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Ultrasonic velocities and isentropic compressibilities of some symmetrical tetraalkylammonium and alkali-metal salts in *N,N*-dimethylacetamide–water mixture at 298.15 K

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Abstract

The ultrasonic velocities of tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr), sodium tetraphenylborate (NaBPh_4), and sodium bromide (NaBr) in *N,N*-dimethylacetamide + water (50% v/v) mixture have been measured in the concentration range $0.01\text{--}0.10\text{ mol dm}^{-3}$ at 298.15 K. Apparent molar isentropic compressibilities (κ_ϕ) of these electrolytes were derived from these data supplemented with their density values. The limiting apparent molar isentropic compressibilities (κ_ϕ^0) have been obtained by the method of extrapolation from the linear plots of apparent molar isentropic compressibilities (κ_ϕ) against the square root of the molal concentration. The limiting apparent molar isentropic compressibility (κ_ϕ^0) values were separated into approximate limiting ionic compressibilities ($\kappa_\phi^0 \pm$) on the basis of the assumption that the limiting ionic compressibility of the bromide ion is zero. The results have been interpreted in terms of electrostriction and penetration effects. © 2004 Elsevier B.V. All rights reserved.

Keywords: Ultrasonic velocity; Apparent molar isentropic compressibility; *N,N*-dimethylacetamide + water mixture; Electrolyte

1. Introduction

The thermodynamic properties (e.g., volume, expansibility, compressibility, heat capacity etc.) are generally convenient parameters for interpreting solute–solute, and solute–solvent interactions occurring in solution phase. The compressibility behavior of solutes, which is the second derivative of the Gibbs energy, is a very sensitive indicator of molecular interactions and can provide useful information about these phenomena [1–8]. Very recently [9], we have reported the results of our compressibility measurements on some selected symmetrical tetraalkylammonium bromides in *N,N*-dimethylacetamide at 298.15 K. The present paper reports the study of the apparent molar isentropic compressibility behavior of some tetraalkylammonium and alkali salts in *N,N*-dimethylacetamide + water (50% v/v) mixture at 298.15 K to elucidate the nature of interactions prevailing in these salt solutions.

2. Experimental

N,N-Dimethylacetamide (G.R.E. Merck, India, >99.5%) was distilled twice in an all-glass distillation set immediately before use and the middle fraction was collected. The purified solvent had a specific conductance of about 10^{-6} S cm^{-1} at 298.15 K. The properties of the purified solvent agree well with the literature values [10]. Triply distilled water with a specific conductance of less than 10^{-6} S cm^{-1} at 298.15 K was used for the preparation of the mixed solvent.

For the preparation of the solution of each salt, a different batch of solvent was used and the properties of the mixed solvent used in each case are recorded in Table 1.

The tetraalkylammonium bromides (Fluka, purissimum) were purified as described in the literature [11]. They were further purified by recrystallization and the two higher homologues (Bu_4NBr and Pen_4NBr) were recrystallized twice [12] to ensure maximum purity. Sodium tetraphenylborate (Fluka, purissimum) was recrystallized from acetone and dried in vacuo at 353.15 K for 72 h. Sodium bromide (Fluka, purum) was dried in vacuo for 72 h and was used

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Table 1

Concentration (c), density (ρ), ultrasonic velocity (u), and apparent molar isentropic compressibility (κ_ϕ) of the electrolyte solutions in *N,N*-dimethylacetamide + water mixture (50% v/v) at 298.15 K

c (mol dm ⁻³)	ρ (g cm ⁻³)	u (cm s ⁻¹)	$10^{10} \kappa_\phi$ (cm ³ mol ⁻¹ bar ⁻¹)	c (mol dm ⁻³)	ρ (g cm ⁻³)	u (cm s ⁻¹)	$10^{10} \kappa_\phi$ (cm ³ mol ⁻¹ bar ⁻¹)
Et ₄ NBr				Pr ₄ NBr			
0.00000	0.99877	173,938	—	0.00000	0.99877	173,938	—
0.00873	0.99922	174,058	-12.74	0.00877	0.99919	174,032	19.90
0.02037	0.99979	174,177	-6.36	0.02046	0.99970	174,130	24.28
0.03201	1.00030	174,284	-1.50	0.03216	1.00020	174,208	28.09
0.05238	1.00120	174,423	4.62	0.05262	1.00100	174,326	32.94
0.07276	1.00210	174,517	9.80	0.07309	1.00170	174,424	37.04
0.10186	1.00320	174,624	15.85	0.10233	1.00270	174,513	41.97
Bu ₄ NBr				PenNBr			
0.00000	0.99854	173,818	—	0.00000	0.99841	173,770	—
0.00897	0.99888	173,880	52.07	0.00877	0.99858	173,840	81.68
0.02094	0.99930	173,954	56.77	0.02047	0.99877	173,929	84.24
0.03290	0.99969	174,020	59.55	0.03217	0.99893	174,010	86.49
0.05385	1.00030	174,117	63.68	0.05264	0.99914	174,139	89.79
0.07479	1.00090	174,189	66.87	0.07310	0.99929	174,253	92.61
0.10470	1.00160	174,274	70.87	0.10235	0.99942	174,400	95.79
NaPh ₄ B				NaBr			
0.00000	0.99853	173,696	—	0.00000	0.99831	173,842	—
0.00890	0.99891	173,575	137.77	0.00939	0.99915	173,815	-13.64
0.02077	0.99939	173,381	144.30	0.02191	1.00020	173,781	-12.28
0.03264	0.99984	173,168	149.14	0.03442	1.00120	173,752	-11.43
0.05341	1.00060	172,753	155.93	0.05633	1.00280	173,720	-10.41
0.07418	1.00130	172,300	161.48	0.07824	1.00440	173,683	-9.57
0.10386	1.00220	171,611	168.17	0.10954	1.00650	173,648	-8.55

without further purification. Because of the hygroscopic nature of these salts, they were stored in a vacuum dessicator over calcium chloride and were dried for 3–4 h at 373.15 K immediately prior to use.

In order to minimize the moisture contamination, all solutions were prepared in a dehumidified room with utmost care. A stock solution (with an approximate concentration of 0.1 mol kg⁻¹) for each salt was prepared by mass and the working solutions were prepared by mass dilution from the stock. The conversion of molality to molarity was performed using the density values, measured with an Ostwald–Sprenkel type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 0.1 cm.

The velocities of sound were measured with an accuracy of 0.3%, using a single-crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at 4 MHz. The interferometer was calibrated with water, methanol and benzene. The temperature stability was maintained within ± 0.01 K by circulating thermostated water around the measuring cell.

3. Results and discussion

Adiabatic compressibility coefficients were derived from the following equation

$$\kappa_S = \frac{1}{u^2 \rho} \quad (1)$$

where ρ is the density and u is the velocity of sound in the solution. The apparent molar isentropic compressibility (κ_ϕ) of the electrolyte solutions was then calculated from the relationship

$$\kappa_\phi = \frac{M\kappa_S^0}{\rho_0} + \frac{1000(\kappa_S\rho_0 - \kappa_S^0\rho)}{m\rho\rho_0} \quad (2)$$

where m is the molal concentration of the salt solution and the other symbols have their usual significance.

The molarity (c), the density (ρ), the sound velocity (u), and the apparent molar isentropic compressibility (κ_ϕ) of the electrolyte solutions at 298.15 K are reported in Table 1.

The limiting apparent molar isentropic compressibilities (κ_ϕ^0) have been obtained (as shown in Fig. 1) by extrapolating the linear plots of κ_ϕ vs. the square root of the molal concentration of the solutes to zero concentration by the method of least-squares

$$\kappa_S = \kappa_S^0 + S_K \sqrt{m} \quad (3)$$

where S_K is the experimental slope. The values of the limiting apparent molar isentropic compressibilities (κ_ϕ^0), and the experimental slopes (S_K) are listed in Table 2.

The limiting apparent molar isentropic compressibilities (κ_ϕ^0) of the tetraalkylammonium salts investigated here are found to increase in the order:



It is also interesting to note that the κ_ϕ^0 values of Et₄NBr and NaBr are only partly negative while those of the other three

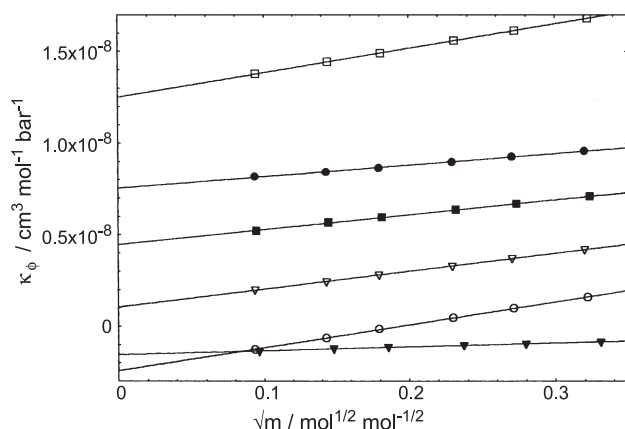


Fig. 1. Plot of apparent molar isentropic compressibilities against the square root of the molal concentrations of solutions of NaBr, Et₄NBr, Pr₄NBr, Bu₄NBr, Pen₄NBr and NaPh₄B in *N,N*-dimethylacetamide + water mixture (50% v/v) at 298.15 K (from bottom to top).

tetraalkylammonium bromides and NaBPh₄ are found to be positive.

The negative κ_{ϕ}^0 values of the electrolytes can be interpreted in terms of a loss of compressibility of the solvent due to the presence of these solutes in solution. The positive κ_{ϕ}^0 values, on the other hand, indicate an increase in the compressibility of the solution compared to the pure solvent.

Several factors may contribute to the compressibility of the electrolyte solutions and we will now examine the important factors in order to elucidate the effects of the solutes on the solvent structure and their role on compressibility.

The bromide ion is found to remain unsolvated in the mixed *N,N*-dimethylacetamide + water system under investigation from our conductivity study [13]. Moreover, it is not a molecular ion, thus ruling out the possibility of having intrinsic compressibility. This ion, therefore, does not influence the compressibility of the medium. The sodium ion, however, is found to be solvated from conductivity study [13]. This ion will, therefore, cause a loss of solvent compressibility resulting from the electrostriction of the solvent molecules around the ion.

Most of the interpretations of the limiting apparent molar isentropic compressibilities in terms of solvation effects [1,2,14–18] assume that κ_{ϕ}^0 of unsolvated ions is negligibly small, although Conway and Verrall [1] recognized that large organic ions could have some intrinsic compressibility due to the intermolecular free space which makes the medium more compressible. This could also be expected for the unsolvated large tetraalkylammonium and tetraphenylborate ions investigated in this study.

Another effect which is possible for large organic ions is the penetration of the solvent molecules within the intraionic free space. This is the result of the interaction of the positively charged nitrogen central atom of the tetraalkylammonium ions (or of the negatively charged boron central atom in the case of the tetraphenylborate ion) with the neighboring

solvent molecules. This is essentially an electrostriction effect and causes constriction of the solution volumes, thus resulting in a more compact and, hence, a less compressible medium.

In view of the factors delineated above which control the compressibility of the electrolyte solutions, it can be concluded that, since the bromide ion has no influence on the compressibility of the solution, the interplay of the other factors would actually determine the overall compressibility of the solution.

The negative limiting apparent molar isentropic compressibility value for Et₄NBr solution can be attributed to the predominance of the penetration effect over the effect of the intrinsic compressibility of the tetraethylammonium ions. For Pr₄NBr, Bu₄NBr, and Pen₄NBr solutions exhibiting positive κ_{ϕ}^0 values, on the other hand, the effect of intrinsic compressibility of the large tetraalkylammonium ions overrides the penetration effect. This observation is quite expected since the extent of penetration of the solvent molecules should be maximum for tetraethylammonium ion with the lowest crystal radius and hence the highest surface charge density among the tetraalkylammonium ions studied here. For higher homologues, the surface charge density decreases with the radius, thus lowering the possibility of penetration.

For NaBr solution, however, the negative κ_{ϕ}^0 value arises from the loss of solvent compressibility caused by the sodium ions.

The positive κ_{ϕ}^0 value for NaBPh₄ solution indicates that the intrinsic compressibility of the tetraphenylborate ion is playing the major role when compared to the penetration effect of this ion and the electrostriction effect of the sodium ion.

In order to investigate the behavior of the individual ions comprising these electrolytes, it is necessary to split the limiting apparent molar isentropic compressibilities into their ionic components. However, there exists no reliable method for the division of κ_{ϕ}^0 values into ionic contributions. Millero [18] has suggested a method for the division of the limiting partial molar volumes of the “reference electrolyte” tetraphenylarsonium tetraphenylborate (Ph₄As⁺Ph₄B[−]) into ionic parts, but such a method cannot be used here since we do not know the ratio of the compressibilities of the pure (solid or gaseous) ions. A similar model based on another “reference electrolyte” tetrabutylammonium tetraphenylborate (Bu₄N⁺Ph₄B[−]) originally used for the splitting of the

Table 2
Limiting apparent molar isentropic compressibilities (κ_{ϕ}^0), and the experimental slopes (S_K) of the electrolyte solutions in *N,N*-dimethylacetamide + water mixture (50% v/v) at 298.15 K

Electrolyte	$10^{10} \kappa_{\phi}^0$ (cm ³ mol ^{−1} bar ^{−1})	$10^{10} S_K$ (cm ³ mol ^{−3/2} kg ^{1/2} bar ^{−1})
Et ₄ NBr	−24.41 ± 0.20	125.63 ± 0.92
Pr ₄ NBr	10.49 ± 0.20	98.16 ± 0.93
Bu ₄ NBr	44.72 ± 0.29	81.21 ± 1.31
Pen ₄ NBr	75.40 ± 0.31	63.30 ± 1.41
NaPh ₄ B	124.83 ± 0.83	134.44 ± 0.38
NaBr	−15.09 ± 0.01	19.73 ± 0.05

viscosity B -coefficients of electrolytes into the contributions from individual ions was attempted [19] to split the κ_ϕ^0 values. This approach is inappropriate since it assumes that the ratio of the volumes of these ions is equal to the ratio of their compressibilities. However, the compressibilities of these large ions are not a simple function of their volumes. The extrapolation method as suggested by Conway et al. [20] for volumes can also not be used for the division of the κ_ϕ^0 values in view of the large contribution of the compressibilities of the tetraalkylammonium ions which does not seem to be a simple function of the size of the ion. Interestingly, we tried both the extrapolation method and the “reference electrolyte” method using tetrabutylammonium tetraphenylborate ($\text{Bu}_4\text{N}^+\text{Ph}_4\text{B}^-$) to perform the division of the κ_ϕ^0 values into ionic components. However, unfortunately, the results obtained by these two methods differ appreciably. The ionic κ_ϕ^0 values obtained from the extrapolation method for Et_4N^+ , Pr_4N^+ , Bu_4N^+ , Na^+ and Br^- ions are, respectively, 13.85, 48.75, 82.98, 113.66, 23.17 and $-38.26 \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$, whereas those obtained from the “reference electrolyte” method are, respectively, 76.55, 111.45, 145.68, 176.36, 38.96, 85.86 and $-100.96 \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$. The method used by Davidson et al. [3] for acetonitrile, which assumes the limiting ionic compressibility of the tetraphenylborate ion to be zero is also not appropriate as the tetraphenylborate ion is large (its crystal radius is 0.535 nm), and therefore, its intrinsic compressibility contribution cannot be taken as zero.

Under these circumstances, and also in view of the compressibility behavior of the bromide ion in the mixed solvent system under study as discussed above, the choice of $\kappa_\phi^0(\text{Br}^-) = 0$ seems to be the best at this moment. Ionic κ_ϕ^0 values based on this assumption for the tetraalkylammonium ions are equal to the limiting molar isentropic compressibilities of the corresponding tetraalkylammonium bromide salts while those for the Na^+ , Br^- and Ph_4B^- ions are respectively, -15.09 , 0.00 and $139.92 \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$, which fit quite well with the discussion made above on the basis of the κ_ϕ^0 values of the electrolytes as a whole thus substantiating the present protocol for the division of limiting apparent molar isentropic compressibilities of these electrolytes in N,N -dimethylacetamide + water mixed solvent system.

4. Conclusion

Apparent molar isentropic compressibilities of some symmetrical tetraalkylammonium and alkali-metal salts in

N,N -dimethylacetamide + water (50% v/v) mixture have been obtained from precise ultrasonic velocity measurements at 298.15 K. The limiting apparent molar isentropic compressibility values were obtained by the method of extrapolation of the linear plots of the limiting apparent molar isentropic compressibility versus molal concentration. The effect of penetration of the solvent molecules into the intraionic free space of the tetraethylammonium ions has been found to predominate over the effect of their intrinsic compressibility for tetraethylammonium bromide solution. For sodium bromide solution, however, the negative κ_ϕ^0 value arises from the loss of solvent compressibility caused by the sodium ions. For tetrapropylammonium bromide, tetrabutylammonium bromide, and tetrapentylammonium bromide solutions exhibiting positive κ_ϕ^0 values, on the other hand, the effect of intrinsic compressibility of the large tetraalkylammonium ions overrides the penetration effect. The positive κ_ϕ^0 value for sodium tetraphenylborate solution indicates that the intrinsic compressibility of the tetraphenylborate ion is playing the major role when compared to the penetration effect of this ion and the electrostriction effect of the sodium ion.

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