

## CHAPTER III

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

## Introduction

The volumetric behaviour 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<sup>1,2</sup> on ion-ion, ion-solvent, and solvent-solvent interactions. In this chapter, 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<sup>3-5</sup> only at 298.15 K. 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<sup>1,6-10,20</sup> at one temperature. The solvent acetonitrile has drawn attention in recent years because of its use in technological applications, namely, in battery systems and plating techniques<sup>11,12</sup>.

## Experimental

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,  $\rho_0$ , and viscosity,  $\eta_0$  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 12h. 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<sup>3</sup> 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  $\pm 0.01$  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<sup>-3</sup>.

## Results

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

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

where  $m$  is the molality of the electrolyte solution,  $M$  is the molecular weight of the solute, and  $\rho$  and  $\rho_0$  are the densities of the solution and solvent, respectively.

The molal concentrations ( $m$ ), densities ( $\rho$ ), and apparent molar volumes ( $\phi_v$ ) 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

$$\phi_v = \phi_v^0 + S_v^* m^{1/2} \quad (2)$$

where  $\phi_v^0$  is the apparent molar volume of the salt at infinite dilution, and  $S_v^*$  is the experimental slope.

The limiting apparent molar volumes  $\phi_v^0$ , (equal to the partial molar volumes at infinite dilution,  $V_2^0$ ), were obtained by the least-squares fitting of  $\phi_v$  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 equation

$$\phi_v = \phi_v^0 + A_v m^{1/2} + b_v m \quad (3)$$

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.

## Discussion

For all salts, plots of  $\phi_v$  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  $\phi_v^0$  values. These observations suggest that the electrolytes remain nearly fully dissociated in acetonitrile in the concentration range investigated. This also justified 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  $\bar{V}_2^0$  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 where the concentrations employed were sufficiently high (as high as 0.615 43 mol.kg<sup>-1</sup>) to exhibit this phenomenon.

The limiting apparent molar volumes ( $\phi_v^0$ ) 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<sup>17</sup> in several nonaqueous solvents as well as in water and heavy water. The  $\phi_v^0$  values for tetraethyl-, tetrapropyl-, tetrabutyl-, and tetrapentylammonium bromides are available in the literature<sup>3-5</sup> only at 298.15 K and our values are found to be in good agreement with these (Table 3).

The temperature dependence of  $\phi_v^0$  can be expressed as

$$\phi_v^0 = A + BT + CT^2 \quad (4)$$

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

$$\phi_E^0 = (\partial \phi_v^0 / \partial T)_p = B + 2CT \quad (5)$$

The  $\phi_E^0$  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 values of these electrolytes are found to be 17.58, 17.60, and 17.76  $\text{cm}^3 \cdot \text{mol}^{-1}$ , respectively. The values are in good agreement<sup>17</sup> with those in other nonaqueous solvents which range from 17.33  $\text{cm}^3 \cdot \text{mol}^{-1}$  at 298.15 K to 17.81  $\text{cm}^3 \cdot \text{mol}^{-1}$  at 347.15 K. The  $\phi_E^0$  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 behaviour has also been observed<sup>6,18-20</sup> in other solvents, e.g., water, N-methylacetamide, dimethyl sulfoxide and dimethylformamide, 2-methoxyethanol, etc.

## References

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**Table 1. Properties of Acetonitrile**

T/K	$\rho_0 / \text{g.cm}^{-3}$		$\eta_0 / \text{mPa.s}$	
	this work	literature	this work	literature
298.15	0.776 86	0.776 85 <sup>a</sup>	0.3446	0.341 <sup>a</sup>
		0.775 9 <sup>b</sup>		0.344 <sup>b</sup>
		0.776 82 <sup>c</sup>		
308.15	0.765 64	0.765 81 <sup>a</sup>	0.3125	0.314 <sup>a</sup>
		0.766 2 <sup>b</sup>		0.314 <sup>b</sup>
		0.765 60 <sup>d</sup>		
318.15	0.754 98	0.752 71 <sup>a</sup>	0.2893	0.293 <sup>a</sup>
		0.755 9 <sup>b</sup>		0.289 <sup>b</sup>

<sup>a</sup> ref.13, <sup>b</sup> ref.14, <sup>c</sup> ref. 15, <sup>d</sup> ref. 16.

**Table 2. Molal Concentration (m), Density ( $\rho$ ), and Apparent Molar Volume ( $\phi_v$ ) for Tetraalkylammonium Bromides in Acetonitrile at 298.15, 308.15, and 318.15K**

$m/\text{mol.kg}^{-1}$	$\rho/\text{g. cm}^3$	$\phi_v/\text{cm}^3\text{mol}^{-1}$	$m/\text{mol.kg}^{-1}$	$\rho/\text{g. cm}^3$	$\phi_v/\text{cm}^3\text{mol}^{-1}$
T = 298.15 K					
Et <sub>4</sub> NBr			Pr <sub>4</sub> NBr		
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	0.77883	215.39
0.032026	0.779 32	143.72	0.03239	0.77933	215.71
0.038 67	0.779 80	144.00	0.038 95	0.77982	216.01
0.045 24	0.780 29	144.26	0.045 40	0.78030	216.24
0.051 87	0.780 78	144.57	0.052 15	0.78080	216.47
Bu <sub>4</sub> NBr			Pen <sub>4</sub> NBr		
0.01293	0.77789	282.61	0.01272	0.77789	352.56
0.02594	0.77891	283.28	0.02618	0.77896	353.33
0.03238	0.77941	283.56	0.03239	0.77945	353.53
0.03913	0.77993	283.86	0.03904	0.77997	353.79
0.04551	0.78042	284.06	0.04572	0.78049	353.99
0.05220	0.78093	284.30	0.05220	0.78099	354.22
Hex <sub>4</sub> NBr			Hept <sub>4</sub> NBr		
0.01277	0.77790	423.92	0.01303	0.77794	493.64
0.02603	0.77896	424.61	0.02604	0.77900	494.13
0.03261	0.77948	424.87	0.03264	0.77953	494.42
0.03923	0.78000	425.09	0.03928	0.78006	494.63
0.04585	0.78052	425.16	0.04571	0.78057	494.81
0.05227	0.78102	425.53	0.05272	0.78112	495.05



T = 308.15 K

	Et <sub>4</sub> NBr			Pr <sub>4</sub> NBr	
0.01288	0.76660	147.16	0.01292	0.76662	218.11
0.02586	0.76755	148.12	0.02578	0.76758	218.85
0.03246	0.76803	148.42	0.03240	0.76807	219.14
0.03896	0.76850	148.71	0.03894	0.76855	219.49
0.04537	0.76896	149.01	0.04551	0.76903	219.73
0.05210	0.76944	149.33	0.05225	0.76952	219.98
	Bu <sub>4</sub> NBr			Pen <sub>4</sub> NBr	
0.01288	0.76664	288.24	0.01265	0.76664	359.02
0.02598	0.76764	288.98	0.02615	0.76769	359.65
0.03245	0.76813	289.22	0.03239	0.76817	359.91
0.03911	0.76863	289.51	0.03894	0.76867	360.18
0.04553	0.76911	289.73	0.04567	0.76918	360.45
0.05226	0.76961	289.97	0.05263	0.76966	360.65
	Hex <sub>4</sub> NBr			Hep <sub>4</sub> NBr	
0.01279	0.76667	429.68	0.01290	0.76670	500.05
0.02607	0.76772	430.36	0.02608	0.76776	500.86
0.03259	0.76823	430.60	0.03273	0.76829	501.06
0.03929	0.76875	430.85	0.03932	0.76881	501.31
0.04578	0.76925	431.08	0.04582	0.76932	501.50
0.05232	0.76975	431.31	0.05262	0.76985	501.67

T = 318.15 K

	Et <sub>4</sub> NBr			Pr <sub>4</sub> NBr		
0.01273	0.75591	150.02	0.01270	0.75593	221.17	
0.02584	0.75685	151.03	0.02562	0.75688	222.02	
0.03245	0.75732	151.39	0.03221	0.75736	222.35	
0.03896	0.75778	151.72	0.03870	0.75783	222.64	
0.04536	0.75823	152.01	0.04538	0.75831	222.96	
0.05206	0.75870	152.25	0.05208	0.75879	223.21	
	Bu <sub>4</sub> NBr			Pen <sub>4</sub> NBr		
0.01279	0.75597	292.20	0.01260	0.75597	363.01	
0.02607	0.75694	292.99	0.02620	0.75702	363.74	
0.03251	0.75744	293.30	0.03235	0.75749	363.99	
0.03912	0.75793	292.56	0.03896	0.75799	364.33	
0.04550	0.75840	293.80	0.04558	0.75849	364.53	
0.05219	0.75889	294.05	0.05187	0.75896	364.79	
	Hex <sub>4</sub> NBr			Hep <sub>4</sub> NBr		
0.01281	0.75601	433.99	0.01286	0.75604	504.65	
0.02613	0.75706	434.80	0.02610	0.75711	505.36	
0.03253	0.75756	435.01	0.03274	0.75764	505.66	
0.03926	0.75808	434.33	0.03931	0.75816	505.91	
0.04575	0.75858	435.52	0.04580	0.75867	506.14	
0.05230	0.75908	435.74	0.05257	0.75920	506.30	

**Table 3. Limiting Apparent Molar Volume ( $\phi_v^0$ ) and Experimental Slope ( $S_v^*$ ) of Tetraalkylammonium Bromides in Acetonitrile at 298.15, 308.15, and 318.15K**

Salt	$\phi_v^0 / \text{cm}^3 \cdot \text{mol}^{-1}$			$S_v^* / \text{cm}^3 \cdot \text{L}^{1/2} \cdot \text{mol}^{-3/2}$		
	298.15	308.15	318.15	298.15	308.15	318.15
Et <sub>4</sub> NBr	140.64 ( 140.75, <sup>a</sup> 140.49, <sup>b</sup> 141.60, <sup>c</sup>	145.08	147.87	17.13	18.56	19.41
Pr <sub>4</sub> NBr	212.77 ( 212.48, <sup>a</sup> 212.80, <sup>b</sup> 213.0 )	246.24	219.18	16.30	16.33	17.67
Bu <sub>4</sub> NBr	280.89, <sup>b</sup> 281.30 ) 280.89, <sup>b</sup> 281.30, <sup>c</sup>	286.55	290.40	14.76	14.94	15.97
Pen <sub>4</sub> NBr	350.99 ( 350.69, <sup>a</sup> 350.70	357.39	361.27	14.14	14.22	15.37
Hex <sub>4</sub> NBr	422.45	428.09	432.31	13.23	13.98	15.07
Hep <sub>4</sub> NBr	492.21	498.53	503.02	12.29	13.92	14.47

<sup>a</sup>ref. 3, <sup>b</sup>ref. 4,5. <sup>c</sup>ref. 5.

**Table 4. Correlation Coefficients (r)**

salt	r		
	298.15 K	308.15 K	318.15 K
Et <sub>4</sub> NBr	0.9997	0.9990	0.9990
Pr <sub>4</sub> NBr	0.9997	0.9996	0.9999
Bu <sub>4</sub> NBr	0.9997	0.9997	0.9987
Pen <sub>4</sub> NBr	0.9989	0.9986	0.9990
Hex <sub>4</sub> NBr	0.9934	0.9997	0.9986
Hep <sub>4</sub> NBr	0.9962	0.9959	0.9993

**Table 5. Limiting Partial Molar Expansibilities ( $\phi_E^0$ ) in Acetonitrile**

salt	$\phi_E^0/\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$		
	298.15 K	308.15 K	318.15 K
Et <sub>4</sub> NBr	0.526	0.361	0.196
Pr <sub>4</sub> NBr	0.373	0.320	0.267
Bu <sub>4</sub> NBr	0.652	0.474	0.296
Pen <sub>4</sub> NBr	0.766	0.513	0.260
Hex <sub>4</sub> NBr	0.635	0.493	0.351
Hep <sub>4</sub> NBr	0.723	0.540	0.357