheptylammonium bromide, 4368-51-8; 2-methoxyethanol, 109-86-4; tetraethylammonium, 66-40-0; tetrapropylammonium, 13010-31-6; tetrabutylammonium, 10549-76-5; tetrapentylammonium, 15959-61-2; tetrahexylammonium, 20256-54-6; tetraheptylammonium, 35414-25-6.

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