

List of Publications

1. Study of Ion-Solvent Interactions of Some Alkali Metal Chlorides in Tetrahydrofuran + Water Mixture at Different Temperatures. *J. Chem. Eng. Data.* 2001, **46**, 1327.
2. Limiting Apparent Molar Volumes, their Temperature Derivatives and Viscosity B-Coefficients for some Alkali Metal Chlorides in aqueous Tetrahydrofuran Mixture. *J. Indian Chem. Soc.* 2002, **79**, 148.
3. Volumetric, Viscometric and Ultrasonic Studies of some Nitrate Compounds in Aqueous Binary Mixture of Tetrahydrofuran at Various Temperatures. *J. Indian Chem. Soc.* 2003, **80**, 1.
4. Studies on Thermodynamics and Transport Properties of Two Binary Mixtures formed by Water, Methanol and Tetrahydrofuran at Different Temperatures. *J. T. R. C.* (in press). Acceptance letter enclosed.
5. Studies on the Densities, Viscosities and Adiabatic Compressibilities of some Mineral Salts in Water at Different Temperatures. *J. Chem. Eng. Data.* (in press). Acceptance letter enclosed.

Study of Ion-Solvent Interactions of Some Alkali Metal Chlorides in Tetrahydrofuran + Water Mixture at Different Temperatures

Mahendra Nath Roy,* Rabindra Dey, and Anupam Jha

Department of Chemistry, North Bengal University, Darjeeling 734 430, India

The apparent molar volumes and viscosities of three alkali metal chlorides, namely, lithium chloride, sodium chloride, and potassium chloride, have been determined in a 40 mass % tetrahydrofuran + water mixture at 303, 308, 313, and 318 K. The limiting apparent molar volumes (V_ϕ°) and slopes (S_ϕ^*) have been interpreted in terms of ion-solvent and ion-ion interactions, respectively. Structure-making/-breaking capacities of various electrolytes have been inferred from the sign of ($d^2V_\phi^\circ/dT^2$), dB/dT , and the B coefficient for all electrolytes studied. The viscosity data have been analyzed using the Jones-Dole equation. The results show that the three electrolytes act as structure promoters in this solvent mixture.

Introduction

The volumetric behavior of solutes has been proven to be very useful in elucidating the various interactions occurring in aqueous and nonaqueous solutions.¹ Studies on the apparent and partial molar volumes of electrolytes and the dependence of viscosity on concentration of solutes and temperature of solutions have been employed as a function of studying ion-ion and ion-solvent interactions.² It has been found by a number of workers³⁻⁵ that the addition of electrolyte could either break or make the structure of a liquid. Because a liquid's viscosity depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures.

In this paper, we report the limiting apparent molar volumes (V_ϕ°), experimental slopes (S_ϕ^*), limiting apparent molar expansibilities (ϕ_E°), and viscosity B coefficients for three alkali metal chlorides, namely, lithium chloride, sodium chloride, and potassium chloride, in a 40 mass % tetrahydrofuran (THF) + water solvent mixture at different temperatures.

Experimental Section

Tetrahydrofuran (Merck, India) was kept for several days over KOH, refluxed for 24 h, and distilled over LiAlH_4 .⁶ The boiling point (66 °C), density (0.8807 $\text{g}\cdot\text{cm}^{-3}$), and viscosity ($\eta_0 = 0.0046$ P) compared well with the literature values.⁷ The specific conductance of THF was $0.81 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ at 25 °C.

Alkali metal chlorides (Fluka) were of purum or puriss grade and purified by us as described earlier.^{8,9}

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

The densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of ~ 0.1 cm. The pycnometer was calibrated at 298, 308, and 318 K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at ± 0.01 K of the desired temperature by means of

Table 1. Properties of Pure Tetrahydrofuran (THF) and a 40 Mass % THF + H_2O Solvent Mixture at Different Temperatures

T/K	mass %	$\rho/\text{g}\cdot\text{cm}^{-3}$		η/cP	
		this work	lit.	this work	lit.
298	100 (pure THF)	0.88072	0.88072 ^a 0.88070 ^c	0.46300	0.46300 ^b 0.46000 ^c
303	100	0.87595		0.44536	
308	100	0.87116	0.87116 ^c	0.42770	0.42770 ^b
313	100	0.86627		0.40893	
318	100	0.86140	0.86140 ^a	0.39017	0.39017 ^b
298	40	0.96640	0.96640 ^a	1.73210	1.73210 ^b
303	40	0.96391		1.52760	
308	40	0.96120	0.96120 ^a	1.32310	1.32310 ^b
313	40	0.95359		1.18412	
318	40	0.94598	0.94598 ^a	1.04516	1.04516 ^b

^a r_0 ,^{9,10,22} ^b h_0 ,^{9,10} ^c r_0 , h_0 .⁷

a mercury in glass thermoregulator, and the absolute temperature was determined by a calibrated platinum resistance 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. An average of triplicate measurements was taken into account. The density values are reproducible to $\pm 3 \times 10^{-6} \text{g}\cdot\text{cm}^{-3}$. Details were given earlier in a publication from our laboratory (Das and Roy, 1993).

The viscosities were measured by means of a suspended-level Ubbelohde (Suindells and Godfrey, 1952) viscometer at the desired temperature (accuracy of ± 0.01 °C). The precision of the viscosity measurement was 0.05%. We have previously given the details.¹⁰

The experimental values of densities (ρ_0) and viscosities (η_0) of pure THF and 40 mass % THF + water at 298, 303, 308, 313, and 318 K are given in Table 1.

Results

The apparent molar volumes, V_ϕ , of the solutes were calculated from the densities of the solutions by using the equation

$$V_\phi = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \quad (1)$$

B Journal of Chemical and Engineering Data

Table 2. Limiting Apparent Molar Volumes (V_ϕ°) and Experimental Slopes (S_v^*) of Different Salts in 40 Mass % THF + Water at Different Temperatures

salt	V_ϕ° at various temps ($\text{cm}^3 \text{mol}^{-1}$)				S_v^* at various temps ($\text{cm}^3 \text{L}^{1/2} \text{mol}^{-3/2}$)			
	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K
LiCl	-191.75	-240.502	-443.849	-633.905	388.194	525.746	971.602	1355.919
NaCl	-224.461	-285.361	-502.611	-719.110	466.507	650.985	1039.870	1620.59
KCl	-464.253	-541.196	-770.164	-982.70	1024.510	1234.66	1753.641	2243.321

Table 3. Limiting Apparent Molar Expansibilities (ϕ_E°) for Various Salts in 40 Mass % THF + Water at Different Temperatures

electrolyte	limiting apparent molar expansibilities ϕ_E° ($\text{cm}^3 \text{mol}^{-1} \text{K}^{-1}$)			
	303 K	308 K	313 K	318 K
LiCl	-14.656	-41.998	-39.340	-36.682
NaCl	-13.675	-43.525	-43.375	-43.225
KCl	-50.722	-47.436	-44.149	-40.863

where M is the molecular weight of the solute, ρ_0 and ρ are the densities of the solvent mixture and the solution, respectively, and c is the concentration in molarity. The correction to V_ϕ° due to hydrolysis of salts may be negligible, because the strong H-bonding¹¹ between THF and water will reduce the hydrolysis of these salts by free water molecules considerably.

Because the data concerning the pressure dependence of the dielectric constant of the THF + water mixture are not available, the limiting apparent molar volume (V_ϕ°) was calculated by using the equation¹²

$$V_\phi = V_\phi^\circ + S_v^* c^{1/2} \quad (2)$$

where S_v^* is a constant dependent on charge and salt type and can be related to ion-ion interactions and V_ϕ° is the limiting apparent molar volumes. These values were estimated by Microsoft Excel, which is a computerized least-squares method. Values of V_ϕ° and S_v^* are given in Table 2.

The temperature dependence of V_ϕ° for various electrolytes studied here in the above solvent mixture can be expressed by the equation

$$V_\phi^\circ = a_0 + a_1 T + a_2 T^2 \quad (3)$$

where T is the temperature in degrees kelvin.

The limiting apparent molar expansibilities (ϕ_E°) can be obtained by differentiating eq 3 with respect to temperature.

$$\phi_E^\circ = (dV_\phi^\circ/dT)_p = a_1 + 2a_2 T \quad (4)$$

The ϕ_E° values of the electrolytes at 303, 308, 313, and 318 K are given in Table 3.

The relative viscosities of solutions for various electrolytes, namely, LiCl, NaCl, and KCl, in a 40 mass % THF + H₂O mixture at different temperatures were also determined. The data were analyzed by using the Jones-Dole¹³ equation

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc$$

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

where $\eta = (Kt - l/t) \times \rho$, η_0 and η are the viscosities of the solvent mixture and solution, respectively, A and B are constants, ρ is the density of the particular solvent mixture

or solution, and K and L are constants for a particular viscometer.

The values of A and B were calculated by a computerized least-squares method. Molar concentrations, densities, viscosities, apparent molar volumes, and values of the B coefficient and A are recorded in Table 4.

Discussion

The values of S_v^* shown in Table 2 are large and positive for the alkali metal chlorides studied here in a 40 mass % THF + H₂O mixture at all of the temperatures investigated. This is an indication of strong ion-ion interactions in this solvent mixture medium.^{14,15} This type of behavior of alkali metal chlorides and some common salts has been also observed in propylene glycol-water mixtures.¹⁶ A possible explanation for the positive slopes in the 40 mass % THF + H₂O mixture may be that the ionic association would become quite appreciable in this medium as the concentration of the electrolyte is increased, thereby weakening the ion-solvent interactions.

As a consequence, contraction of the solvent mixture would be gradually lowered with the increase in concentration of the added solute. The S_v^* values (ion-ion interactions) increase as the size of the cation increases as well as with increase in temperature. Exactly the same conclusion regarding the ion association behavior of these electrolytes in THF and DME has been drawn from our conductometric studies.⁶ The limiting apparent molar volumes V_ϕ° shown in Table 2 are large and negative, and these values decrease as the size of the alkali metal ion increases (from Li⁺ to K⁺) as well as with increase in temperature (from 303 to 318 K). This indicates that there is a large amount of electrostriction occurring in these solutions, and this electrostrictive solvation is greater at higher temperature and with larger metal ion. Similar results are reported for some metal sulfates in different DMF + H₂O mixtures at different temperatures.¹⁵ It is evident from Table 3 that the ϕ_E° values of all the salts in this solvent mixture increase with increase of temperature. The increase in magnitude per degree of temperature is positive, indicating that the behavior of all of these salts is similar to that of symmetrical quaternary ammonium alkyl salts.^{1,17}

It is also found that $[d^2V_\phi^\circ/dT^2]$ values for solutions of all studied salts here are positive, showing that these studied electrolytes (LiCl, NaCl, and KCl) behave as structure promoters^{15,16,18} in this medium.

Perusal of Table 4 shows that the values of B for all of the electrolytes are positive and large, indicating that all of these alkali metal chlorides (LiCl, NaCl, and KCl) act as structure makers in this mixed solvent system. The structure-making tendencies of the salts are in the order lithium salt > sodium salt > potassium salt. A similar trend was reported by other workers.^{19,20}

It has been reported by a number of workers that the (dB/dT) value is a better criterion²¹ for determining the structure-making/-breaking nature of any electrolyte rather than simply the B coefficients. It is found that B values are positive and decrease with a rise in temperature

Table 4. Molar Concentrations, Densities, Viscosities, Apparent Molar Volumes, and Values of the B Coefficient and A in 40 Mass % THF + Water Mixture at Different Temperatures

c	ρ	η	V_a	B	A
mol dm ⁻³	g cm ⁻³	cP	dm ³ mol ⁻¹	dm ³ mol ⁻¹	dm ^{3/2} mol ^{-1/2}
303 K, LiCl					
0.01313	0.96575	0.99243	-145.56		
0.04595	0.97219	1.00110	-110.11		
0.08535	0.97404	1.02710	-80.58	7.205	-3.512
0.13131	0.97402	1.03799	43.13		
0.18383	0.97670	1.06218	-28.82		
303 K, NaCl					
0.01398	0.96677	1.06336	-160.05		
0.04896	0.97332	1.03639	-141.22		
0.08393	0.97510	1.05111	-87.62	6.281	-3.108
0.12589	0.97756	1.05706	-52.82		
0.174858	0.97876	1.07656	-28.19		
303 K, KCl					
0.04821	0.98263	1.05443	-240.01		
0.07231	0.98200	1.06487	-196.84		
0.09642	0.98330	1.08155	-132.52	4.665	-2.411
0.12052	0.98517	1.09379	-106.70		
0.14462	0.98592		-81.37		
308 K, LiCl					
0.01305	0.96394	0.90829	-175.11		
0.04569	0.96786	0.91471	-107.52		
0.08505	0.97067	0.92137	-71.78	6.419	-3.119
0.13087	0.97157	0.92823	-38.33		
0.18318	0.97325	0.93587	-24.37		
308 K, NaCl					
0.01395	0.96477	0.96952	-205.02		
0.04886	0.97142	0.94613	-156.94		
0.08369	0.97303	0.95573	-86.29	6.261	-2.957
0.12543	0.97393	0.96265	-44.85		
0.17420	0.97512		-22.36		
308 K, KCl					
0.04800	0.97846	0.89552	-293.53		
0.07208	0.97990	0.91118	-195.14		
0.09610	0.98013	0.92732	-128.86	4.434	-2.314
0.12028	0.98322	0.93389	-113.54		
0.14445	0.98440		-92.67		
313 K, LiCl					
0.01300	0.95838	0.81882	-340.51		
0.04563	0.96646	0.83169	-251.30		
0.08479	0.96770	0.84274	-130.12	6.376	-3.067
0.13040	0.96613	0.86306	-72.52		
0.18281	0.97131	0.89269	-57.19		
313 K, NaCl					
0.01394	0.96300	0.84957	-375.55		
0.04884	0.97103	0.85564	-313.25		
0.08357	0.971585	0.89418	-164.52	6.223	-2.669
0.12536	0.973463	0.90996	-104.95		
0.17394	0.973660	0.94027	-59.71		
313 K, KCl					
0.04791	0.97666	0.83841	-426.72		
0.07186	0.97690	0.85276	-262.02		
0.09597	0.97881	0.87157	-198.50	4.364	-2.184
0.11990	0.98019	0.88391	-155.00		
0.14423	0.98331		-137.96		
318 K, LiCl					
0.01299	0.95230	0.73823	-475.66		
0.04555	0.96472	0.74545	-390.28		
0.08454	0.96489	0.76479	-191.72	6.170	-2.964
0.13005	0.96547	0.76495	-113.61		
0.18248	0.96957	0.79444	-91.86		
318 K, NaCl					
0.01380	0.95396	0.76986	-540.561		
0.04862	0.96609	0.79606	-358.62		
0.08316	0.96692	0.79824	-204.62	5.308	-2.523
0.12477	0.96843	0.80578	-131.84		
0.17318	0.96942	0.82426	-81.34		
318 K, KCl					
0.04779	0.97417	0.73289	-544.48		
0.07167	0.97424	0.75281	-338.04		
0.09559	0.97490	0.79315	-241.05	4.299	-2.105
0.11963	0.97794	0.82595	-203.61		
0.14382	0.98051		-175.02		

(negative dB/dT), suggesting a structure-promoting tendency of alkali metal chlorides. The same conclusion is

obtained by determining $[d^2V_a/dT^2]$ values as mentioned above. Besides, the positive B values and negative dB/dT values show the absence of a firm layer of solvent mixture around the ion in their cosphere.

Literature Cited

- (1) Millero, F. J. *Chem. Rev.* 1971, 71, 147.
- (2) Millero, F. J. In *Structure and Transport Process in Water and Aqueous Solutions*; Horne, R. A., Ed.; New York, 1972.
- (3) Stokes, H. H.; Mills, R. *International Encyclopaedia of Physical Chemistry and Chemical Physics*; New York, 1965; p 3.
- (4) Nikam, P. S.; Hasan, Mehdi. Density and Viscosity Studies of some metal halides in (DMSO + water) mixtures at 25 °C. *J. Chem. Eng. Data* 1988, 33, 165.
- (5) Nikam, P. S.; Hiray, A. R. Viscosity B co-efficients of R₄NBr in 2-methoxy ethanol at 25 and 35 °C. *J. Indian Chem. Soc.* 1989, 66, 883.
- (6) Nandi, D.; Roy, M. N.; Hazra, D. K. Electrical conductances of tetraalkylammonium bromides, LiBF₄ and LiAsF₆ in tetrahydrofuran at 25 °C. *J. Indian Chem. Soc.* 1993, 70, 305-310.
- (7) Covington, A. K.; Dickinson, T. *Physical Chemistry of Organic Solvent Systems*; Plenum: New York, 1973; p 5.
- (8) Nandi, D.; Das, S.; Hazra, D. K. Viscosities of alkali metal chlorides and bromides in 2-methoxy ethanol at 25 and 35 °C. *J. Chem. Soc., Faraday Trans. 1* 1989, 85, 1531-1535.
- (9) Roy, M. N.; Nandi, D.; Hazra, D. K. Conductance Studies of alkali metal chlorides and bromides in aqueous binary mixture of tetrahydrofuran at 25 °C. *J. Indian Chem. Soc.* 1993, 70, 123-126.
- (10) Das, B.; Roy, M. N.; Hazra, D. K. Densities and Viscosities of the binary aqueous mixtures of tetrahydrofuran and 1,2 dimethoxyethane at 298, 308 and 318 K. *Indian J. Chem. Technol.* 1994, 1, 93-97.
- (11) Pikkariainen, L. Viscosities of the Binary Solvent Mixtures of N,N-Diethylmethane-Sulfonamide with Aliphatic Alcohols. *J. Chem. Eng. Data* 1988, 33, 299-301.
- (12) Masson, D. O. Ion-Solvent Interactions. *Philos. Mag.* 1929, 8, 218.
- (13) Jones, C. I.; Dole, M. Density and Viscosity Studies on Some R₄NX in DMF + water mixtures at different temperatures. *J. Am. Chem. Soc.* 1929, 51, 2950.
- (14) Das, B.; Hazra, D. K. Apparent and Partial Molal Volumes of Selected Symmetrical Tetraalkylammonium Bromides in 2-Methoxy 1-ethanol at 25 °C. *J. Chem. Eng. Data* 1991, 36, 403-406.
- (15) Nikam, P. S.; Sawant, A. B.; Aher, J. S.; Khairnar, R. S. Limiting apparent Molar Volumes and Their Temperature Derivatives for Ammonium Sulfate, Potassium Sulfate and Aluminium Sulfate in aqueous dimethylformamide. *J. Indian Chem. Soc.* 2000, 77, 197-200.
- (16) Parmar, M. L.; Chauhan, M. K. A Study of Ion-Solvent interactions of some tetraalkyl and multivalent electrolytes in propylene glycol-water mixtures. *Indian J. Chem.* 1995, 34A, 434-439.
- (17) Millero, F. J.; Drost, H. W. Apparent molal volumes of NH₄Cl and some R₄NCl at various temperatures. *J. Phys. Chem.* 1968, 72, 1758-1762.
- (18) Helper, L. G. Studies on viscosities and densities of R₄NX in ME + water mixtures of different temperatures. *Can J. Chem.* 1969, 47, 4613-4616.
- (19) Gill, D. S.; Cheema, T. S. Preferential solvation of ions in Mixed Solvents. *Z. Phys. Chem. (Neue Folge)* 1984, 140, 139-148.
- (20) Prasad, B. N.; Babu, S. B.; Subba, M. C. S.; Rao, K. C. Equivalent Conductance, Viscosity and apparent molar volumes Studies of alkali metal propionate in propionic acid + ethanol mixture at 30 °C. *J. Indian Chem. Soc.* 2000, 77, 8-10.
- (21) Gurney, R. W. *Ionic Processes in Solutions*; McGraw-Hill: New York, 1954.
- (22) Roy, M. N. Studies on Adiabatic Compressibilities of Some Alkali Metal Chlorides and Bromides in THF + H₂O mixtures at 25 °C. *North Bengal Univ. Rev. (Sci. Technol.)* 1997, 8, 54-58.

Received for review January 17, 2001. Accepted June 14, 2001.

Limiting apparent molar volumes, their temperature derivatives and viscosity *B*-coefficients for some alkali-metal chlorides in aqueous tetrahydrofuran mixture

Anupam Jha, Rabindra Dey and Mahendra Nath Roy*

Department of Chemistry, University of North Bengal, Darjeeling-734 430, India

Fax : 91-0353-581546

Manuscript received 16 February 2001, accepted 31 May 2001

Density and viscosity of lithium chloride, sodium chloride and potassium chloride have been measured in tetrahydrofuran (THF) + water mixture (60%, w/w) at different concentrations and at 303, 308, 313 and 318 K. From density data apparent molar volumes have been derived and analyzed using Masson equation. The limiting apparent molar volume (ϕ_v^0) and slope (S_v^*) are interpreted in terms of ion-solvent and ion-ion interactions, respectively. The viscosity data have been analyzed using Jones-Dole equation. The structure-making/breaking capacities of the salts have been inferred from the Hepler's and Sharma and Ahluwalia's criterion.

Thermodynamic investigations play an important role in understanding the type and extent of the patterns of molecular associations that exist in liquid mixtures and their sensitivities to variations in composition, temperature, pressure and chemical nature¹. The limiting apparent molar volume of a salt is an important thermodynamic property. Since viscosity is a property of the liquid which depends upon the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures. In the present work, we have carried out a systematic study on the limiting apparent molar volumes (ϕ_v^0), experimental slopes (S_v^*) and *B*-coefficients of alkali metal chlorides MCl (M = Li, Na, K) in tetrahydrofuran (THF) + water mixture (60%, w/w) at 303, 308, 313 and 318 K.

Results and Discussion

The experimental values of densities (ρ_0), viscosities (η_0) and relative permittivities (*D*) of tetrahydrofuran + water at 298 K are not available at the relevant compositions. Their available values are therefore, plotted against the mole-fractions of tetrahydrofuran, and the values at all the desired compositions have been generated from the smooth master curves and are given in Table 1. The results reveal that η_0 of the solvent mixture (THF + H₂O) increases rapidly to a maximum at about 0.143 mole-fraction or 40 wt% of THF and thereafter decreases. Such characteristics in the viscosity vs composition curve is a manifestation of strong specific interaction² between unlike molecules predominated by hydrogen bonding interaction.

The apparent molar volume (ϕ_v) were calculated from the density of the solution using eqn. (1).

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

where *c* is the molarity of the electrolyte solution, *M* the molecular weight of the solute and ρ and ρ_0 are the densities of the solution and solvent, respectively. The limiting apparent molar volumes (ϕ_v^0) were calculated by the Masson equation³.

$$\phi_v = \phi_v^0 + S_v^*c^{1/2} \quad (2)$$

where S_v^* is a constant dependent on charge and salt type and can be related to ion-ion interactions and ϕ_v^0 is the limiting apparent molar volume which is related to ion-solvent interactions. The plots of ϕ_v against $c^{1/2}$ were linear in

Table 1. Density (ρ), viscosity (η_0), relative permittivities (*D*) and specific conductance (L_0) for tetrahydrofuran + water at 298 K

Wt. %	ϵ_2	<i>D</i>	ρ_0 g cm ⁻³	η_0 cP	$10^6 L_0$ $\Omega^{-1} \text{cm}^{-1}$
0	0	78.54	0.99797	0.8903	1.01
20	0.059	57.25	0.98668	1.4900	3.20
40	0.143	44.50	0.96640	1.7321	2.60
60	0.273	32.00	0.94600	1.4904	1.35
80	0.500	19.50	0.91592	0.9237	1.18
100	1.000	7.58	0.88072	0.4630	0.81

all cases and from the intercept and slope one can obtain the values of ϕ_v^0 and S_v^* , respectively. The values are given in Table 2.

The experimental S_v^* values (Table 2), at different temperatures are all large and positive in THF + water mixture (60%, w/w) for all electrolytes studied, indicating the presence of strong solute-solute interactions. This type of behavior of alkali metal chlorides and some common salts has also been observed in propylene glycol-water mix-

Table 2. Limiting apparent molar volume (ϕ_v^0) and experimental slopes (S_v^1) for various salts in 60% (w/w) tetrahydrofuran + water mixture at different temperatures*

Salts	ϕ_v^0 (cm ³ mol ⁻¹)				S_v^1 (L ^{1/2} mol ^{-3/2})			
	303	308	313	318 K	303	308	313	318 K
LiCl	-268.186 (± 0.01)	-311.532 (± 0.01)	-480.479 (± 0.02)	-641.178 (± 0.01)	759.865 (± 0.01)	875.099 (± 0.01)	1301.100 (± 0.02)	1678.604 (± 0.01)
NaCl	-346.804 (± 0.02)	-371.254 (± 0.01)	-554.387 (± 0.01)	-727.152 (± 0.02)	1112.941 (± 0.02)	1144.796 (± 0.01)	1700.396 (± 0.01)	2264.464 (± 0.01)
KCl	-528.192 (± 0.02)	-561.238 (± 0.01)	-782.683 (± 0.02)	-990.201 (± 0.01)	1747.011 (± 0.01)	1835.353 (± 0.01)	2541.661 (± 0.01)	3260.971 (± 0.01)

*Standard error in parenthesis.

tures⁴. The possible explanation for the positive slopes in the studied solvent-mixture may be that the ionic association would become quite appreciable in this medium as the concentration of the electrolyte is increased thereby weakening the solute-solvent interactions. As a result, contraction of the solvent mixture would be gradually lowered with increase in concentration of the added solute. Exactly the same conclusion regarding the ion-association behavior

The variation of ϕ_v^0 with temperature of the electrolytes in this solvent-mixture follows the polynomial equation,

$$\phi_v^0 = a_0 + a_1T + a_2T^2 \quad (3)$$

over the temperature range under the investigation. The coefficients a_i 's are determined and the following equations are obtained,

$$\phi_v^0 = 25998.407 - 136.229 T + 0.1650 T^2 \quad (4) \text{ for LiCl}$$

$$\phi_v^0 = 30900.072 - 165.397 T + 0.2074 T^2 \quad (5) \text{ for NaCl}$$

$$\phi_v^0 = 39932.144 - 217.262 T + 0.2785 T^2 \quad (6) \text{ for KCl}$$

The limiting apparent molar expansibilities, $[\phi_E^0 = (\delta\phi_v^0/\delta T)_p]$, calculated from eqn. (4-6) for different electrolytes at different temperatures are given in Table 3. It is found that the values of ϕ_E^0 increase with increase in temperature for all studied electrolytes, which can be ascribed to the presence of caging or packing effect⁷.

For determining structure-making and structure-breaking capacities of solutes in different solvents, the equation of Hepler⁸ was used,

$$(\delta\phi_E^0/\delta T) = -(\delta^2\phi_v^0/\delta T^2)_p \quad (7)$$

According to Hepler, structure-making solutes should positive value and structure-breaking solutes negative value of the term of $(\delta^2\phi_v^0/\delta T^2)_p$ respectively. It has been observed from eqns. (4)-(6) that $(\delta^2\phi_v^0/\delta T^2)_p$ for solutions of all studied electrolytes are positive, indicating thereby that

Table 4. Values of *A* (cm^{3/2} mol^{-1/2}) and *B* (cm³ mol⁻¹) parameters for various salts in 60% (w/w) THF + water mixture at different temperatures*

Salts	<i>B</i> values				<i>A</i> values			
	303	308	313	318 K	303	308	313	318 K
LiCl	7.5703 (± 0.01)	7.5674 (± 0.02)	6.9095 (± 0.01)	6.3137 (± 0.02)	-3.1879 (± 0.01)	-3.1679 (± 0.01)	-2.9562 (± 0.02)	-2.6028 (± 0.01)
NaCl	7.3934 (± 0.01)	7.1393 (± 0.01)	6.7490 (± 0.01)	6.1779 (± 0.01)	-3.1465 (± 0.02)	-2.9801 (± 0.01)	-2.8421 (± 0.01)	-2.5769 (± 0.01)
KCl	5.8806 (± 0.02)	4.9455 (± 0.01)	4.9388 (± 0.02)	4.9037 (± 0.01)	-2.1897 (± 0.02)	-2.1309 (± 0.01)	-2.1157 (± 0.01)	-2.0728 (± 0.02)

*Standard errors are given in parenthesis.

these electrolytes (LiCl, NaCl and KCl) behave as structure-makers in this solvent-mixture.

The viscosity data of solution for the electrolytes (LiCl, NaCl and KCl) in THF + H₂O mixture (60%, w/w) have been analyzed using Jones-Dole equation⁹,

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc \quad (8)$$

where η and η_0 are the viscosities of the solution and solvent, respectively, and c is the concentration of solution. The values of A and B were calculated by the method of least-squares by fitting the experimental data in the Jones-Dole equation and these values are given in Table 4. It is evident from Table 4 that the values of B -coefficient for all the studied electrolytes are positive and large and the values decrease from LiCl to KCl as well as with increase in temperature and this behavior shows that all alkali metal chlorides (LiCl, NaCl and KCl) act as structure-promoters in this solvent-mixture system. The structure-promoting tendencies of the electrolytes are in the order : Li-salt > Na-salt > K-salt. A similar trend was reported by other workers¹⁰ in case of viscosities of perchlorates of lithium and sodium in propionic acid-ethanol mixture.

It has been reported by a number of workers that dB/dT is a better criterion¹¹ for determining the structure-making/breaking nature of any electrolyte rather than simply the B -coefficient. Table 3 shows that the value of B are positive and decreases with increase in temperature (from 303 to 318) which gives negative values of dB/dT suggesting that these electrolytes (LiCl, NaCl and KCl) behave as structure-promoters in this mixed solvent system. These conclusions are in excellent agreement with that drawn from $(\delta^2\phi_V/\delta T^2)_p$ discussed earlier.

Experimental

Tetrahydrofuran (THF; Merck) was kept several days over KOH, then refluxed for 24 h and distilled over LiAlH₄ as described earlier¹². The boiling point (66°), density (0.88072 g cm³) and viscosity (0.0046 P) compared well with the literature values¹³. The specific conductance of tetrahydrofuran was ca $0.81 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ at 25°.

Alkali-metal chlorides (Fluka, Puris or Purum) were purified as described earlier¹⁴.

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

Density (ρ) was measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298, 308 and 318 K with double-distilled water and benzene¹². Viscosity was measured by means of a suspended-level Ubbelohde¹⁵ viscometer with a flow time of about 539 s. For distilled water at 298 K, the time of the reflux was measured with a stop-watch capable of recording ± 0.1 s. Details have been described earlier¹².

References

1. F. J. Millero, *Chem. Rev.*, 1971, 71, 147.
2. L. Pikkariainen, *J. Chem. Eng. Data*, 1988, 33, 299.
3. D. O. Masson, *Phil. Mag.* 1929, 8, 218.
4. M. L. Parmar and M. K. Chauhan, *Indian J. Chem., Sect. A*, 1995, 34, 434.
5. M. N. Roy, D. Nandi and D. K. Hazra, *J. Indian Chem. Soc.*, 1993, 70, 123.
6. R. M. Fuoss, *J. Phys. Chem.*, 1978, 82, 2427.
7. F. J. Millero in "Water and Aqueous Solution : Structure, Thermodynamics and Transport Processes", ed. R. A. Home, Wiley-Interscience, New York, 1972, Chap. 13.
8. L. G. Hepler, *Can. J. Chem.*, 1968, 47, 4613.
9. G. Jones and M. Dole, *J. Am. Chem. Soc.*, 1929, 51, 2950.
10. D. S. Gill and J. S. Cheema, *Z. Phys. Chem. (Neue Folge)*, 1984, 140, 149.
11. T. S. Sharma and J. C. Ahluwalia, *Rev. Chem. Soc.*, 1973, 2, 217; R. W. Gurney, "Ionic Processes in Solutions", McGraw Hill, New York, 1954.
12. M. N. Roy, B. Das and D. K. Hazra, *Indian J. Chem. Technol.*, 1984, 1, 93.
13. A. K. Covington and T. Dickinson, "Physical Chemistry of Organic Solvent Systems", Plenum, New York, 1973.
14. D. Nandi, S. Das and D. K. Hazra, *J. Chem. Soc., Faraday Trans. 1*, 1989, 1531; M. N. Roy, D. Nandi and D. K. Hazra, *J. Indian Chem. Soc.*, 1993, 70, 305.
15. J. R. Suindells and T. B. Godfray, *J. Res. Natl. Bur. Stand.*, 1952, 48, 1.

364/2002
3

Volumetric, viscometric and ultrasonic studies of some nitrate compounds in aqueous binary mixture of tetrahydrofuran at various temperatures

Anupam Jha, Ankan Choudhury, Mrinmay Jha, Bhoj Bahadur Gurung and Mahendra Nath Roy*

Department of Chemistry, North Bengal University, Darjeeling-734430, India

E-mail : mahendraroy2002@yahoo.co.in

Manuscript received 12 December 2002, revised 4 April 2003, accepted 23 May 2003

The densities, viscosities and ultrasonic velocities of NH_4NO_3 , KNO_3 , $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ in a 20 mass % tetrahydrofuran + water mixture have been measured at 303, 308, 313, 318 and 323 K. Apparent molar volumes (V_ϕ), viscosity B -coefficients and adiabatic compressibility of these electrolyte solutions are derived from these data supplemented with their densities, viscosities and ultrasonic velocities respectively. The limiting apparent molar volumes (V_ϕ^∞) and experimental slopes (S_ϕ^∞) obtained from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The viscosity data have been analyzed using the Jones-Dole equation. The results show that these electrolytes have structure breaking capacities in this solvent-mixture. The compressibility data also indicate the electrostriction of solvent molecules around the metal ions.

In continuation of the work¹⁻³ on the classical nature of solutes and their mutual and specific interactions with the solvent molecules, we report here in the density, viscosity and ultrasonic velocity measurements in a 20 mass % tetrahydrofuran (THF) + water mixture of ammonium nitrate, potassium nitrate, magnesium nitrate and calcium nitrate as a function of temperature. The nature of various types of interactions prevailing in these electrolyte solutions are also discussed.

Results and discussion

The apparent molar volume (V_ϕ) of liquid solutions was calculated from the relation

$$V_\phi = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \quad (1)$$

where c is the molarity of the solution and the other symbols have their usual significance. The correction to V_ϕ due to hydrolysis of electrolytes only may be negligible, since the strong hydrogen bonding⁴ between THF and H_2O will reduce the hydrolysis of these electrolytes by free water molecules considerably.

Application of the Redlich-Meyer equation was not possible due to the lack of data on the compressibility and pressure variation of dielectric constant, necessary to calculate the theoretical limiting slope (S_ϕ^∞). Thus, the limiting apparent molar volume (V_ϕ^∞) and experimental slope (S_ϕ^∞) were obtained by a least square method. Within experimental error, values for (V_ϕ^∞) varied linearly with \sqrt{c} to follow the following equation⁵.

Table 1. Physical properties of pure tetrahydrofuran (THF) and 20 mass % THF + H_2O solvent mixture at different temperatures

T/K	Mass%	$\rho/\text{g cm}^{-3}$		η/cP	
		Present work	Lit.	Present work	Lit.
298	100 (Pure THF)	0.88072	0.88072 ^a	0.46300	0.46300 ^a
303	"	0.87595	0.88070 ^b	-	0.46000 ^b
308	"	0.87116	0.87116 ^a	0.42770	0.42770 ^a
313	"	0.86627	-	0.40893	-
318	"	0.86140	0.86140 ^a	0.39017	0.39017 ^a
323	"	0.86051	0.86051 ^a	0.38921	0.38921 ^a
298	20	0.98668	0.98668 ^a	1.49002	1.49002 ^a
303	"	0.98488	-	1.31155	-
308	"	0.98488	-	1.31435	-
313	"	0.98019	-	1.05991	-
318	"	0.97730	0.97730 ^a	0.89670	0.89670 ^a
323	"	0.97631	0.97631 ^a	0.89535	0.89535 ^a

^aRefs. 1-4, ^bRef. 16

$$V_\phi^\infty = V_\phi^\infty + S_\phi^\infty \sqrt{c} \quad (2)$$

where S_ϕ^∞ is a constant, dependent on charge and salt type and can be related to solute-solute interactions and V_ϕ^∞ is the limiting apparent molar volume which is related to solute-solvent interactions. The V_ϕ^∞ values along with the experimental slopes (S_ϕ^∞) are listed in Table 2.

The variation of V_ϕ^∞ with temperature of the electrolytes in this solvent mixture follows the polynomial equation.

$$V_\phi^\infty = a_0 + a_1 T + a_2 T^2 \quad (3)$$

Table 2. Limiting apparent molar volumes (V_ϕ^0) and experimental Slopes (S_ϕ^*) together with standard errors of different salts in 20 mass % tetrahydrofuran + water at different temperatures

salts	V_ϕ^0 at various temp. ($\text{cm}^3 \text{mol}^{-1}$)					S_ϕ^* at various temp. ($\text{L}^{1/2} \text{mol}^{-3/2}$)				
	303K	308K	313K	318K	323K	303K	308K	313K	318K	323K
NH_4NO_3	0.933 (± 0.2)	9.157 (± 0.5)	17.115 (± 0.3)	19.751 (± 0.2)	21.062 (± 0.5)	76.239 (± 0.6)	75.378 (± 0.6)	70.059 (± 0.8)	67.6.3 (± 0.3)	65.715 (± 0.2)
KNO_3	4.731 (± 0.4)	16.532 (± 0.3)	20.726 (± 0.4)	23.049 (± 0.4)	23.155 (± 0.1)	62.311 (± 0.8)	41.510 (± 0.2)	39.029 (± 0.2)	37.668 (± 0.1)	35.437 (± 0.1)
$\text{Ca}(\text{NO}_3)_2$	1.746 (± 0.3)	7.019 (± 0.4)	14.771 (± 0.5)	21.310 (± 0.4)	26.293 (± 0.1)	242.21 (± 0.1)	237.87 (± 0.2)	226.18 (± 0.3)	219.42 (± 0.2)	214.53 (± 0.1)
$\text{Mg}(\text{NO}_3)_2$	44.297 (± 0.5)	50.449 (± 0.4)	57.154 (± 0.4)	61.684 (± 0.7)	67.329 (± 0.5)	221.71 (± 0.5)	219.59 (± 0.7)	214.54 (± 0.5)	208.17 (± 0.1)	200.54 (± 0.6)

(Values in the parenthesis are standard errors.)

Where T is the temperature in Kelvin. The coefficients u_0 , a_1 and a_2 are determined and the following equations are obtained.

$$V_\phi^0/\text{cm}^3 \text{mol}^{-1} = -6477.95/\text{cm}^3 \text{mol}^{-1} + 40.70 T / \text{cm}^3 \text{mol}^{-1} \text{K}^{-1} - 0.063 T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for ammonium nitrate (4)

$$V_\phi^0/\text{cm}^3 \text{mol}^{-1} = -5506.53/\text{cm}^3 \text{mol}^{-1} + 34.25 T / \text{cm}^3 \text{mol}^{-1} \text{K}^{-1} - 0.053 T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for potassium nitrate (5)

$$V_\phi^0/\text{cm}^3 \text{mol}^{-1} = -105.71/\text{cm}^3 \text{mol}^{-1} + 5.93 T / \text{cm}^3 \text{mol}^{-1} \text{K}^{-1} - 0.007 T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for calcium nitrate. (6)

$$V_\phi^0/\text{cm}^3 \text{mol}^{-1} = -1578.27/\text{cm}^3 \text{mol}^{-1} + 9.29 T / \text{cm}^3 \text{mol}^{-1} \text{K}^{-1} - 0.013 T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for magnesium nitrate (7)

The apparent molar expansibilities (ϕ_E^0) can be obtained by differentiating equation (3) with respect to temperature

$$\phi_E^0 = (\delta V_\phi^0 / \delta T)_p = a_1 + 2a_2 T \quad (8)$$

The ϕ_E^0 values of the studied electrolytes at 303, 308, 313, 318 and 323 K are determined and recorded in Table 3.

The viscosity data of solutions for various electrolytes viz. ammonium nitrate, potassium nitrate, magnesium nitrate and calcium nitrate

Table 3. Limiting apparent molar expansibilities (ϕ_E^0) for various salts in 20 mass % tetrahydrofuran + water at different temperatures

Electrolytes	Limiting apparent molar expansibilities ϕ_E^0 ($\text{cm}^3 \text{mol}^{-1} \text{K}^{-1}$)				
	303K	308 K	313 K	318 K	323 K
NH_4NO_3	2.292	1.662	1.032	0.402	-0.228
KNO_3	2.130	1.600	1.070	0.540	0.610
$\text{Ca}(\text{NO}_3)_2$	1.387	1.312	1.237	1.162	1.087
$\text{Mg}(\text{NO}_3)_2$	1.416	1.286	1.156	1.026	0.896

in 20 mass % THF + H_2O mixture have been analyzed using the Jones-Dole⁶ equation,

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc \quad (9)$$

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{c}$$

where $\eta = (Kt - Lt) \times \rho$

where η_0 and η are the viscosities of the solvent-mixture and solution respectively, A and B are constants, ρ is the density of the solvent-mixture and K and L are constants for a particular viscometer. The value of A and B are estimated by least squares method and recorded in Table 4.

Adiabatic compressibility coefficients, β were derived from the relation

$$\beta = 1/u^2 \rho \quad (10)$$

where ρ is the solution density and u is the sound velocity in the solution. The apparent molal adiabatic compressibility (ϕ_{κ}) of the liquid solutions was calculated from the relation,

$$\phi_{\kappa} = M/\rho_0 + 1000 (\beta\rho_0 - \beta_0\rho)/m\rho_0 \quad (11)$$

The limiting apparent molal adiabatic compressibilities (ϕ_{κ}^0) were obtained by extrapolating the plots of ϕ_{κ} versus the square root of molal concentration of the solute to zero concentration by the computerised least squares method,

$$\phi_{\kappa} = \phi_{\kappa}^0 + S_{\kappa}^* m^{1/2} \quad (12)$$

The values of β , ϕ_{κ} , ϕ_{κ}^0 and S_{κ}^* are reported in Table 5.

The S_{κ}^* values shown in Table 2 are positive for all metal nitrates studied here in 20 mass % THF + H_2O mixture indicating strong solute-solute interactions in this mixture medium. This type of behaviour of alkali metal chlorides, tetraalkylammonium halides and some common salts has also been observed in different solvents and solvent-mixture systems. may be that ionic association would become quite appreciable in this medium as the concentration of the

© The possible explanation for the positive slopes in the studied solvent mixture have magnetic

Jha *et al.* : Volumetric, viscometric and ultrasonic studies of some nitrate compounds *etc.*

Table 4. Molar concentrations, densities, viscosities, apparent molar volumes and values of *B*-coefficient and *A* in 20 mass % tetrahydrofuran + water mixture at different temperatures.

<i>c</i> /mol dm ⁻³	ρ_0 /g.cm ⁻³	η_0 /cP	V_ϕ /cm ³ mol ⁻¹	<i>B</i> /cm ³ mol ⁻¹	<i>A</i> /cm ^{3/2} mol ^{-1/2}
T = 303 K					
NH ₄ NO ₃					
0.03601	0.98719	1.01332	16.009		
0.07801	0.98952	0.91590	20.887		
0.12002	0.99143	0.92989	25.887	2.627	-1.744
0.16203	0.99299	0.94730	30.445	(±0.2)	(±0.3)
0.19083	0.99325	0.98824	35.404		
← KNO ₃					
0.03612	0.98791	0.99892	17.487		
0.07825	0.99117	0.92404	21.076		
0.12039	0.99398	0.92845	25.906	2.786	-1.805
0.16253	0.99656	0.94908	29.321	(±0.1)	(±0.2)
0.18841	0.99782	0.98214	32.928		
Ca(NO ₃) ₂					
0.03845	0.99203	1.00406	50.998		
0.08333	0.99881	0.96954	69.998		
0.12820	1.00413	0.96404	87.314	2.842	-1.744
0.17307	0.99858	1.00372	109.534	(±0.1)	(±0.1)
0.20640	1.01033	1.04275	114.578		
Mg(NO ₃) ₂					
0.03862	0.99141	0.94475	88.765		
0.08369	0.99741	0.90561	108.328		
0.12876	1.00248	0.91895	121.564	3.755	-2.164
0.17383	1.00602	0.97568	136.866	(±0.2)	(±0.2)
0.20602	1.00802	1.05038	1.05038	146.302	
T = 308 K					
NH ₄ NO ₃					
0.03593	0.98512	0.86371	23.889		
0.07781	0.98702	0.79055	29.986		
0.11961	0.98860	0.79783	34.558	2.629	-1.775
0.16159	0.98984	0.80516	38.926	(±0.2)	(±0.3)
0.19029	0.99028	0.82720	42.992		
KNO ₃					
0.03604	0.98586	0.86044	24.767		
0.07798	0.98883	0.79626	28.017		
0.12021	0.99165	0.79833	30.455	2.827	1.825
0.16213	0.99428	0.81730	32.651	(±0.1)	(±0.2)
0.18798	0.99554	0.84815	35.479		
Ca(NO ₃) ₂					
0.03823	0.99005	0.87511	55.067		
0.08311	0.99668	0.84673	73.867		
0.12747	1.00180	0.84938	90.876	2.994	-1.750
0.17268	1.00593	0.89725	105.653	(±0.2)	(±0.3)
0.20595	1.00815	0.93424	116.438		

			Mg(NO ₃) ₂			
0.03851	0.9896	0.79941	95.324			
0.08352	0.99533	0.73764	111.747			
0.12843	0.99973	0.77527	129.032	3.888		-2.286
0.17333	1.00377	0.82594	134.453	(±0.2)		(±0.1)
0.20577	1.00490	0.86226	152.986			
			T = 313 K			
			NH ₄ NO ₃			
0.03584	0.98198	0.76496	30.564			
0.07750	0.98359	0.70052	36.893			
0.11913	0.98501	0.69735	40.365	2.631		-1.818
0.16096	0.98596	.69509	45.086	(±0.3)		(±0.2)
0.18947	0.98640	0.72982	48.220			
			KNO ₃			
0.03599	0.98281	0.76737	28.777			
0.07786	0.98569	0.70947	31.098			
0.11981	0.8838	0.70972	33.376	2.861		-1.849
0.16166	0.99078	0.72696	36.324	(±0.1)		(±0.1)
0.18730	0.99207	0.75573	38.444			
			Ca(NO ₃) ₂			
0.03809	0.98692	0.78333	60.563			
0.08292	0.99344	0.82371	77.956			
0.12711	0.99843	0.83728	94.554	3.492		-1.769
0.17323	1.00261	0.87629	108.089	(±0.2)		(±0.2)
0.20548	1.00475	0.90497	118.998			
			Mg(NO ₃) ₂			
0.03845	0.98621	0.71287	101.756			
0.08336	0.99208	0.64351	116.098			
0.12818	0.99639	0.68470	132.645	3.955		-1.335
0.17304	0.99987	0.72788	145.543	(±0.1)		(±0.1)
0.20540	1.00124	0.77054	157.032			
			T = 318 K			
			NH ₄ NO ₃			
0.03576	0.97901	0.66412	32.981			
0.07731	0.98062	0.61610	38.001			
0.11873	0.98180	0.61585	43.099	2.872		-1.916
0.16055	0.98293	0.61252	46.008	(±0.2)		(±0.3)
0.18913	0.98319	0.64157	50.032			
			KNO ₃			
0.03582	0.97985	0.67594	30.555			
0.07768	0.98263	0.62620	33.221			
0.11949	0.98520	0.62569	35.777	2.880		-1.862
0.16148	0.98768	0.64070	37.676	(±0.2)		(±0.2)
0.18712	0.98889	0.66384	40.099			
			Ca(NO ₃) ₂			
0.03795	0.98382	0.64805	65.876			
0.08244	0.99017	0.66379	81.897			

Table 5. Adiabatic compressibility (β), apparent molal adiabatic compressibility (ϕ_k), limiting apparent molal adiabatic compressibility (ϕ_k^∞) and experimental slope (S_k^*) of some metal nitrates in 20 mass % THF + water mixture at various temperature.

$B \times 10^7$ Pa^{-1}	$\phi_k \times 10^4$ $\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1}$	$\phi_k^\infty \times 10^4$ $\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1}$	$S_k^* \times 10^4$ $\text{m}^3 \text{mol}^{-3/2} \text{Pa}^{-1} \text{kg}^{1/2}$				
				4.081	-0.788	(±0.1)	(±0.3)
				4.076	-0.635		
						Mg(NO ₃) ₂	
				3.985	-8432		
				3.986	-3.490		
				3.991	-1.890	-7.58	14.95
				4.015	-1.112	(±0.1)	(±0.2)
				4.024	-0.783		
						T = 323 K	
						NH ₄ NO ₃	
4.149	-4.075						
4.184	-1.352						
4.215	-0.583	-3.32	7.15	4.012	-9.168		
4.262	-0.065	(±0.1)	(±0.3)	4.021	-4.009		
4.268	-0.009			4.023	-2.512	-8.63	17.39
				4.076	-1.461	(±0.3)	(±0.1)
				4.130	-0.934		
						KNO ₃	
4.051	-6.710			4.019	-9.001		
4.095	-2.514			4.036	-3.727		
4.248	-0.255	-8.59	22.57	4.042	-2.387	-12.66	25.81
4.350	0.464	(±0.2)	(±0.1)	4.045	-1.748	(±0.1)	(±0.2)
4.422	0.815			4.074	-1.340		
						Ca(NO ₃) ₂	
4.104	-5.044			4.091	-5.831		
4.107	-1.782			4.118	-1.569		
4.079	-1.298	-3.38	5.89	4.102	-0.493	-5.59	11.65
4.078	-0.768	(±0.3)	(±0.1)	4.090	0.171	(±0.2)	(±0.2)
4.067	-0.594			4.061	0.326		
						Mg(NO ₃) ₂	
3.975	-8.161			3.975	-9.362		
4.008	-2.967			3.969	-4.099		
3.993	-1.730	-6.18	11.95	3.964	-2.403	-8.44	15.90
4.017	-0.997	(±0.1)	(±0.2)	3.975	-1.479	(±0.1)	(±0.1)
4.023	-0.673			3.979	-1.148		
						T = 313 K	
						NH ₄ NO ₃	
4.087	-6.341						
4.088	-2.730						
4.089	-1.687	-5.22	9.95				
4.105	-1.096	(±0.2)	(±0.2)				
4.120	-0.805						
						KNO ₃	
4.039	-7.684						
4.059	-3.192						
4.064	-1.927	-10.88	23.89				
4.059	-1.362	(±0.1)	(±0.3)				
4.082	-1.055						
						Ca(NO ₃) ₂	
4.076	-5.746						
4.095	-2.351						
4.103	-1.130	-5.16	10.09				

solutes in different solvents and in different solvent-mixtures, equation of Hepler¹¹ was used,

$$(\delta\phi_k^*/\delta T)_p = -(\delta^2 V_\phi^*/\delta T^2)_p \quad (13)$$

According to Hepler, structure-making solutes should have a positive value and structure breaking solutes a negative value of the term of $(\delta^2 V_\phi^*/\delta T^2)_p$ respectively. It has been observed that the values of $(\delta^2 V_\phi^*/\delta T^2)_p$ for solutions of all electrolytes are negative indicating the structure-breaking behaviours of these electrolytes viz. Ammonium nitrate, potassium nitrate, magnesium nitrate and calcium nitrate in this solvent-mixture.

The molar concentrations (c), densities (ρ), viscosities (η), apparent molar volumes (V_ϕ) and values of A and B are

Jha *et al.* : Volumetric, viscometric and ultrasonic studies of some nitrate compounds *etc.*

0.12656	0.99508	0.68592	97.911	4.086	-2.158
0.17130	0.99867	0.70403	113.978	(±0.2)	(±0.1)
0.20494	1.00149	0.76626	120.844		
			Mg(NO ₃) ₂		
0.03827	0.98319	0.62645	104.777		
0.08323	0.98892	0.56411	119.543		
0.12801	0.99336	0.59812	134.021	3.990	-2.364
0.17276	0.99677	0.63586	147.022	(±0.3)	(±0.2)
0.20510	0.99800	0.67741	159.118		
			T = 323 K		
			NH ₄ NO ₃		
0.03565	0.97448	0.59991	33.785		
0.07722	0.97605	0.58833	39.067		
0.11860	0.97728	0.60955	43.423	3.933	-1.937
0.16030	0.97830	0.65284	46.999	(±0.1)	(±0.2)
0.18889	0.97869	0.70751	50.209		
			KNO ₃		
0.03581	0.97526	0.60649	33.312		
0.07732	0.97794	0.58776	35.555		
0.11939	0.98045	0.61386	38.045	3.853	-1.893
0.16134	0.98282	0.65285	40.111	(±0.2)	(±0.3)
0.18706	0.98405	0.71605	42.119		
			Ca(NO ₃) ₂		
0.03782	0.97916	0.57644	69.987		
0.08242	0.98544	0.56608	85.118		
0.12636	0.99016	0.59773	101.543	4.468	-2.192
0.17068	0.99384	0.65358	116.045	(±0.1)	(±0.2)
0.20455	0.99643	0.72632	123.978		
			Mg(NO ₃) ₂		
0.03825	0.97856	0.56695	108.671		
0.08312	0.98410	0.54860	123.855		
0.12794	0.98865	0.58493	136.231	4.955	-2.378
0.17209	0.99202	0.66867	148.776	(±0.1)	(±0.1)
0.20459	0.99306	0.74379	161.787		

Values in the parenthesis are standard errors.

electrolyte is increased thereby weakening the solute-solvent interactions. As a consequence, contraction of the solvent-mixture would be gradually lowered with increasing concentration of the electrolyte, resulting in a net positive volume change per mole of the added solute. As expected, the S_v^* values decrease with increasing temperature in this solvent mixture for the studied electrolytes, which is attributed to more violent thermal agitation at higher temperature resulting in diminishing the force of solute-solute interactions (ionic dissociation)¹⁰.

To examine the solute-solvent interactions, the V_ϕ^0 values

can be used. Table 2 reveals that V_ϕ^0 values are negative and increase with increasing temperature. This indicates the presence of weak solute-solvent interaction and the solvent molecules are loosely attached to solute which expands with increase in temperature, thus resulting in higher values of V_ϕ^0 at higher temperature in this solvent mixture system.

It is evident from Table 3 that ϕ_E^0 values increase with increasing temperature for all electrolytes and the positive increase in ϕ_E^0 with increasing temperature can be ascribed to the presence of caging or packing effect¹⁰.

For determining structure making/breaking capacities of

recorded in Table 4.

A perusal of Table 4 shows that the values of B -coefficients for all studied electrolytes are positive and large and these values increase with increasing temperature. This indicates that these electrolytes, NH_4NO_3 , KNO_3 , $\text{K}_2(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$ act as structure-breaker in this solvent-mixture. A similar result was reported by other workers¹² in the case of viscosities of perchlorate of lithium and sodium in propionic acid + ethanol mixture.

It has been reported by a number of workers that dB/dT is a better criterion^{13,14} for determining the structure-making/breaking nature of any electrolyte rather than simply the B -coefficient. It is evident from Table 2 that the values of B are positive and increase with rise in temperature (positive dB/dT) suggesting structure-breaking tendencies of all electrolytes in this mixed solvent system. These conclusions are in excellent agreement with that drawn from $(\delta^2 V_{\phi}^0 / \delta T^2)_p$ illustrated earlier.

It is seen from Table 5 that all the salts studied here have negative apparent molal adiabatic compressibilities, ϕ_K^0 which become more negative on increasing the temperature. Negative ϕ_K^0 values of the salts are interpreted in terms of the loss of compressibility of THF + water mixture due to electrostrictive forces in the vicinity of the ions. On rising the temperature of the system, the metal ions lose some solvent molecules from their first coordination sphere in a process which is expected to increase the compressibility. But at higher temperature, breakdown of the intermolecular hydrogenbonds in the THF + water mixed system also takes place more effectively resulting in a loss of compressibility. Thus it may be concluded that for the salts solutions under study, the later effect is growing faster and overriding the former as far as the present temperature range is concerned. From Table 5, it is also evident that limiting experimental slopes, S_K^* have positive values indicating the existence of strong solute-solute interactions in the studied solvent system which resembles the agreement drawn from S_K^* discussed earlier. A similar result was reported by worker¹⁵ in the case of ultrasonic studies of some alkali metal fluorides and bromides in THF + water mixture.

Experimental

The purification of tetrahydrofuran (Merck, India), ammonium nitrate, potassium nitrate, magnesium nitrate and calcium nitrate (AR Sd. fine chemicals) and density measurements of various solutions are described earlier¹⁶. The binary aqueous solutions of tetrahydrofuran as well as solutions of nitrates were made by mass and conversion of molality into molarity was done¹⁷.

The viscosities were measured by means of suspended-level Ubbelohde¹⁸ viscometer at the desired temperature (accuracy ± 0.01 K). The precision of the viscosity measurements was 0.05%. Details have been described earlier².

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 ± 0.01 K by circulating thermostated water around the cell by a circulating pump.

The experimental values of densities (ρ_0) and viscosities (η_0) of pure tetrahydrofuran and 20 mass % tetrahydrofuran + water mixture at 303, 308, 313, 318 and 323 K are recorded (Table 1).

Acknowledgement

The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No 540 /6/ DRS/ 2002, SAP-1) for financial support.

References

1. M. N. Roy, A. Jha and R. Dey, *J. Chem. Eng. Data*, 201, 46, 1247.
2. B. Das, M. N. Roy and D. K. Hazra, *Indian J. Chem. Technol.*, 1994, 1, 93.
3. M. N. Roy, D. Nandi and D. K. Hazra, *J. Indian Chem. Soc.*, 993, 70, 123.
4. M. N. Roy, D. Nandi and D. K. Hazra, *J. Indian Chem. Soc.*, 1993, 70, 305.
5. D. O. Masson, *Phil. Mag.*, 1929, 8, 218.
6. G. Jones and M. Dole, *J. Am. Chem. Soc.*, 1929, 51, 2950.
7. B. Das and D. K. Hazra, *J. Chem. Eng. Data*, 1991, 36, 403.
8. B. E. Conway, R. E. Verrel and J. E. Desnoyers, *Trans. Faraday Soc.*, 1966, 62, 2738.
9. P. S. Nikam, A. B. Sawant and J. S. Aher, *J. Indian Chem. Soc.*, 2000, 77, 197.
10. F. J. Millero, in "Structure and Transport Process in Water and Aqueous Solutions", ed. R. A. Horne, Wiley Interscience, New York, 1972, Chap. 4, 13.
11. L. G. Hepler, *Can. J. Chem.*, 1969, 478, 4613.
12. M. L. Parmar and M. K. Chauhan, *Indian J. Chem., Sect. A*, 1995, 34, 434.
13. R. Gopal and M. A. Siddiqui, *J. Phys. Chem.*, 1969, 72, 1814.
14. N. Saha and B. Das, *J. Eng. Chem. Data*, 1997, 42, 277.
15. M. N. Roy, *North Bengal University Review (Sci. and*

- Technol.*, 1997, 8, 54.
16. A. Choudhury, Anupam Jha and M. N. Roy, *J. Indian Chem. Soc.* (in press).
17. D. P. Shoemaker and C. W. Garland, 'Experiments in Physical Chemistry', McGraw-Hill, New York, 1967, p. 131.
18. J. R. Suindells and T. B. Godtray, *J. Res. Natl. Bur. Stand.*, 1952, 48, 1.

JOURNAL OF TEACHING AND RESEARCH IN CHEMISTRY

DEPARTMENT OF CHEMISTRY

UTKAL UNIVERSITY , BHUBANESWAR

Title of the Paper submitted :

Studies on Thermodynamic

at Different Temperatures

Authors : Jha et al

The paper has been accepted for publication in J T R C
and will come out in the December Issue , 2003.

U.N. Dash
12.11.03

(Prof U.N.DASH)

EDITOR, J T R C

J. T. R. C,
Department of Chemistry,
Utkal University,
Bhubaneswar - 751004.

