

**CHAPTER VII**

# Isentropic Compressibilities of Some Symmetrical Tetraalkylammonium Bromides in Methanol + Acetonitrile Mixtures

## Introduction

Thermodynamic properties are generally convenient parameters for interpreting solute-solvent interactions in solution phase. The partial molar volume-the 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 various compounds. The compressibility-the second derivative of Gibbs energy-is also a sensitive indicator of molecular interactions and can help provide an unequivocal interpretation of these interactions. Although the compressibility studies of electrolytes are available in the literature in pure nonaqueous solvents and in their aqueous mixtures, comparatively little attention has been paid to such investigations in mixed nonaqueous solvents (chapter I, page 47). In chapters III and IV of this dissertation, we reported the study of the apparent molar volumes and viscosity of some tetraalkylammonium salts in acetonitrile, methanol and their binary mixtures. The present chapter reports the compressibility behaviour of four tetraalkylammonium bromides e.g., tetraethylammonium bromide ( $\text{Et}_4\text{NBr}$ ), tetrapropylammonium bromide ( $\text{Pr}_4\text{NBr}$ ), tetrabutylammonium bromide, ( $\text{Bu}_4\text{NBr}$ ) and tetrapentylammonium bromide ( $\text{Pen}_4\text{NBr}$ ) in methanol+acetonitrile mixtures in order to supplement our earlier volume studies.

## Experimental

The purifications of the solvents-methanol and acetonitrile, and those of the electrolytes have been described in chapter II.

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

The densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with triply distilled water and benzene. The temperature of the bath was controlled to  $\pm 0.01$  K. Details have been described earlier (chapter H).

Sound velocities ( $u$ ) were measured using a single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 5 MHz which was calibrated with water, methanol and acetonitrile at 298.15 K. The maximum uncertainty in the velocity measurements in all cases was  $\pm 0.03\%$ .

The solvent properties are reported in Table 1.

## Results

The isentropic compressibility of each electrolyte solution was calculated from the ultrasonic velocity ( $u$ ) and density ( $\rho$ ) using the equation :

$$K_s = u^{-2} \rho^{-1} \quad (1)$$

The isentropic compressibilities are found to decrease with increasing solute concentration for all the salts. The addition of electrolyte lowers the compressibility of the solvent due to orientation of the solvent molecules around the incorporated ions, which normally increases the internal pressure.

The apparent molar isentropic compressibilities,  $K_o$  of all the electrolytes in different methanol-acetonitrile mixtures have been calculated using the equation :

$$K_o = [ 1000 (\beta\rho_o - \beta_o\rho) / (m\rho\rho_o) ] + M\beta_o\rho_o^{-1} \quad (2)$$

where  $m$  is the molality of the solution,  $M$  is the molar mass (g.mol<sup>-1</sup>) of the solute,  $\beta_o$  and  $\beta$  are the isentropic compressibilities of the pure solvent and solution, and  $\rho_o$  and  $\rho$  are densities of pure solvent and solution respectively.

The ultrasonic velocities ( $u$ ), isentropic compressibilities ( $K_s$ ), and apparent molar isentropic compressibilities ( $K_\phi$ ) of the salts as a function of concentration in various methanol+acetonitrile mixtures at 298.15 K are given in Table 2.

The limiting apparent molar isentropic compressibilities ( $K_\phi^0$ ) of the electrolytes were obtained from the extrapolation of the linear plots of  $K_\phi$  vs.  $m^{1/2}$  by the method of least-squares using the relationship :

$$K_\phi = K_\phi^0 + A_\phi m^{1/2} \quad (3)$$

Here  $A_\phi$  is the experimental slope. Plots of  $K_\phi$  vs.  $m^{1/2}$  are found to be linear in all cases. The experimental  $K_\phi^0$  and  $A_\phi$  values are reported in Table 3.

## Discussion

Table 3 shows that the  $K_\phi^0$  values in acetonitrile and in methanol+acetonitrile mixtures are negative for  $\text{Et}_4\text{NBr}$  and  $\text{Pr}_4\text{NBr}$ , while these are positive for the other two electrolytes,  $\text{Bu}_4\text{NBr}$  and  $\text{Pen}_4\text{NBr}$ .

Also included in this Table are the  $K_\phi^0$  values for  $\text{Et}_4\text{NBr}$ ,  $\text{Pr}_4\text{NBr}$ ,  $\text{Bu}_4\text{NBr}$  and  $\text{Pen}_4\text{NBr}$  in acetonitrile at 298.15 K obtained from the literature<sup>6</sup>.

Since there is no reliable method for the division of  $K_\phi^0$  values into ionic contributions in the methanol+acetonitrile mixed solvent systems, it was not possible to obtain the ionic  $K_\phi^0$  values in these solvents. However, from a careful examination of the various factors which influence the apparent molar isentropic compressibilities, some important generalisations can be made regarding the behaviour of the constituting ions in the mixed solvent media.

From our conductivity studies (chapter VIII), it has been established that these tetraalkylammonium ions are scarcely solvated whereas the bromide ion is strongly solvated in methanol+acetonitrile mixtures.

Owing to high surface charge density on the bromide ion, significant electrostriction of the solvent molecules will occur around it. This will cause loss of solvent compressibility thus resulting in a negative  $K_{\phi}^0$  value for this ion. On the other hand, the probability of such type of electrostriction around the tetraalkylammonium ions (with lower surface charge density on them) is, however, less and becomes highly unlikely with increasing size of the tetraalkylammonium ions. These cations could have some intrinsic compressibility arising from some free space present in solution between the ions and the solvent molecules and / or from conformational changes in the structure of the tetraalkylammonium cations. For a large tetraalkylammonium ion, a positive  $K_{\phi}^0$  value is expected due to changes of configuration from long chains into a coiled or spherical configuration by the application of pressure from the ultrasonic waves. The effect should decrease with decreasing size of the tetraalkylammonium cation. This later-mentioned effect for the ttrabutylammonium and tetrapentylammonium predominate over the electrostriction effect of the bromide ion, thus making the  $K_{\phi}^0$  value for  $\text{Bu}_4\text{NBr}$  and  $\text{Pen}_4\text{Br}$  positive. For  $\text{Et}_4\text{Br}$  and  $\text{Pr}_4\text{Br}$ , on the other hand, the electrostriction effect of the bromide ion is playing the major role which makes the  $K_{\phi}^0$  values for these salts negative.

The  $K_{\phi}^0$  value for all these electrolytes in the methanol-acetonitrile mixtures decreases with increasing methanol content. It has been established earlier (chapter V) that when methanol is added to acetonitrile, some of the hydrogen bonds in methanol cleaves followed by the formation of hydrogen bonds between acetonitrile and methanol molecules. This results in a more compact structure compared to pure acetonitrile. The mixtures will, therefore, become more and more compressible with the increase in methanol concentration. This is reflected in the  $K_{\phi}^0$  values of the electrolytes in the mixed solvent media.

## References

1. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions*, Reinhold, New York, Chapter 8, 1943.
2. C. Tanford, *Hydrophobic Effect, Formation of Micelles & Biological Membranes*, Wiley-Interscience, New York, 1980
3. E. Vikingstad, *Aggregation Process in Solutions*, Ed. E. Wyn-Janes and J. Gormally, Elsevier, Amsterdam, p. 100, 1983.
4. R. W. Gurney, *Ionic Processes in Solutions*, McGraw Hill, New York, 1954.
5. J. E. Desnoyers, M. Arel, G. Perron and C. Jolicoeur, *J. Phys. Chem.* **73**, 3347, 1969.
6. I. Davidson, G. Perron and J. E. Desnoyers, *Can. J. Chem.*, **59**, 2212, 1981.

**Table 1. Solvent Properties of Methanol + Acetonitrile Mixtures at 298.15 K<sup>a</sup>**

	x = 0.20	x = 0.40	x = 0.60	x = 0.80
$\rho_0 / \text{g.cm}^{-3}$	0.78680	0.78465	0.78212	0.77952
$u_0 / \text{m s}^{-1}$	1140.20	1181.64	1215.85	1251.10

<sup>a</sup> x = mole fraction of acetonitrile

**Table 2. Molality (m), Density ( $\rho$ ), Sound Velocity (u), Isentropic Compressibility ( $K_s$ ) and Apparent Molar Isentropic Compressibility ( $K_\phi$ ) for Tetraalkylammonium Bromides in Methanol + Acetonitrile Mixtures at 298.15 K.**

$m / \text{mol kg}^{-1}$	$\rho / \text{g.cm}^{-3}$	$u / \text{m.s}^{-1}$	$K_s / 10^{-6} \text{ bar}^{-1}$	$K_\phi / 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$
$x = 0.20$				
Et <sub>4</sub> NBr				
0.01075	0.78758	1140.91	97.539	13.893
0.02084	0.78830	1141.56	97.420	16.847
0.02557	0.78863	1141.85	97.311	18.210
0.03105	0.78902	1142.20	97.229	19.315
0.03505	0.78930	1142.45	97.138	20.736
0.03992	0.78964	1142.75	96.998	22.174
0.04539	0.79002	1143.09	96.954	22.508
0.05060	0.79038	1143.41	96.850	23.824
0.05626	0.79077	1143.76	96.747	24.999
0.06049	0.79106	1144.02	96.662	25.902
0.06561	0.79141	1144.32	96.545	25.746
Pr <sub>4</sub> NBr				
0.00463	0.78714	1140.50	97.669	-42.463
0.01041	0.78756	1140.88	97.552	-42.216
0.02045	0.78828	1141.51	97.355	-38.014
0.03202	0.78910	1142.22	97.133	-34.499
0.04000	0.78966	1142.71	96.981	-32.953
0.04904	0.79029	1143.25	96.812	-30.889
0.05991	0.79104	1143.86	96.618	-27.589

<sup>a</sup> mole fraction of acetonitrile



Bu<sub>4</sub>NBr

0.01069	0.78161	1140.92	97.539	13.893
0.02196	0.78845	1141.65	97.311	18.210
0.03064	0.78909	1142.20	97.138	20.736
0.03995	0.78977	1142.79	96.954	22.508
0.05073	0.79055	1143.45	96.747	24.999
0.06106	0.79129	1144.11	96.545	25.746

Pen<sub>4</sub>NBr

0.01638	0.78801	1141.45	97.399	69.547
0.02161	0.78839	1141.84	97.286	70.997
0.02479	0.78862	1142.07	97.218	72.287
0.02966	0.78897	1142.43	97.114	73.226
0.04116	0.78979	1143.27	96.870	75.405
0.04526	0.79008	1143.56	96.786	76.448
0.05010	0.79042	1143.90	96.687	77.568
0.05432	0.79073	1144.22	96.595	78.103
0.06055	0.79115	1144.64	96.472	79.321
0.06690	0.79159	1145.08	96.345	80.498

x = 0.40

Et<sub>4</sub>NBr

0.00588	0.78508	1182.05	91.162	-109.739
0.01979	0.78608	1183.00	90.900	-105.268
0.03499	0.78712	1183.97	90.631	-101.199
0.05430	0.78850	1185.25	90.277	-97.123
0.06068	0.78894	1185.66	90.165	-96.103
0.06578	0.78929	1185.96	90.079	-94.559

Pr<sub>4</sub>NBr

0.01024	0.78540	1182.32	91.083	-38.442
0.01883	0.78602	1182.87	90.927	-35.021
0.02499	0.78646	1183.26	90.896	-33.388
0.03203	0.78696	1183.70	90.691	-31.502
0.04582	0.78793	1184.55	90.449	-28.794
0.05502	0.78857	1185.11	90.291	-27.206
0.06515	0.78927	1185.71	90.119	-25.532

Bu<sub>4</sub>NBr

0.00509	0.78504	1181.99	91.176	12.288
0.00984	0.78540	1182.31	91.085	14.333
0.01608	0.78587	1182.72	90.967	17.044
0.01942	0.78612	1182.94	90.905	17.865
0.03114	0.78699	1183.69	90.689	21.131
0.03548	0.78731	1183.96	90.611	22.387
0.05056	0.78841	1184.90	90.341	24.245

Pen<sub>4</sub>NBr

0.01097	0.78547	1182.46	91.054	70.730
0.01980	0.78612	1183.09	90.882	74.689
0.03344	0.78711	1184.06	90.619	77.460
0.03901	0.78751	1184.44	90.514	78.992
0.04996	0.78829	1185.19	90.310	81.074
0.06089	0.78906	1185.93	90.110	82.828
0.06575	0.78940	1186.27	90.019	83.137

$x = 0.60$ 
Et<sub>4</sub>NBr

0.00818	0.78272	1216.45	86.339	-108.584
0.01605	0.78329	1217.00	86.198	-104.165
0.02134	0.78367	1217.37	86.104	-102.671
0.03144	0.78439	1218.07	85.926	-100.406
0.04448	0.78513	1218.96	85.700	-97.867
0.05435	0.78600	1219.62	85.532	-96.020
0.06531	0.78676	122.36	85.346	-94.459

Pr<sub>4</sub>NBr

0.01031	0.78288	1216.55	86.307	-37.758
0.01940	0.78354	1217.15	86.149	-34.983
0.02495	0.78394	1217.51	86.054	-33.497
0.03601	0.78473	1218.21	85.869	-30.651
0.04605	0.78544	1218.84	85.703	-28.740
0.05517	0.78608	1219.41	85.553	-27.344

Bu<sub>4</sub>NBr

0.00978	0.78287	1216.51	86.314	16.353
0.02063	0.78369	1217.22	86.123	19.594
0.02986	0.78438	1217.81	85.964	21.797
0.04027	0.78515	1218.46	85.788	24.060
0.05050	0.78590	1219.09	85.617	25.920
0.05585	0.78629	1219.39	85.533	27.766

Pen<sub>4</sub>NBr

0.01034	0.78290	1216.59	86.299	74.263
0.01935	0.78357	1217.22	86.136	76.609
0.02997	0.78435	1217.93	85.950	79.978
0.03960	0.78505	1218.58	85.782	81.477
0.05017	0.78581	1219.28	85.600	83.706
0.06325	0.78674	1220.10	85.384	85.882

$$x = 0.80$$

Et<sub>4</sub>NBr

0.00963	0.78025	1251.80	81.789	-105.694
0.02007	0.78103	1252.54	81.611	-102.679
0.02587	0.78146	1252.94	81.514	-100.953
0.03225	0.78193	1253.38	81.408	-99.594
0.03552	0.78217	1253.60	81.354	-98.746
0.04086	0.78256	1253.96	81.267	-97.644
0.04456	0.78283	1254.21	81.207	-96.973
0.05186	0.78336	1254.70	81.088	-95.740
0.05421	0.78358	1254.78	81.055	-95.482
0.05962	0.78392	1255.21	80.965	-94.347

Pr<sub>4</sub>NBr

0.01512	0.78066	1252.10	81.707	-34.851
0.02145	0.78113	1252.51	81.605	-33.522
0.03258	0.78195	1253.21	81.428	-30.843
0.04039	0.78252	1253.69	81.306	-29.162
0.04977	0.78320	1254.26	81.162	-27.437
0.05812	0.78380	1254.75	81.036	-25.679

Bu<sub>4</sub>NBr

0.01308	0.78054	1251.96	81.738	17.656
0.01971	0.78105	1252.38	81.630	19.643
0.03034	0.78186	1253.03	81.461	22.707
0.03549	0.78225	1253.35	81.379	23.455
0.04534	0.78299	1253.93	81.226	25.372
0.06000	0.78408	1254.80	81.001	27.807

Pen<sub>4</sub>NBr

0.01092	0.78038	1251.80	81.776	77.225
0.01581	0.78076	1252.10	81.697	79.122
0.03064	0.78190	1252.99	81.462	82.901
0.04158	0.78273	1253.63	81.292	84.979
0.04983	0.78335	1254.10	81.167	86.500
0.05908	0.78404	1254.62	81.028	88.001

**Table 3. Limiting Apparent Molar Isentropic Compressibilities ( $K_\phi^0$ ) and Slope of Eqn. (3) for Tetraalkylammonium Bromides in Methanol + Acetonitrile Mixtures at 298.15 K**

	x = 0.20	x = 0.40	x = 0.60	x = 0.80	x = 1.00 <sup>a</sup>
Et <sub>4</sub> NBr					
$K_\phi^0 / 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$	-121.06	-116.57	-115.19	-114.00	-112.4
$10^4 A_\phi$	88.62	83.80	82.36	80.48	64.0
Pr <sub>4</sub> NBr					
$K_\phi^0 / 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$	-49.84	-46.52	-44.95	-44.73	44.4
$10^4 A_\phi$	86.55	82.51	79.68	77.94	79.6
Bu <sub>4</sub> NBr					
$K_\phi^0 / 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$	5.56	6.57	8.12	8.82	9.4
$10^4 A_\phi$	84.38	81.15	80.54	77.88	82.9
Pen <sub>4</sub> NBr					
$K_\phi^0 / 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$	58.85	62.71	66.08	69.32	71.8
$10^4 A_\phi$	83.00	81.30	78.50	77.03	78.6

<sup>a</sup> from Davidson *et al.*, **59**, 2212, 1981.