

## Apparent molar volumes and apparent molar adiabatic compressibilities of some symmetrical tetraalkylammonium bromides in 1,2-dimethoxyethane

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Apparent molar volumes ( $\phi_v$ ) and apparent molar adiabatic compressibilities ( $\phi_K$ ) of four symmetrical tetraalkylammonium bromides have been determined in 1,2-dimethoxyethane from precise density and sound velocity measurements. Limiting apparent molar volumes and adiabatic compressibilities of the salts obtained from the concentration dependence of  $\phi_v$  and  $\phi_K$  data are separated into ionic contributions. The data have been quantitatively interpreted in terms of solute-solvent and solute-solute interactions. Strong electrostriction occurs around bromide ions whereas the larger tetraalkylammonium ions which are scarcely solvated in 1,2-dimethoxyethane, cause a greater degree of disorder in the solvent structure.

Thermodynamic properties are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution phase. The partial molar volume, pressure derivative of partial molar Gibbs energy, is a useful parameter for studying solute-solvent interactions in solution. Various concepts regarding molecular processes in solutions such as electrostriction<sup>1</sup>, hydrophobic hydration<sup>2</sup>, micellization<sup>3</sup>, and cosphere overlap during solute-solvent interactions<sup>4,5</sup> have to some extent been derived from the partial molar volume data of diverse compounds. The compressibility, a second derivative of Gibbs energy, is also a sensitive indicator of molecular interactions and can provide useful information in such cases where partial molar volume data alone fail to provide an unequivocal interpretation of these interactions. The present paper reports the study of the apparent molar volumes and adiabatic compressibilities of some tetraalkylammonium bromides in 1,2-dimethoxyethane to explicate the nature of solute-solvent interactions in this medium. The importance of this solvent lies in the fact that it has found a wide range of applications as solvent and solubilizing agent in organic syntheses and electrochemical studies<sup>6,7</sup>.

### Materials and Methods

The purification of 1,2-dimethoxyethane (Fluka, purum) has been described earlier<sup>8</sup>. The solvent was shaken well with FeSO<sub>4</sub> (AR, BDH) for 1-2 h, decanted and distilled. The distillate was

refluxed for 12 h and redistilled over metallic sodium. The properties of the purified solvent at different temperatures along with the available literature<sup>9</sup> values are recorded in Table 1. A fair agreement in density and viscosity values at 25°C between the two is observed.

Tetraalkylammonium bromides were either of purum or puriss grade (Fluka). Tetrabutylammonium and tetrapentylammonium bromides were recrystallized from acetone-ether and dried *in vacuo* at 60°C for two days. Tetrahexylammonium and tetraheptylammonium bromides were washed with distilled ether and dried *in vacuo* at room temperature for two days.

A stock solution of each salt was prepared by weight and working solutions were obtained by weight dilution. The conversion of molality into molarity was done by using the density values.

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume

Table 1—Solvent properties

Temperature (°C)	Density (g cm <sup>-3</sup> )	Viscosity (mPa s)
25	0.86132 (0.86120) <sup>a</sup>	0.4236 (0.4095) <sup>a</sup>
35	0.85129	0.3847
45	0.84076	0.3496

<sup>a</sup>Values in the parenthesis are taken from ref. 9

of about 25 cm<sup>3</sup> and an internal diameter of capillary of about 1 mm. The pycnometer was calibrated at 25, 35 and 45°C with doubly distilled water. Measurements were made using a single pan Mettler balance (Switzerland, model H20) with an accuracy of ±0.00001 g. The temperature of the thermostatic bath was controlled to ±0.01°C of the desired temperature. The reproducibility of density measurements was ±3 × 10<sup>-5</sup> g cm<sup>-3</sup>.

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 the cases was ±0.03%.

**Results and Discussion**

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

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

Table 2—Concentration (*c*), density ( $\rho$ ), and apparent molar volume ( $\phi_v$ ) for tetraalkylammonium bromides in 1,2-dimethoxyethane at 25, 35 and 45°C

<i>c</i> (mol dm <sup>-3</sup> )	$\rho$ (g cm <sup>-3</sup> )	$\phi_v$ (cm <sup>3</sup> mol <sup>-1</sup> )	<i>c</i> (mol dm <sup>-3</sup> )	$\rho$ (g cm <sup>-3</sup> )	$\phi_v$ (cm <sup>3</sup> mol <sup>-1</sup> )
25°C					
Bu <sub>4</sub> NBr			Pen <sub>4</sub> NBr		
0.01204	0.86207	301.96	0.00496	0.86163	366.86
0.02005	0.86254	303.64	0.01050	0.86197	367.55
0.02496	0.86282	304.51	0.01494	0.86224	367.92
0.02996	0.86310	305.31	0.01975	0.86254	368.29
0.04004	0.86365	306.73	0.02493	0.86284	368.63
0.05007	0.86418	307.97	0.02998	0.86314	368.94
Hex <sub>4</sub> NBr			Hep <sub>4</sub> NBr		
0.00997	0.86182	446.55	0.01019	0.86182	512.73
0.02004	0.86224	451.47	0.02022	0.86225	516.30
0.02512	0.86243	453.47	0.02524	0.86245	517.72
0.02998	0.86260	455.20	0.03023	0.86264	519.00
0.04004	0.86292	458.38	0.04003	0.86299	521.26
0.04489	0.86306	459.77	0.05004	0.86332	523.29
35°C					
Bu <sub>4</sub> NBr			Pen <sub>4</sub> NBr		
0.01187	0.85203	305.46	0.00490	0.85160	370.28
0.01994	0.85250	307.41	0.01041	0.85194	371.25
0.02473	0.85277	308.40	0.01469	0.85220	371.83
0.02963	0.85304	309.32	0.01934	0.85248	372.32
0.03953	0.85357	310.94	0.02438	0.85278	372.80
0.04943	0.85408	312.39	0.02938	0.85307	373.23
Hex <sub>4</sub> NBr			Hep <sub>4</sub> NBr		
0.00997	0.85178	451.70	0.01003	0.85180	516.68
0.01972	0.85218	457.48	0.01994	0.85224	520.44
0.02453	0.85235	459.73	0.02480	0.85244	521.94
0.02913	0.85250	461.70	0.02963	0.85263	523.29
0.03878	0.85278	465.36	0.03911	0.85298	525.65
0.04345	0.85290	466.97	0.04879	0.85331	527.77

Table 2—Concentration ( $c$ ), density ( $\rho$ ), and apparent molar volume ( $\phi_v$ ) for tetraalkylammonium bromides in 1,2-dimethoxyethane at 25, 35 and 45°C—Contd

$c$ (mol dm <sup>-3</sup> )	$\rho$ (g cm <sup>-3</sup> )	$\phi_v$ (cm <sup>3</sup> mol <sup>-1</sup> )	$c$ (mol dm <sup>-3</sup> )	$\rho$ (g cm <sup>-3</sup> )	$\phi_v$ (cm <sup>3</sup> mol <sup>-1</sup> )
45°C					
Bu <sub>4</sub> NBr			Pen <sub>4</sub> NBr		
0.01178	0.84150	308.72	0.00480	0.84107	373.35
0.01970	0.84196	310.99	0.01021	0.84141	374.44
0.02436	0.84222	312.15	0.01441	0.84167	375.05
0.02912	0.84248	313.19	0.01901	0.84195	375.71
0.03881	0.84299	315.10	0.02383	0.84224	376.29
0.04854	0.84348	316.79	0.02854	0.84252	376.82
Hex <sub>4</sub> NBr			Hep <sub>4</sub> NBr		
0.00960	0.84125	456.18	0.00976	0.84127	521.41
0.01928	0.84164	462.60	0.01956	0.84171	525.86
0.02385	0.84180	465.02	0.02418	0.84190	527.55
0.02822	0.84194	467.16	0.02878	0.84208	529.07
0.03744	0.84220	471.14	0.03813	0.84242	531.85
0.04191	0.84231	472.90	0.04749	0.84273	534.29

Table 3—Limiting apparent molar volume ( $\phi_v^0$ ),  $d\phi_v^0/dT$  values and experimental slope ( $S_v^*$ ) of tetraalkylammonium bromides in 1,2-dimethoxyethane at 25, 35 and 45°C

Salt	$\phi_v^0$ , (cm <sup>3</sup> mol <sup>-1</sup> )			$d\phi_v^0/dT$		$S_v^*$ , (cm <sup>3</sup> L <sup>1/2</sup> mol <sup>-3/2</sup> )		
	25°C	35°C	45°C	(25-35)°C	(35-45)°C	25°C	35°C	45°C
Bu <sub>4</sub> NBr	296.18 (±0.01)	298.79 (±0.02)	300.87 (±0.02)	0.261	0.208	52.71 (±0.06)	61.15 (±0.13)	72.25 (±0.15)
Pen <sub>4</sub> NBr	365.46 (±0.03)	368.30 (±0.04)	370.92 (±0.04)	0.284	0.262	20.10 (±0.20)	29.02 (±0.32)	34.78 (±0.34)
Hex <sub>4</sub> NBr	434.77 (±0.01)	437.90 (±0.06)	440.83 (±0.01)	0.313	0.293	117.97 (±0.59)	140.44 (±0.35)	156.66 (±0.08)
Hep <sub>4</sub> NBr	504.06 (±0.02)	507.48 (±0.01)	510.74 (±0.01)	0.342	0.326	85.94 (±0.10)	91.85 (±0.07)	108.14 (±0.04)

where  $c$  is the molarity 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 molar concentrations, densities and the apparent and partial molar volumes of the various electrolyte solutions in 1,2-dimethoxyethane at 25, 35 and 45°C are given in Table 2.

From the  $\phi_v$  data,  $\phi_v$  versus  $\sqrt{c}$  curves have been drawn and the plots were found to be linear in all the cases with positive slopes. Obviously, the Masson's empirical relation<sup>10</sup>, namely,

$$\phi_v = \phi_v^0 + S_v^* \sqrt{c} \quad \dots (2)$$

is applicable within the temperature and concentration ranges studied here. The limiting apparent

molar volumes,  $\phi_v^0$ , (equal to the partial molar volumes at infinite dilution,  $\bar{v}_2^0$ ) are obtained by the least-squares fitting of  $\phi_v$  values to the above equation and these values along with the experimental  $S_v^*$  values have been reported in Table 3.

Though our experimental results of apparent molar volumes can be well represented by the Masson's equation i.e., Eq. 2, we also tried to analyze these data on the basis of Redlich-Mayer equation<sup>11</sup>

$$\phi_v = \phi_v^0 + S_v \sqrt{c} + b_v c \quad \dots (3)$$

where  $S_v$  is the coefficient given by Debye-Huckel theory and  $b_v$  is a fitting constant empirically determined. However, the evaluation of  $S_v$  requires the knowledge of the pressure dependence of the

dielectric constant of the solvent which was not available in the literature for the present system and our attempts were not successful.

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  $\phi_v^0$  values can be used and from Table 3 we see that these values are large and positive, and 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<sup>12</sup>.

Ionic limiting partial molar volumes have been calculated following the extrapolation method suggested by Conway and coworkers<sup>13</sup>. Zana *et al.*<sup>14,15</sup> have also 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 1,2-dimethoxyethane, we have used the extrapolation technique<sup>13</sup>. Following this procedure, the  $\bar{V}_2^0$  values for the tetraalkylammonium bromides in 1,2-dimethoxyethane at 25, 35, and 45°C were plotted against the formula weight of the corresponding tetraalkylammonium ions. An excellent linear relationship was observed at all the temperatures. The ionic partial molar volumes ( $\bar{V}_{ion}^0$ ) thus obtained have been presented in Table 4. The  $\bar{V}_{ion}^0$  values for the tetraalkylammonium ions are positive and have been found to increase regularly from  $Bu_4N^+$  to  $Hep_4N^+$ . The  $V_{ion}^0$  values in 1, 2-dimethoxyethane are found to be almost similar to those in other nonaqueous solvents<sup>16-19</sup>. This fact indicates that the large tetraalkylammonium ions are scarcely solvated in this solvent medium.

It may be noted from Table 3 that for all the salts,  $\phi_v^0$  values increase with the rise in tempera-

ture, although  $d\phi_v^0/dT$  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  $\phi_v^0$  values at the higher temperature. Again, 1,2-dimethoxyethane is a non-hydrogen bonded solvent and the ion-solvent dipole interaction energy in this medium would be appreciable and the attachment of the solvent molecules in the primary solvation layer of  $R_4N^+$  ions may not be loose. Thus, some solvent molecules may permanently be associated with the  $R_4N^+$  ions while outside the primary region 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  $d\phi_v^0/dT$  would decrease with the rise in temperature.

Adiabatic compressibility coefficients,  $\beta$ , were derived from the relation

$$\beta = 1/u^2 d \quad \dots (4)$$

where  $u$  is the velocity of sound in the solution.

The apparent molar adiabatic compressibility ( $\phi_k$ ) of liquid solutions was calculated from the relation

$$\phi_k = \frac{1000}{cd_0} (d_0\beta - d\beta_0) + \beta_0 \frac{M}{d_0} \quad \dots (5)$$

where  $\beta_0$  and  $\beta$  are the compressibility coefficients of the solvent and solution, respectively. The molar concentration ( $c$ ), adiabatic compressibility ( $\beta$ ) and apparent molar adiabatic compressibilities ( $\phi_k$ ) for all the salts in 1,2-dimethoxyethane are given in Table 5.

The concentration dependence of apparent molar adiabatic compressibility is given by

$$\phi_k = \phi_k^0 + S_k \sqrt{c} \quad \dots (6)$$

where  $S_k$  is an experimentally determined slope and  $\phi_k^0$  is the limiting apparent molar adiabatic compressibility. The  $\phi_k^0$  and  $S_k$  values are presented in Table 6.

Data reported here indicate that all the compounds studied in this work, except  $Bu_4NBr$ , have positive compressibilities. It is well established<sup>20,21</sup> that solutes causing electrostriction lead to a decrease in compressibility of the solution. Therefore, the negative  $\phi_k^0$  value of  $Bu_4NBr$  indicate an overall constriction in the solution volumes caused by electrostriction over other effects. But

Table 4—Ionic limiting partial molar volume ( $\phi_v^0$ ) in 1,2-dimethoxyethane at 25, 35 and 45°C

Ion	$\bar{V}_{ion}^0$ ( $cm^3 mol^{-1}$ )		
	25°C	35°C	45°C
$Bu_4N^+$	299.49	300.64	302.26
$Pen_4N^+$	368.77	370.13	372.31
$Hex_4N^+$	438.08	439.57	442.22
$Hep_4N^+$	507.37	509.33	512.12
$Br^-$	-3.31	-1.85	-1.39

Table 5—Concentration ( $c$ ), density ( $\rho$ ), adiabatic compressibility coefficient ( $\beta$ ), and apparent molar adiabatic compressibility ( $\phi_K$ ) of the tetraalkylammonium bromides in 1,2-dimethoxyethane at 25°C

Salt	$c$ (mol dm <sup>-3</sup> )	$\rho$ (g cm <sup>-3</sup> )	$\beta$ (10 <sup>13</sup> Pa <sup>-1</sup> )	$\phi_K$ (10 <sup>15</sup> m <sup>3</sup> mol <sup>-1</sup> Pa <sup>-1</sup> )
Bu <sub>4</sub> NBr	0.01204	0.86207	89.012	7.28
	0.02005	0.86254	88.807	11.39
	0.02496	0.86282	88.683	13.60
	0.02996	0.86310	88.557	15.38
	0.04004	0.86365	88.305	18.50
	0.05007	0.86418	88.058	21.46
Pen <sub>4</sub> NBr	0.00496	0.86163	89.173	15.20
	0.01050	0.86197	89.001	16.89
	0.01494	0.86224	88.864	18.80
	0.01975	0.86253	88.715	18.60
	0.02493	0.86284	88.556	19.62
	0.02998	0.86318	88.401	20.36
Hex <sub>4</sub> NBr	0.00997	0.86182	88.984	53.86
	0.02004	0.86224	88.651	65.47
	0.02512	0.86243	88.487	70.28
	0.02998	0.86260	88.332	74.40
	0.04004	0.86292	88.016	81.79
	0.04489	0.86306	87.867	85.24
Hep <sub>4</sub> NBr	0.01019	0.86182	88.926	63.50
	0.02022	0.86225	88.541	71.98
	0.02524	0.86245	88.351	75.38
	0.03023	0.86264	88.164	78.56
	0.04003	0.86299	87.800	83.92
	0.05004	0.86332	87.434	88.95

Table 6—Limiting apparent molar adiabatic compressibilities ( $\phi_K^0$ ) and experimental slopes ( $S_k$ ) of tetraalkylammonium bromides in 1,2-dimethoxyethane at 25°C

	$\phi_K^0$ (10 <sup>13</sup> m <sup>3</sup> mol <sup>-1</sup> Pa <sup>-1</sup> )	$S_k$ (10 <sup>15</sup> m <sup>3</sup> mol <sup>-3/2</sup> Pa <sup>-1</sup> kg <sup>1/2</sup> )
Bu <sub>4</sub> NBr	-6.12 (±0.28)	123.54 (±1.66)
Pen <sub>4</sub> NBr	11.98 (±0.72)	49.04 (±0.55)
Hex <sub>4</sub> NBr	25.94 (±0.13)	279.57 (±0.79)
Hep <sub>4</sub> NBr	42.56 (±0.12)	207.02 (±0.71)

for the remaining solutions solvent structure becomes more compressible in the presence of the these solutes.

In order to gain more insight regarding ion-solvent interaction, we have divided the salt  $\phi_K^0$  va-

lues into their ionic contributions in the same way as done for ionic  $\phi_V^0$  values. Thus, the intercept in the plot of apparent molar adiabatic compressibilities of R<sub>4</sub>N<sup>+</sup> ions versus cation formula weights is the ionic apparent molar adiabatic compressibility of the Br<sup>-</sup> ion. Individual ionic compressibilities of Bu<sub>4</sub>N<sup>+</sup>, Pen<sub>4</sub>N<sup>+</sup>, Hex<sub>4</sub>N<sup>+</sup>, Hep<sub>4</sub>N<sup>+</sup> and Br<sup>-</sup> are 68.43, 86.53, 100.49, 117.11 and -74.55 (10<sup>15</sup> m<sup>3</sup> mol<sup>-1</sup> Pa<sup>-1</sup>) respectively. The results show that ionic apparent molar adiabatic compressibility value for Br<sup>-</sup> ion is large negative whereas those for the tetraalkylammonium ions are large positive. The negative compressibility of Br<sup>-</sup> ion is obviously due to the electrostriction of solvent molecules around this ion arising from its relatively high charge density value. But for the tetraalkylammonium ions, the electrostriction effect will be quite negligible because of their very low surface charge density. The poor fit of the tetraalkylammonium ions into the solvent structure appear to be responsible for causing a more

compressible environment in the solution thus giving rise to positive  $\phi_k^0$  values for these ions. It is also seen that as the size of the tetraalkylammonium ion increases, the ionic  $\phi_k^0$  values go on increasing. It can be argued that as the size of the ion increases, it becomes increasingly difficult for the solute to be accommodated in the solvent structure. Consequently, it appears to cause a greater degree of disorder in the solvent. The compressibility of such disordered structures is expected to be higher than that of the ordered structures. This explains the observed trend for the ionic  $\phi_k^0$  values of the tetraalkylammonium ions.

The investigation thus indicates that all the salts studied here exhibit strong ionic interactions, apparently due to the low dielectric constant of the solvent. Bromide ion causes electrostriction of the solvent molecules around it, but for the large tetraalkylammonium ions size effects predominate and cause more compressible environment in the solvent medium.

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