Apparent Molar Volumes of Some Symmetrical Tetraalkylammonium Bromides in Acetonitrile at (298.15, 308.15, and 318.15) K

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The apparent molar volumes of six symmetrical tetraalkylammonium bromides (Et_4NBr to Hep_4NBr) have been determined in acetonitrile at (298.15, 308.15, and 318.15) K from precise density measurements. The apparent molar volumes have been extrapolated to zero concentration to obtain the limiting values at infinite dilution. The infinite dilution partial molar expansibilities have also been calculated from the temperature dependence of the limiting apparent molar volumes.

Introduction

The volumetric behavior of solutes has been proved to be very useful in elucidating the various interactions occurring in aqueous and nonaqueous solutions. Studies on the effect of concentration and temperature on the apparent molar volumes of electrolytes have been extensively used to obtain information on ion−ion, ion−solvent, and solvent−solvent interactions (Millero, 1972; Popovych and Tomkins, 1981). In this paper, an attempt is made to reveal the nature of various types of interactions prevailing in solutions of six symmetrical tetraalkylammonium bromides, R_4NBr ($R = C_2H_5$ to n-C_7H_{15}), in acetonitrile from precise apparent molar volume data at (298.15, 308.15, and 318.15) K. A survey of the literature reveals that of the six salts investigated here, the apparent molar volumes of the first four have been reported only at 298.15 K (Zana et al., 1979; Bottomley and Bremers, 1986; Marcus et al., 1994). The temperature dependence of the apparent molar volumes of these electrolytes in acetonitrile is capable of giving more insight regarding ion−ion and ion−solvent interactions which cannot be obtained from molar volume measurements at one temperature (Millero, 1972; Gopal et al., 1973; Pogue and Atkinson, 1988; Das and Hazra, 1991, 1995; Das, 1995; Muhuri et al., 1996). The solvent acetonitrile has drawn attention in recent years because of its use in technological applications, namely, in battery systems and plating techniques (Janz and Tomkins, 1973; Jasinski, 1967).

Experimental Section

Acetonitrile (E. Merck, 99%) was distilled from P_2O_5 and then from CaH_2 in an all-glass distillation apparatus. The middle fraction was collected. The purity of the solvent was verified by the measurements of its density, ρ_0, and viscosity, η_0, which are reported in Table 1 and compared with the literature data. Freshly distilled solvent was always used for preparing the solutions.

Tetraalkylammonium bromides were of Fluka purum of puriss grade. The salts were purified by recrystallization, and the higher homologues starting from tetrapentylammonium bromide were recrystallized twice to ensure the 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 373.15 K prior to use.

A stock solution for each salt was prepared by mass, and working solutions were obtained by mass dilution. 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, which was calibrated with deionized, double-distilled water at each temperature. The pycnometer with the test solution was equilibrated in a water bath maintained at ±0.01 K 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 pycnometer was then removed from the thermostatic bath, properly dried, and weighed. The evaporation losses remained insignificant during the time of actual measurements. An average of triplicate measurements were taken into account. The density values are reproducible to $\pm 3 \times 10^{-5}$ g·cm^{-3}.

Table 1. Properties of Acetonitrile

	ρ_0/g·cm^{-3}		η_0/mPa·s	
T/K	this work	lit.	this work	lit.
298.15	0.776 86	0.776 85[a] 0.775 9[b] 0.776 82[c]	0.3446	0.341[a] 0.344[b]
308.15	0.765 64	0.765 81[a] 0.766 2[b] 0.765 60[d]	0.3125	0.314[a] 0.314[b]
318.15	0.754 98	0.752 71[a] 0.755 9[b]	0.2893	0.293[a] 0.289[b]

[a] Gill et al. (1995). [b] Moumouzias et al. (1991). [c] Mato and Berro (1991). [d] Sandhu et al. (1986).

Results and Discussion

The apparent molar volumes (ϕ_v) were calculated from the densities of the solutions using the following equation

$$\phi_v = M/\rho - 1000(\rho - \rho_0)/m\rho\rho_0 \qquad (1)$$

where m is the molality of the electrolyte solution, M is the molecular weight of the solute, and ρ and ρ_0 are the densities of the solution and solvent, respectively.

The molal concentrations (m), densities (ρ), and apparent molar volumes (ϕ_v) of the various electrolyte solutions in acetonitrile at (298.15, 308.15, and 318.15) K are given in Table 2.

The apparent molar volume of each salt shows a linear dependence on the square root of its molal concentration at all temperatures according to the following equation

$$\phi_v = \phi_v{}^\circ + S_v{}^* m^{1/2} \qquad (2)$$

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Table 2. Molal Concentration (m), Density (ρ), and Apparent Molar Volume (ϕ_v) for Tetraalkylammonium Bromides in Acetonitrile at (298.15, 308.15, and 318.15) K

m/mol·kg^{-1}	ρ/g·cm^{-3}	ϕ_v/cm^3·mol^{-1}	m/mol·kg^{-1}	ρ/g·cm^{-3}	ϕ_v/cm^3·mol^{-1}
		298.15 K			
	Et_4NBr			Pr_4NBr	
0.012 84	0.777 85	142.59	0.013 09	0.777 87	214.62
0.025 88	0.778 84	143.39	0.025 74	0.778 83	215.39
0.032 26	0.779 32	143.72	0.032 39	0.779 33	215.71
0.038 67	0.779 80	144.00	0.038 95	0.779 82	216.01
0.045 24	0.780 29	144.26	0.045 40	0.780 30	216.24
0.051 87	0.780 78	144.57	0.052 15	0.780 80	216.47
	Bu_4NBr			Pen_4NBr	
0.012 93	0.777 89	282.61	0.012 72	0.777 89	352.56
0.025 94	0.778 91	283.28	0.026 18	0.778 96	353.33
0.032 38	0.779 41	283.56	0.032 39	0.779 45	353.53
0.039 13	0.779 93	283.86	0.039 04	0.779 97	353.79
0.045 51	0.780 42	284.06	0.045 72	0.780 49	353.99
0.052 20	0.780 93	284.30	0.052 20	0.780 99	354.22
	Hex_4NBr			Hep_4NBr	
0.012 77	0.777 90	423.92	0.013 03	0.777 94	493.64
0.026 03	0.778 96	424.61	0.026 04	0.779 00	494.13
0.032 61	0.779 48	424.87	0.032 64	0.779 53	494.42
0.039 23	0.780 00	425.09	0.039 28	0.780 06	494.63
0.045 85	0.780 52	425.16	0.045 71	0.780 57	494.81
0.052 37	0.781 02	425.53	0.052 72	0.781 12	495.05
		308.15 K			
	Et_4NBr			Pr_4NBr	
0.012 88	0.766 60	147.16	0.012 92	0.766 62	218.11
0.025 86	0.767 55	148.12	0.025 78	0.767 58	218.85
0.032 46	0.768 03	148.42	0.032 40	0.768 07	219.14
0.038 96	0.768 50	148.71	0.038 94	0.768 55	219.46
0.045 37	0.768 96	149.01	0.045 51	0.769 03	219.73
0.052 10	0.769 44	149.33	0.052 25	0.769 52	219.98
	Bu_4NBr			Pen_4NBr	
0.012 88	0.766 64	288.24	0.012 65	0.766 64	359.02
0.025 98	0.767 64	288.98	0.026 15	0.767 69	359.65
0.032 45	0.768 13	289.22	0.032 39	0.768 17	359.91
0.039 11	0.768 63	289.51	0.038 94	0.768 67	360.18
0.045 53	0.769 11	289.73	0.045 67	0.769 18	360.45
0.052 26	0.769 61	289.97	0.052 03	0.769 66	360.65
	Hex_4NBr			Hep_4NBr	
0.012 79	0.766 67	429.68	0.012 90	0.766 70	500.05
0.026 07	0.767 72	430.36	0.026 08	0.767 76	500.86
0.032 59	0.768 23	430.60	0.032 73	0.768 29	501.06
0.039 29	0.768 75	430.85	0.039 32	0.768 81	501.31
0.045 78	0.769 25	431.08	0.045 82	0.769 32	501.50
0.052 32	0.769 75	431.31	0.052 62	0.769 85	501.67
		318.15 K			
	Et_4NBr			Pr_4NBr	
0.012 73	0.755 91	150.02	0.012 70	0.755 93	221.17
0.025 84	0.756 85	151.03	0.025 62	0.756 88	222.02
0.032 45	0.757 32	151.39	0.032 21	0.757 36	222.35
0.038 96	0.757 78	151.72	0.038 70	0.757 83	222.64
0.045 36	0.758 23	152.01	0.045 38	0.758 31	222.96
0.052 06	0.758 70	152.25	0.052 08	0.758 79	223.21
	Bu_4NBr			Pen_4NBr	
0.012 79	0.755 97	292.20	0.012 60	0.755 97	363.01
0.026 07	0.756 94	292.99	0.026 20	0.757 02	363.74
0.032 51	0.757 44	293.30	0.032 35	0.757 49	363.99
0.039 12	0.757 93	293.56	0.038 96	0.757 99	364.33
0.045 50	0.758 40	293.80	0.045 58	0.758 49	364.53
0.052 19	0.758 89	294.05	0.051 87	0.758 96	364.79
	Hex_4NBr			Hep_4NBr	
0.012 81	0.756 01	433.99	0.012 86	0.756 04	504.65
0.026 13	0.757 06	434.80	0.026 10	0.757 11	505.36
0.032 53	0.757 56	435.01	0.032 74	0.757 64	505.66
0.039 26	0.758 08	434.33	0.039 31	0.758 16	505.91
0.045 75	0.758 58	435.52	0.045 80	0.758 67	506.14
0.052 30	0.759 08	435.74	0.052 57	0.759 20	506.30

Table 3. Limiting Apparent Molar Volume ($\phi_v°$) and Experimental Slope (S_v*) of Tetraalkylammonium Bromides in Acetonitrile at 298.15, 308.15, and 318.15 K

	$\phi_v°$/cm^3·mol^{-1}			S_v*/cm^3·L$^{1/2}$·mol$^{-3/2}$		
salt	298.15	308.15	318.15	298.15	308.15	318.15
Et_4NBr	140.64 (140.75,[a] 140.49,[b] 141.6[c])	145.08	147.87	17.13	18.56	19.41
Pr_4NBr	212.77 (212.48,[a] 212.80,[b] 213.0[c])	216.24	219.18	16.30	16.33	17.67
Bu_4NBr	280.92 (280.62,[a] 280.89,[b] 281.3[c])	286.55	290.40	14.76	14.94	15.97
Pen_4NBr	350.99 (350.69,[a] 350.7[c])	357.39	361.27	14.14	14.22	15.37
Hex_4NBr	422.45	428.09	432.31	13.23	13.98	15.07
Hep_4NBr	492.21	498.53	503.02	12.29	13.92	14.47

[a] Zana et al. (1979). [b] Bottomley and Bremers (1986). [c] Marcus et al. (1994).

Table 4. Correlation Coefficients (r)

	r		
salt	298.15 K	308.15 K	318.15 K
Et_4NBr	0.9997	0.9990	0.9990
Pr_4NBr	0.9997	0.9996	0.9999
Bu_4NBr	0.9997	0.9997	0.9987
Pen_4NBr	0.9989	0.9986	0.9990
Hex_4NBr	0.9934	0.9997	0.9986
Hep_4NBr	0.9962	0.9959	0.9993

where $\phi_v°$ is the apparent molar volume of the salt at infinite dilution, and S_v* is the experimental slope.

The limiting apparent molar volumes, $\phi_v°$ (equal to the partial molar volumes at infinite dilution, $\bar{V}_2°$), were obtained by the least-squares fitting of ϕ_v values to the above equation, and these values along with the experimental S_v* values are reported in Table 3. The corresponding correlation coefficients of the regression analysis are given in Table 4.

Since our experimental results of apparent molar volumes can be well represented by eq 2, we have not analyzed the data on the basis of the equation

$$\phi_v = \phi_v° + A_v m^{1/2} + b_v m \qquad (3)$$

where A_v is the theoretical limiting slope of the Debye–Hückel theory and b_v is a fitting constant determined empirically. Moreover, the evaluation of A_v requires the knowledge of the pressure dependence of the dielectric constant of acetonitrile, which is known only at 298.15 K, rendering analysis of the data at 308.15 and 318.15 K in terms of eq 3 impossible. However, analysis at 298.15 K on the basis of eq 2 has also been attempted.

For all salts, plots of ϕ_v against $m^{1/2}$ and of $(\phi_v - A_v m^{1/2})$ against m at 298.15 K give essentially straight lines which extrapolate to approximately the same $\phi_v°$ values. These observations suggest that the electrolytes remain nearly fully dissociated in acetonitrile in the concentration range investigated. This also justifies the applicability of eq 2 for the analysis of our data. When, on the other hand, association occurs, $(\phi_v - A_v m^{1/2})$ increases sharply with m at low concentration, and then levels off or goes through a maximum at higher concentration. This happens since the $\bar{V}_2°$ of the free ions are expected to be smaller than those of the ion pairs. Actually, this is believed to be the case for tetrabutylammonium bromide in acetonitrile at 298.15 K (Zana et al., 1979) where the concentrations employed were sufficiently high (as high as 0.615 43 mol·kg^{-1}) to exhibit this phenomenon.

The limiting apparent molar volumes ($\phi_v°$) are large and positive, and the values increase with the increasing size of the cations. This is found to be in agreement with earlier findings in several nonaqueous solvents as well as in water and heavy water (Krumgalz, 1980). The $\phi_v°$ values for tetraethyl-, tetrapropyl-, tetrabutyl-, and tetrapentylammonium bromides are available in the literature only at 298.15 K (Zana et al., 1979; Bottomley and Bremers, 1986; Marcus et al., 1994), and our values are found to be in good agreement with these (Table 3).

Table 5. Limiting Partial Molar Expansibilities (ϕ_E°) in Acetonitrile

	ϕ_E°/cm^3·mol^{-1}·K^{-1}		
salt	298.15 K	308.15 K	318.15 K
Et_4NBr	0.526	0.361	0.196
Pr_4NBr	0.373	0.320	0.267
Bu_4NBr	0.652	0.474	0.296
Pen_4NBr	0.766	0.513	0.260
Hex_4NBr	0.635	0.493	0.351
Hep_4NBr	0.723	0.540	0.357

The temperature dependence of ϕ_v° can be expressed as

$$\phi_v^\circ = A + BT + CT^2 \tag{4}$$

where T is the temperature in degrees Kelvin.

The infinite dilution partial molar expansibilities can be obtained by differentiating eq 4 with respect to temperature

$$\phi_E^\circ = (\partial\phi_v^\circ/\partial T)_P = B + 2CT \tag{5}$$

The ϕ_E° values of the electrolytes at (298.15, 308.15, and 318.15) K are given in Table 5. It may be noted that the thermal expansion of each salt decreases with rising temperature. This suggests that the liquid structure of acetonitrile is weakened by the elevation of temperature. The electrostriction around the ions relatively increases with the rise in temperature.

The methylene group contributions to the limiting partial molar volumes of these electrolytes are found to be (17.58, 17.60, and 17.76) cm^3·mol^{-1}, respectively. The values are in good agreement with those in other nonaqueous solvents which range from 17.33 cm^3·mol^{-1} at 298.15 K to 17.81 cm^3·mol^{-1} at 347.15 K (Krumgalz, 1980). The ϕ_E° values of the tetraalkylammonium bromides are not a linear function of the formula weight of the cation, R_4N^+ (Table 5). Hence, the methylene group contribution to the limiting partial molar expansibilities could not be calculated. This type of behavior has also been observed in other solvents, e.g., water (Millero and Drost-Hansen, 1968), *N*-methylacetamide (Gopal et al., 1973), dimethyl sulfoxide and dimethylformamide (Gopal and Siddiqi, 1969), 2-methoxyethanol (Das and Hazra, 1995), etc.

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