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## THERMODYNAMIC AND ULTRASONIC STUDIES OF SOME AMMONIUM SALTS IN AQUEOUS POLAR AND NON-POLAR SOLVENTS AT 303K

T. Sumathi\* and U. Gnanasheela

Department of Physics, DDE, Annamalai University, Annamalai Nagar – 608 002, Tamilnadu, India.

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### ABSTRACT

In the present communication, experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and speeds of sound ( $U$ ) of ammonium salts in aqueous 2-methoxyethanol and 1,4-Dioxane in 10, 20, 30 and 40% were measured at 303K. From these experimental data, acoustical parameters such as adiabatic compressibility ( $\beta$ ), free volume ( $V_f$ ), internal pressure ( $\pi_i$ ), Falkenhagen coefficient A and Jones-Dole coefficient B have been calculated. The results are interpreted in terms of strong/weak ion-ion and solute-solvent interaction and the structure breaking/making abilities of ammonium salts with polar and non-polar solvents.

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### INTRODUCTION

Knowledge of the state of association of electrolytes in solution and of their interaction with the solvent molecules is essential for a proper understanding of their behavior in solution. The study of intermolecular interaction plays an important role in the development of molecular sciences. A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like infrared, Raman effect, nuclear magnetic resonance, dielectric constant, ultraviolet and ultrasonic method. Ultrasonic investigation of liquid mixtures consisting of polar and non-polar components is of considerable importance in understanding intermolecular interaction between the component molecules and they find application in several industrial and technological processes (Arul and Palaniappan, 2005). The ultrasonic velocity studies carried out in the present investigation reveal that the velocity varies with concentration due to the solute-solvent interactions through molecular association. The existing particle-particle resistance initiates some more interactions and this is supported by the measured parameters.

Study of electrolytes in alkoxy ethanol solution is much interesting because of their common use as solvent of various industrial processes. The investigation regarding the molecular association in organic ternary mixtures having alcohol as one of the components of particular interest, since, alcohols are highly polar and self associated through hydrogen bonding in pure state

(Kannappan et al., 2008). Another solvent 1,4-Dioxane is a aprotic and non polar solvent, which has two lone pairs of electrons on each of these two hydrogen atoms. The 1,4-Dioxane-water mixtures is a well studied solvent of binary mixtures of water. These systems are important in fundamental research and technology because properties such as viscosity, free volume, internal pressure etc, can be continuously changed with solvent composition (Akhtar, 2007).

In this paper an attempt has been made to reveal the nature of various type of interactions prevailing in solutions of some ammonium salts in 2-methoxyethanol-water and 1,4-Dioxane-water at 303K by using volumetric measurements. The accurate measurement of ultrasonic velocity, density, viscosity and other derived parameters such as adiabatic compressibility ( $\beta$ ), free volume ( $V_f$ ), internal pressure ( $\pi_i$ ) etc., are useful parameters in elucidating the state of affairs in a solutions. There are various types of interaction that exist between the components of electrolytes; the solute-solvent interactions are more significant.

### MATERIALS AND METHODS

All the chemicals used in present work are analytical (AR) reagent grade of minimum assay 99.9% obtained from Aldrich, E-Merck, Germany and Sd Fines chemicals, India and are used as such without further purification. Water used in these experiments was deionized, distilled and degassed prior to making solutions. The required quantity of ammonium salts for give molality was dissolved in binary mixture of aqueous

\* Corresponding author: +91

E-mail address: tsumathi92@yahoo.com.

2-methoxyethanol and 1,4-Dioxane and similar procedure has been adopted for different molalities of ammonium salts. For each concentration, the mass of the ammonium salts can be measured using electronic digital balance having an accuracy of  $\pm 0.1$  mg (Model: SHIMADZU AX-200). The speeds of sound waves were obtained using ultrasonic interferometer (model: F:81, M/s Mittal Enterprises, New Delhi) at a fixed frequency of 3MHz with an accuracy of  $\pm 2$   $\text{ms}^{-1}$ . An Ostwald's viscometer which is of 10 ml capacity is used for the viscosity measurement of liquid mixtures. The viscometer is calibrated with fresh conductivity water immersed in the water bath, which is kept at the experimental temperature. The time flow of solution are measured with digital stop clock having an accuracy of 0.01s (model: Racer Hs-10W) of the bath. By knowing the flow time of reference liquid (water), the viscosity of the mixture can be determined. The measured viscosity values are accurate to  $\pm 0.0001$   $\text{Nsm}^{-2}$ . A specific gravity bottle with 5 ml capacity is cleaned well and dried and filled with reference liquid (conductivity water) and then suspended in temperature controlled water bath. An electronically digital operated constant temperature bath (Raaga Industries, Chennai-61) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature.

### RESULTS AND DISCUSSION

The various acoustical parameters such as adiabatic compressibility ( $\beta$ ), free volume ( $V_f$ ), internal pressure ( $\pi_i$ ), Falkenhagen co-efficient, A and B Jones Dole or viscosity B-coefficient were determined using the following equations (Sumathi et al., 2011; Anilkumar Nain et al., 2011; Santhosh et al., 2010).

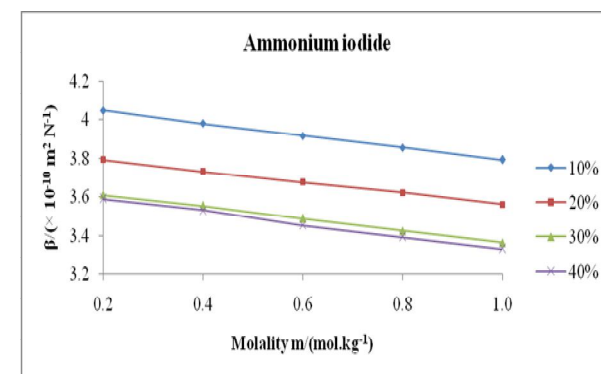
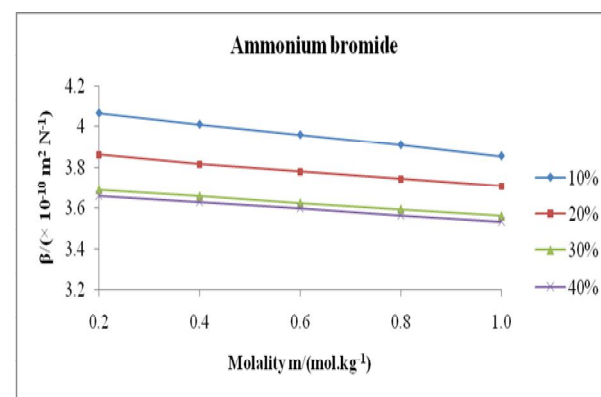
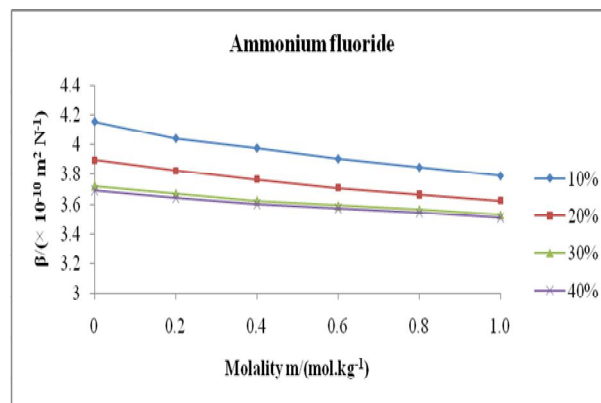
$$\beta = \frac{1}{U^2 \rho} \dots\dots\dots (1)$$

$$\pi_i = bRT \left( \frac{K\eta}{U} \right)^{1/2} \left( \frac{\rho^{2/3}}{M_{\text{eff}}^{7/6}} \right) \dots\dots\dots (2)$$

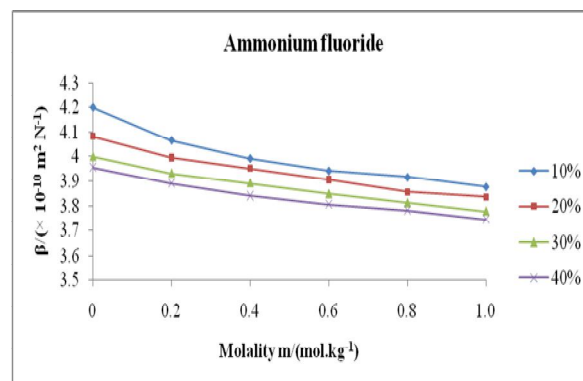
$$V_f = \left( \frac{M_{\text{eff}} U}{K\eta} \right)^{3/2} \dots\dots\dots (3)$$

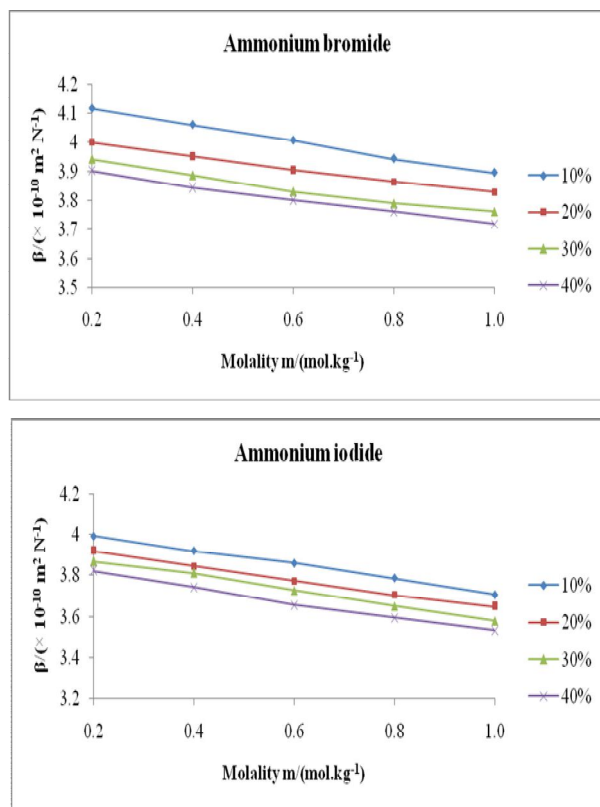
$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \dots\dots\dots (4)$$

where b is constant which is 2 for cubic packing, R the gas constant and T is temperature in Kelvin, K is the temperature independent constant ( $K = 4.28 \times 10^9$ ),  $M_{\text{eff}}$  is the effective molecular weight of the solution  $\eta$  and  $\eta_0$  are the viscosities of the solution and solvent, m is the molal concentration of the solute. A and B are constants for a given solute solvent system.



**Fig. 1** Values of Adiabatic compressibility ( $\beta$ ) of ammonium salts in 2-methoxyethanol-water mixtures at 303K





**Fig. 2** Values of Adiabatic compressibility ( $\beta$ ) of ammonium salts in 1,4-dioxane-water mixtures at 303K

**Table 1** Values of internal pressure ( $\pi_i$ ) and free volume ( $V_f$ ) of ammonium salts in 2-methoxyethanol-water mixtures at 303K

Molality m/(mol.kg <sup>-1</sup> )	$\pi_i/(\times 10^6 \text{ Nm}^{-2})$				$V_f/(\times 10^{-8} \text{ m}^3 \text{ mol}^{-1})$			
	10%	20%	30%	40%	10%	20%	30%	40%
Ammonium fluoride								
0.0	2572.99	2560.72	2554.16	2412.57	1.92	1.66	1.41	1.36
0.2	2593.01	2579.14	2573.22	2424.17	1.89	1.64	1.39	1.36
0.4	2622.44	2602.65	2593.19	2460.68	1.84	1.61	1.36	1.31
0.6	2645.08	2620.09	2613.59	2514.36	1.80	1.58	1.34	1.23
0.8	2681.18	2656.78	2648.58	2558.97	1.73	1.52	1.29	1.17
1.0	2688.98	2673.15	2669.39	2621.83	1.71	1.49	1.26	1.09
Ammonium bromide								
0.2	2548.25	2537.73	2528.22	2431.83	1.99	1.71	1.46	1.34
0.4	2485.86	2480.38	2476.90	2386.44	2.12	1.80	1.51	1.39
0.6	2433.89	2431.57	2429.26	2350.42	2.22	1.89	1.58	1.44
0.8	2381.63	2376.62	2374.60	2310.46	2.33	1.99	1.67	1.48
1.0	2328.81	2327.71	2319.02	2280.65	2.47	2.09	1.77	1.52
Ammonium iodide								
0.2	2521.05	2512.55	2415.88	2412.79	2.02	1.75	1.64	1.35
0.4	2523.04	2514.31	2424.25	2414.26	1.96	1.69	1.58	1.30
0.6	2530.92	2518.86	2436.30	2417.18	1.89	1.64	1.52	1.27
0.8	2543.75	2536.48	2438.41	2422.36	1.82	1.56	1.46	1.22
1.0	2597.76	2572.96	2445.88	2424.40	1.67	1.46	1.42	1.19

The values of adiabatic compressibility ( $\beta$ ), decreases with increasing concentration of salts in both the solvents (Figs. 1 and 2). Adiabatic compressibility ( $\beta$ ) exhibits reverse trend to that of ultrasonic velocity ( $U$ ) studied. When the molal concentration of ammonium salts increases,  $\beta$  decreases gradually because 2-methoxyethanol is a polar, protic solvent and when polar solvents are added, the association of solute and solvent molecules occurs resulting in close packing and clinging of molecules. Therefore, the solution becomes less compressible and thereby

decreasing  $\beta$  values. Whereas in 1,4-Dioxane, which is a non polar, aprotic solvent having higher density, already packing of Dioxane molecules occurs in the structure and hence in become less compressible nature of solution (Sachin. D. Zade, 2011). By comparing the  $\beta$  values in 2-methoxyethanol and 1,4-Dioxane, it is clearly observed that  $\beta$  values in 2-methoxyethanol is smaller than that of 1,4-Dioxane solvent. The increasing electrostritive compression of water around the molecules results in a large decrease in the compressibility of 2-methoxyethanol solvent. The decrease in compressibility implies that there is an enhanced molecular association in the above system upon increase in solute content, as the new entities (formed due to molecular association) become impact and less compressible (Santhosh et al., 2010).

The values of internal pressure ( $\pi_i$ ) are found to be increased and those of free volume ( $V_f$ ) are decreased in system I and system III, whereas, these values are found to be reverse in system II in both aqueous 2-methoxyethanol and 1,4-Dioxane (Tables 1 and 2). The measure of the net adhesive/cohesive forces between the components of the mixture is reflected by the values of the internal pressure (Mahendiran and Palaniappan, 2011). The internal pressure increases with increase in concentration of the salts as a result of ion-solvent interaction increases. It is observed that the free volume ( $V_f$ ) and internal pressure ( $\pi_i$ ) exists in opposite character.

Free volume represents the average volume in which the centre of the molecules can move inside the cell due to the repulsion of surrounding molecule (Ravichandran and Ramanathan, 2010). Free volume decreases with increasing the value of concentration, which clearly indicates the increasing magnitude of interactions (Thirnavukkarasu and Kanagathara, 2011). The decrease in volume again proves that there is a close association between solvent and solute molecules i.e., strong solute-solvent interactions (Shipra Baluja and Falguni Karia, 2012). In system II, the internal

**Table 2** Values of internal pressure ( $\pi_i$ ) and free volume ( $V_f$ ) of ammonium salts in 1,4-dioxane-water mixtures at 303K

Molality m/(mol.kg <sup>1</sup> )	$\pi_i/(\times 10^6 \text{ Nm}^{-2})$				$V_f/(\times 10^{-8} \text{ m}^3 \text{ mol}^{-1})$			
	10%	20%	30%	40%	10%	20%	30%	40%
<b>Ammonium fluoride</b>								
0.0	2457.26	2332.90	2220.49	2107.70	2.23	2.21	2.14	2.04
0.2	2479.93	2351.44	2241.18	2121.18	2.19	2.18	2.10	2.01
0.4	2496.65	2393.24	2264.35	2129.52	2.15	2.07	2.04	1.99
0.6	2515.20	2413.52	2284.87	2156.37	2.11	2.02	1.99	1.92
0.8	2538.79	2437.85	2307.58	2189.18	2.05	1.97	1.94	1.84
1.0	2559.75	2451.18	2324.80	2219.18	2.00	1.93	1.89	1.77
<b>Ammonium bromide</b>								
0.2	2526.85	2403.74	2309.86	2174.47	2.05	2.02	1.90	1.85
0.4	2446.66	2339.20	2275.19	2133.93	2.24	2.17	1.96	1.93
0.6	2414.31	2297.87	2246.46	2103.84	2.31	2.27	2.02	1.99
0.8	2374.78	2261.45	2205.95	2071.90	2.40	2.34	2.10	2.07
1.0	2340.42	2232.07	2152.30	2044.22	2.47	2.40	2.23	2.12
<b>Ammonium iodide</b>								
0.2	2379.43	2327.16	2231.46	2028.78	2.43	2.21	2.08	2.24
0.4	2393.84	2341.00	2252.41	2110.06	2.34	2.12	1.98	1.95
0.6	2403.99	2362.81	2272.68	2142.83	2.25	2.01	1.89	1.83
0.8	2413.31	2393.11	2298.97	2181.75	2.16	1.89	1.77	1.69
1.0	2419.41	2399.17	2300.24	2202.43	2.09	1.82	1.72	1.59

pressure decreases and the free volume increases with increasing mole fraction of ammonium bromide. The internal pressure may give information regarding the nature and strength of force existing between the molecules. The increase in free volume and the decrease in internal pressure shows that the strength of interaction decreases gradually with the increase in solute concentration, which may be due to the loosening of cohesive forces leading to breaking up structure of the solvent (Kannappan et al., 2007).

presence of weak ion-ion interaction (Prasanna Pradhan et al., 2009). On the other hand the positive values A in ammonium bromide show the presence of strong ion-ion interaction. The positive values of B-coefficient in ammonium fluoride and ammonium iodide is indicative of water structuring. The B-coefficient is also known as a measure of order or disorder introduced by the solute into the solvent. It is also a measure of solute-solvent interaction and the relative size of the solute and solvent molecules. The behavior of B-coefficient in the systems

**Table 3** Values of A and B parameters of Jones-Dole equation of ammonium salts in 2-methoxyethanol and 1,4-Dioxane-water mixtures at 303K

Water + 2-methoxyethanol	<b>A/</b> ( $\times 10^{-3} \text{ dm}^{3/2} \text{ mol}^{-1/2}$ )	<b>B/</b> ( $\text{dm}^3 \text{ mol}^{-1}$ )	<b>A/</b> ( $\times 10^{-3} \text{ dm}^{3/2} \text{ mol}^{-1/2}$ )	<b>B/</b> ( $\text{dm}^3 \text{ mol}^{-1}$ )
<b>Ammonium fluoride</b>				
10%	-18.1	0.1559	-15.5	0.1070
20%	-32.6	0.1513	-11.8	0.1552
30%	-28.3	0.1328	-8.9	0.1289
40%	-26.1	0.3085	-44.5	0.1729
<b>Ammonium bromide</b>				
10%	29.1	-0.1095	251.2	-0.2570
20%	24.3	-0.1029	277.4	-0.2729
30%	10.1	-0.0819	344.1	-0.2892
40%	74.7	-0.0838	294.0	-0.2544
<b>Ammonium iodide</b>				
10%	-233.7	0.4684	-231.5	0.4462
20%	-219.4	0.4538	-109.2	0.4228
30%	-388.1	0.5454	-064.3	0.3981
40%	-70.9	0.3271	-352.2	0.7324

The values of A and B-coefficients for the electrolytes are estimated by computerized least square method. A is the Falkenhagen coefficient that accounts for the ion-ion interactions. B the Jones-Dole co-efficient is a measure of the structural modification induced by solute-solvent in reactions.

From the Table 3 the values of A are negative and B values are positive in ammonium fluoride and ammonium iodide systems, whereas in ammonium bromide the A values are found to be positive and the B values are negative in both the solvents. Since A is measure of ionic interactions, the negative values of A indicate the

studied suggests the existence of strong ion-solvent interaction. The larger value of B indicates structure making capacities of the solute (Santhosh et al., 2010). Solute with negative B-coefficient in system II is characterized as "surface breaker" indicating weak solute-solvent interaction (Sonar et al., 2010).

## CONCLUSION

The ultrasonic studies provide a comprehensive investigation of molecular association between ammonium salts with aqueous 2-methoxyethanol and 1,4-Dioxane arising

from the ion-solvent and ion-ion interaction. In summary, it can be concluded that the B-coefficient of Jones-Dole viscosity equation for electrolytes ( $\text{NH}_4\text{Br}$ ) is negative for structure breaking ions and positive ( $\text{NH}_4\text{F}$  and  $\text{NH}_4\text{I}$ ) for structure making ions at 303K.

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