Studies on Ion-Solvent and Ion-Ion Interactions and Adiabatic Compressibilities of Some Bromide Salts in Methanol at Different Temperatures

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Abstract. The densities, viscosities and ultrasonic speeds of some tetraalkyl and monovalent electrolytes, such as tetraethylammonium bromide, tetrapropylammonium bromide, tetrabutylammonium bromide, lithium bromide, sodium bromide and ammonium bromide, have been determined in methanol at 303, 308, 313, 318 and 323 K. The limiting apparent molar volumes (V_ϕ^0) and experimental slopes (S_v^*), supplemented with density data, have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The parameters B and A, obtained from the viscosity data analyzed using the Jones-Dole equation, have also been interpreted in terms of solute-solute and solute-solvent interactions, respectively. The results show that these electrolytes have structure-making capacities in this solvent. The compressibility data supplemented with the ultrasonic speeds explain the electrostriction of the solvent molecules around the positive ions.

Keywords: solute-solvent interaction, solute-solute interaction, adiabatic compressibility, structure-making capacities, electrostriction, apparent molar volumes

Introduction

Studies on the thermodynamics, transport properties, and ultrasonic speeds of different electrolytes in different solvents are of great importance to obtain information on the behaviour of ions in solutions. Recent years have, therefore, witnessed increased interest in this topic, as is evident from numerous publications in this field (Roy and Jha, 2001; Roy, 2000; Janz, 1973). In the present work, an attempt has been made to provide an unequivocal interpretation of solute-solvent and solute-solute interactions, and adiabatic compressibilities for some tetraalkylammonium and alkali metal bromides in methanol through the measurements of their densities, viscosities and ultrasonic speeds at various temperatures. Methanol is a protic solvent, which is known to be extensively self-associated through hydrogen bonding in the pure state (Pikkarainen, 1988). The importance of this solvent lies in the fact that it has found its applications in many industrial processes and also as a solvent medium for various electrochemical investigations (Das and Hazra, 1995).

Materials and Methods

Methanol (E. Merck, India, Uvasol grade 99.5% pure) was dried over 3 Å molecular sieves and distilled fractionally. The middle fraction was collected and redistilled. The purified solvent had a density of 0.78140 g/cm³ and a viscosity of 0.51105

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cp at 303 K. These values agreed well with the values reported in literature (Saha and Hazra, 1995; Doe *et al.,* 1990). The purities, as checked by gas chromatography, were found to be 99.8% for methanol. Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were further purified as described earlier (Muhuri and Hazra, 1996). Lithium, sodium and ammonium bromides were of purum or puriss grade and were further purified as described earlier (Roy *et al.,* 1993a). A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution. The conversion of molality into molarity was done using the density values (Shoemaker and Garland, 1967).

The densities (ρ) were measured with an Oswald Sprengel type pycnometer having a bulb volume of 25 cm³ and an internal dia of the capillary of about 0.1 cm. The pycnometer was calibrated at (303, 313 and 323 K) with double distilled water and benzene. The pycnometer was equilibrated with the test solution in a waterbath maintained at ±0.01K of the desired temperature by means of a mercury -in- glass thermoregulator and the temperature was determined by a calibrated 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. The average of triplicate measurements was taken into account. The density values were reproducible to ±3 x 10⁻⁵ g/cm³. Details have been discussed earlier (Nikam and Hasan, 1988).

The viscosities were measured by means of suspended level Ubbelohde viscometer (Suindells and Godfray, 1952) at the desired temperature (accuracy ±0.01K). The precision of the viscosity measurement was 0.05%. Details have been described earlier (Roy and Hazra, 1994).

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

Results and Discussion

The apparent molar volumes (V_ϕ) were calculated from the solution densities using the following relation:

$$V_\phi = M/\rho_0 - 10^3 \, (\rho - \rho_0)/c \, \rho_0 \qquad (1)$$

where:
M = molecular weight of the solute
c = molarity of the solution
other symbols = usual significance

Application of the Redlich-Meyer equation was not possible due to lack of data on the compressibility and pressure variation of the dielectric constant, necessary to calculate the theoretical slopes (S_v^*). Thus, the limiting apparent molar volumes (V_ϕ^0) and experimental slopes (S_v^*) were determined by applying the least square method to the plots of V_ϕ versus $c^{1/2}$ using the Masson equation (Masson, 1929):

$$V_\phi = (V_\phi^0) + S_v^* \, c^{1/2} \qquad (2)$$

where:
the symbols have their usual significance

The values of V_ϕ^0 and S_v^* are reported in Table 1. The S_v^* values, as shown in Table 1, were negative for all the investigated salts, which increased with the rise in temperature. This indicates the presence of weak solute-solute interactions. These interactions, however, increased with the increase of temperature, which may be attributed to the decrease in solvation of ions, which means that more and more solute was accommodated in the void space left in the packing of large associated solvent molecules with the increase in temperature.

It may be further noted from Table 1 that the values of V_ϕ^0 were positive and large for all the salts studied in methanol at various temperatures, indicating the presence of strong solute-solvent interaction. These interactions were further weak-

Table 1. Limiting apparent molar volume V_ϕ^0 (cm^3/mol), experimental slope S_v^* (cm^3/dm$^{1/2}$/mol$^{3/2}$), and values of parameters A (dm$^{3/2}$/mol$^{1/2}$) and B (dm^3/mol) of the Jones-Dole equation for some bromide salts in methanol at various temperatures

Temp (K)	V_ϕ^0 (cm^3/mol)	S_v^* (cm^3/dm$^{1/2}$/mol$^{3/2}$)	B (dm^3/mol)	A (dm$^{3/2}$/mol$^{1/2}$)
LiBr				
303	96.441	-168.902	1.069	-0.021
308	95.181	-167.377	1.016	-0.006
313	93.915	-166.942	0.820	-0.006
318	91.757	-165.140	0.820	0.003
323	89.823	-164.648	0.813	0.013
NaBr				
303	54.661	-81.735	0.704	0.058
308	44.630	-66.371	0.034	0.067
313	37.416	-65.389	0.621	0.103
318	33.049	-64.278	0.502	0.123
323	29.747	-62.968	0.484	0.132
NH$_4$Br				
303	64.559	-69.972	0.426	0.105
308	62.573	-67.936	0.416	0.113
313	61.208	-66.265	0.406	0.129
318	60.081	-65.794	0.399	0.152
323	58.388	-64.494	0.543	0.109
Et$_4$NBr				
303	164.390	-36.977	0.498	0.055
308	162.516	-32.499	0.292	0.068
313	160.804	-31.406	0.280	0.076
318	160.153	-30.033	0.278	0.130
323	159.864	-29.255	0.165	0.133
Pr$_4$NBr				
303	235.089	-32.562	0.308	0.282
308	231.441	-31.468	0.188	0.285
313	230.733	-31.366	0.187	0.398
318	228.119	-30.673	0.181	0.504
323	226.403	-29.377	0.175	0.521
Bu$_4$NBr				
303	302.795	-91.611	0.756	0.092
308	291.782	-79.549	0.732	0.164
313	288.713	-76.452	0.657	0.197
318	285.621	-73.758	0.362	0.465
323	280.457	-70.344	0.358	0.471

LiBr: lithium bronide; NaBr: sodium bromide; NH$_4$Br: ammonium bromide; Et$_4$NBr: tetraethylammonium bromide; Pr$_4$NBr: tetrapropylammonium bromide; Bu$_4$NBr: tetrabutylammonium bromide

ened with the rise in temperature, suggesting more electrostrictive solvation at higher temperatures. Similar results were reported for some 1:1 electrolytes in aqueous DMF (Roy and Jha, 2001; Calvente *et al.,* 1994). The variation of V_ϕ^0 with temperature of the salts in the solvents, followed the polynomial equation over the temperature range under the investigation:

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \qquad (3)$$

The coefficients of a's are presented in Table 2. The apparent molar expansibilities, calculated from the equation, $\phi_E^0 = [\delta V_\phi /\delta T]_p$, for all the salts are given in Table 3. The ϕ_E^0 values for all the salts in methanol solutions increased with the increase of temperature. The increase in magnitude per degree temperature was positive, indicating thereby that the behaviour of these salts in methanol was similar to that of symmetrical quarternary ammoniumalkyl salts in water. This can also be ascribed to 'caging effect' (Mollero, 1972).

It has been emphasized by some workers during the past few years that S_v^* is not the sole criterion for determining the structure-making/breaking nature of any electrolyte. Hepler (1969) developed a technique of examining the sign of $(\delta^2 V_\phi^0 \delta T^2)$ for various electrolytes in terms of long range structure-making and structure-breaking capacities of the electrolytes in methanol solutions using the general thermodynamic expression:

Table 2. Values of various coefficients of equation (3) $[V_\phi^0 = a_0 + a_1 T + a_2 T^2]$ for different salts

Salt*	a_0/cm³/mol	a_1/cm³/mol/K	a_2/cm³/mol/K²
LiBr	1537.253	-9.113	0.014
NaBr	5118.515	-31.221	0.047
NH₄Br	417.655	-1.969	0.002
Et₄NBr	1527.765	-8.508	0.013
Pr₄NBr	379.404	-0.515	0.001
Bu₄NBr	3492.139	-19.352	0.029

* refer Table 1 for nomenclature of salts

Table 3. Limiting apparent molar expansibility ϕ_E^0 (cm³/mol/K) for some bromide salts in methanol at different temperatures

Salt	303	308	313	318	323	(ϕ_E^0)
LiBr	-0.396	-0.252	-0.108	0.035	0.178	(+)ve
NaBr	-2.203	-1.724	-1.245	-0.766	-0.288	(+)ve
NH₄Br	-0.361	-0.335	-0.308	-0.282	-0.255	(+)ve
Et₄NBr	-0.490	-0.358	-0.226	-0.094	-0.038	(+)ve
Pr₄NBr	-0.436	-0.435	-0.434	-0.433	-0.431	(+)ve
Bu₄NBr	-1.699	-1.408	-1.116	-0.825	-0.534	(+)ve

* refer Table 1 for nomenclature of salts; $\phi_E^0 = (\delta^2 V_\phi^0 / \delta T^2)_p$

$$(\delta c_p / \delta p)_T = - (\delta^2 V_\phi^0 \delta T^2)_p \qquad (4)$$

It has been deduced on the basis of this expression that the structure-making electrolytes should have positive value, whereas structure-breaking electrolytes should have negative value.

In the present investigation, it was found that the value of $(\delta^2 V_\phi^0 \delta T^2)_p$ was positive for all the salts studied (Table 3), suggesting thereby that the salts acted as structure-makers in this solvent medium.

The viscosity data of solutions for various electrolytes in methanol have been analyzed using the Jones-Dole equation (Jones and Dole, 1929):

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc$$
$$(\eta/\eta_0 - 1)/c^{1/2} = A + Bc^{1/2} \qquad (5)$$

where:
$\eta = (Kt - L/t) \times \rho$

where:

η and η_0 = viscosities of methanol and solutions, respectively
A and B = contacts
p = the density of the solvent
K and L = constants for a particular viscometer

The values of A and B were estimated by computerized least squares method (Table 1), which show that the values of A were either negative or very small for all the salts studied in methanol at various temperatures, thereby showing the presence of weak solute-solute interactions. In other words, these results indicate that all the salts mixed ideally with water and there was a perfect solvation of these molecules resulting in either the absence or weak solute-solute interactions. It is also evident from Table 1 that the B-coefficients for all the salts studied in methanol at various temperatures were positive, thereby suggesting the presence of strong solute-solvent interactions. The value of B-coefficients also decreased with the increase in temperature for the solutions of all salts, thereby showing that the solute-solvent interactions were further weakened with the increase in temperature, which may be attributed to the decrease in solvation of ions by methanol. A similar result was reported in the case of a study of ion-solvent interactions of some tetraalkyl and multivalent electrolytes in propylene glycol + water mixtures (Parmar and Chauhan, 1995).

It has been reported by a number of workers that dB/dT is a better criterion for determining the structure-making/braking nature of any electrolyte rather than simply the B-coefficient values. It may be noted from Table 1 that the values of B were positive and decreased with the rise in temperature (negative

dB/dT), suggesting structure-making tendencies of all the salts in this solvent system. These conclusions are in excellent agreement with that drawn from $(\delta^2 V_\phi^0/\delta T^2)_p$, as discussed above.

Adiabatic compressibility coefficients β, were derived from the following relation:

$$\beta = 1/(u^2\rho) \quad\quad\quad (6)$$

where:

ρ = density of solution
u = ultrasonic speed in the solution

The apparent molar adiabatic compressibilities (ϕ_k) of the solutions were calculated from the following equation:

$$\phi_k = 1000/m\rho\rho_0(\beta\rho_0 - \beta_0\rho) + \beta \cdot M/\rho_0 \quad\quad (7)$$

The limiting apparent molar adiabatic compressibilities (ϕ_k^0) and experimental slopes (S_v^*) were obtained by extrapolating the plots of ϕ_k versus the square root of molar concentration (vm) of the electrolyte by the computerized least squares method using the following equation (Choudhury and Roy, 2004):

$$\phi_k = \phi_k^0 + S_k^* \cdot m^{1/2} \quad\quad\quad (8)$$

The values of ϕ_k^0 and S_k^* at various temperatures are recorded in Table 4. It may be seen that all the salts studied had negative limiting apparent molar adiabatic compressibilities (ϕ_k^0), which increased in the following order: $Bu_4N^+ > Pr_4N^+ > Et_4N^+$ for tetraalkylammonium salts and $Li^+ > Na^+ > NH_4^+$ for common salts. Negative ϕ_k^0 values of the salts were interpreted in terms of the loss of compressibility of methanol due to electrostrictive forces in the vicinity of the ions. The extent of electrostriction was maximum in the case of Bu_4N^+ ion for tetraalkyl ammonium salts and in the case of Li^+ ion for common salts. This was so, since in the case of larger R_4N^+ ion,

Table 4. Limiting apparent molal adiabatic compressibility (ϕ_k^0) and experimental slope (S_k^*) of some bromide salts at various temperatures

Salts*	$\phi_k^0\ 10^9$			$S_k^*\ 10^9$		
	m^3/ mol/Pa			m^3/mol$^{3/2}$/Pa/kg$^{1/2}$		
	303 K	313 K	323 K	303 K	313 K	323 K
LiBr	-0.994	-1.453	-1.003	0.973	1.727	1.048
NaBr	-1.172	-1.255	-1.013	1.161	1.271	0.979
NH_4Br	-1.274	-0.717	-0.779	1.253	0.575	0.704
Et_4NBr	-1.213	-0.895	-0.861	1.200	0.938	1.234
Pr_4NBr	-1.031	-0.736	-0.602	1.005	1.041	0.991
Bu_4NBr	-0.987	-0.439	-0.600	1.283	0.536	0.935

*refer Table 1 for nomenclature of salts

higher was the penetration of the solvent molecules into the space between the coiled alkyl chains attached to the nitrogen atom, and in the case of smaller Li^+ ion, the stronger was the solute-solvent interactions (Das and Hazra, 1992). This, obviously, causes constriction in the solution volumes.

The positive small values of the limiting slopes, S_k^* (Table 4) indicate the existence of weak solute-solute interactions in methanol. The possible explanation for the positive slopes in methanol may be that the ionic association would become quite appreciable in this medium as the concentration of the electrolyte increased. As a consequence, contraction of the solvent would be gradually lowered with increasing concentration of the electrolytes resulting in a net positive volume change per mole of the added solute. The S_k^* values increased as the size of the cation increased. Exactly the same conclusion was drawn from conductometric studies (Roy *et al.,* 1993b).

Acknowledgment

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