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1. Study of Ion-Solvent Interactions of Some Alkali Metal Chlorides in Tetrahydro furan + Water Mixture at Different Temperatures.

   J. Chem. Eng. Data. 2001, **46**, 1347.

2. Limiting Apparent Molar Volumes, Their Temperatures Derivation and Viscosity B-Co-efficients for some Alkali Metal Chlorides in Aqueous Tetrahydo furan mixture.

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4. Solute-Solute and Solute-Solvent Interactions and Expansibilities of Some Electrolytes in Tetrahydo furan + Water Mixture at Various Temperatures.

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5. Electrical Conductances of Tetraalkylammonium and Alkali Metal Salts in Aqueous Binary Mixtures of Tetrahydro furan at Different Temperatures.

   J. Tech. Res. Chem., 2004, **11**, 61.

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

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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^0) and slopes (S_v^*) 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 ($d^2V_\phi^0/dT^2$), dB/dT, and the *B* coefficient for all electolytes 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 workers[3–5] 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^0), experimental slopes (S_v^*), limiting apparent molar expansibilities (ϕ_E^0), 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 $g \cdot cm^3$), and viscosity (η_0 = 0.0046 P) compared well with the literature values.[7] The specific conductance of THF was 0.81 × 10^{-6} Ω^{-1} cm^{-1} at 25 °C.

Alkali metal chlorides (Fluka) were of purum or puriss grade and purified by us as described earlier.[6,9]

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 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 ±3 × 10^{-5} $g \cdot cm^{-3}$. Details were given earlier in a publication from our laboratory (Das and Roy, 1993).

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

		$\rho_0/g \cdot cm^{-3}$		η_0/cP	
T/K	mass %	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[a]	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	0.96381		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]

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

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

10.1021/je010009w CCC: $20.00

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

salt	V_ϕ^o at various temps ($cm^3\ mol^{-1}$)				S_v^* at various temps ($cm^3\ L^{1/2}\ mol^{-3/2}$)			
	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^o) for Various Salts in 40 Mass % THF + Water at Different Temperatures

electrolyte	limiting apparent molar expansibilities ϕ_E^o ($cm^3\ mol^{-1}\ K^{-1}$)			
	303 K	308 K	313 K	318 K
LiCl	−44.656	−41.998	−39.340	−36.682
NaCl	−43.675	−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- bonding[11] 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^o) was calculated by using the equation[12]

$$V_\phi = V_\phi^o + S_v^* c^{1/2} \tag{2}$$

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

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

$$V_\phi^o = a_0 + a_1 T + a_2 T^2 \tag{3}$$

where T is the temperature in degrees kelvin.

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

$$\phi_E^o = (dV\phi^o/dT)p = a_1 + 2a_2T \tag{4}$$

The ϕ_E^o 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 + H_2O mixture at different temperatures were also determined. The data were analyzed by using the Jones−Dole[13] equation

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

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

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 + H_2O 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 + H_2O 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^o 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 tempearture and with larger metal ion. Similar results are reported for some metal sulfates in different DMF + H_2O mixtures at different temperatures.[15] It is evident from Table 3 that the ϕ_E^o 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 [$d^2V_\phi^o/dT^2$] 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 criterion[21] 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 mol dm^{-3}	ρ g·cm^{-3}	η cP	V_ϕ dm^3 mol^{-1}	B dm^3 mol^{-1}	A 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	0.97482	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	0.97549	1.05111	−87.62	6.281	−3.108
0.12589	0.97766	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	0.98290	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	0.95848	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	0.96813	0.86306	−72.52		
0.18281	0.97131	0.89269	−57.19		
313 K, NaCl					
0.01394	0.96390	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	−388.62		
0.08316	0.96692	0.79824	−204.62	5.308	−2.523
0.12477	0.96883	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 d*B*/d*T*), suggesting a structure-promoting tendency of alkali metal chlorides. The same conclusion is obtained by determining [$d^2V_\phi^\circ/dT^2$] values as mentioned above. Besides, the positive *B* values and negative d*B*/d*T* values show the absence of a firm layer of solvent mixture around the ion in their cosphere.

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

JE010009W

ultrasonic interferometer at 2 MHz frequency at different temperatures in a thermostat (± 0.1°). The accuracy of velocity measurement was ± 0.03%. The density (± 0.024% error) was determined by a bicapillary pyknometer.

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J. Indian Chem. Soc.,
Vol. 79, February 2002, pp. 148-150

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

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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 nature[1]. 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 permitivities (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 + H_2O) 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 interaction[2] 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),

$$\phi_V = M/\rho_0 - 1000\,(\rho - \rho_0)/c\rho_0 \tag{1}$$

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 equation[3],

$$\phi_V = \phi_V^0 + S_V^* c^{1/2} \tag{2}$$

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 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.

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

Wt.%	x_2	D	ρ_0 g cm^{-3}	η_0 cP	$10^6 L_0$ Ω^{-1} 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

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 glycal-water mix-

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

Salts	ϕ_v^o (cm^3 mol^{-1})				S_v^* (L$^{1/2}$ mol$^{-3/2}$)			
	303	308	313	318 K	303	308	313	318 K
LiCl	−268.186	−311.532	−480.479	−641.178	759.865	875.099	1301.100	1678.604
	(±0.01)	(±0.01)	(±0.02)	(±0.01)	(±0.01)	(±0.01)	(±0.02)	(±0.01)
NaCl	−346.804	−371.254	−554.387	−727.152	1112.941	1144.795	1700.396	2264.464
	(±0.02)	(±0.01)	(±0.01)	(±0.02)	(±0.02)	(±0.01)	(±0.01)	(±0.01)
KCl	−528.192	−561.238	−782.683	−990.201	1747.011	1835.353	2541.661	3260.971
	(±0.02)	(±0.01)	(±0.02)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)

*Standard error in parenthesis.

tures[1]. 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 of these electrolytes in aqueous mixtures of THF at 298 K has been drawn from conductometric studies[5]. Fuoss[6] also found similar trends for many of the alkali metal halides in dioxane-water mixtures. The increase of S_v^* with increase of temperature in this solvent-mixture for the studied salt suggests that more and more solute is accommodated in the void space left in the packing of large associated solvent molecules. It is also evident from Table 2 that the limiting apparent molar volumes, ϕ_v^o are large and negative and this negative values increase as the size of the alkali metal ion increases (from Li$^+$ to K$^+$) as well as with increase in temperature (from 303 to 318). This indicates the presence of weak solute-solvent interaction and in this solvent-mixture, the solute-solvent interaction decreases from lithium chloride to potassium chloride.

Table 3. Limiting apparent molar expansibility (ϕ_E^o) for various salts in 60% (w/w) THF + water mixture at different temperature

Salts	ϕ_E^o [ml/(mol)(deg)]			
	303	308	313	318 K
LiCl	−36.264	−34.614	−32.965	−31.315
NaCl	−39.737	−37.663	−35.589	−33.516
KCl	−48.467	−45.682	−42.896	−40.111

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

$$\phi_v^o = a_0 + a_1T + a_2T^2 \tag{3}$$

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

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

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

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

The limiting apprent molar expansibilities, [$\phi_E^o = (\delta\phi_v^o/\delta T)_p$] 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^o increase with increase in temperature for all studied electrolytes, which can be ascribed to the presence of caging or packing effect[7].

For determining structure-making and structure-breaking capacities of solutes in different solvents, the equation of Hepler[8] was used,

$$(\delta\phi_E^o/\delta T) = -(\delta^2\phi_v^o/\delta T^2)_p \tag{7}$$

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

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

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

*Standard errors are given in parenthesis.

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

The visocity data of solution for the electrolytes (LiCl, NaCl and KCl) in THF + H_2O mixture (60%, w/w) have been analyzed using Jones-Dole equation[9],

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc \tag{8}$$

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 workers[10] 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 criterion[11] 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 308 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 $(\delta^2\phi_v^0/\delta T^2)_p$ discussed earlier.

Experimental

Tetrahydrofuran (THF; Merck) was kept several days over KOH, then refluxed for 24 h and distilled over $LiAlH_4$ as described earlier[12]. The boiling point (66°), density (0.88072 g cm^3) and viscosity (0.0046 P) compared well with the literature values[13]. The specific conductance of tetrahydrofuran was *ca* $0.81 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 25°.

Alkali-metal chlorides (Fluka, Puris or Purum) were purified as described earlier[14].

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 cm^3 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 benzene[12]. Viscosity was measured by means of a suspended-level Ubbelohde[15] 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 earlier[12].

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J. Indian Chem. Soc.,
Vol. 79, July 2002, pp. 623-626

A study on ion-solvent interactions of some sulfate compounds in aqueous tetrahydrofuran at different temperatures

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Manuscript received 11 July 2001, revised 1 January 2002, accepted 12 February 2002

The densities and viscosities of ammonium sulfate, sodium sulfate, magnesium sulfate and aluminium sulfate in 40 mass% tetrahydrofuran + water mixture have been measured at temperatures 303, 308, 313 and 318 K. Apparent molar volumes (V_ϕ) and viscosity *B*-coefficients of these electrolytes are derived from these data supplemented with their densities and viscosities, respectively. The limiting apparent molar volumes (V_ϕ°) and experimental slopes (S_V^*) obtained from Masson equation have been interpreted in terms of ion-solvent and ion-ion interactions, respectively. The viscosity data have been analyzed using Jones-Dole equation. The V_ϕ° values vary with temperature as a power of series of temperature. The structure-making/breaking capacities of the electrolytes studied here have been inferred from the Hepler's criterion.

The volumetric behavior of solutes has been proved to be very useful in elucidating the various interactions occurring in aqueous and non-aqueous solutions[1]. It has been found by a number of workers[2] that the addition of electrolyte could either break or make the structure of a liquid. 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.

Tetrahydrofuran (THF), commercially known as cellosolves, is a good industrial solvent. It figures prominently in the high energy battery industry and has been found its application in the organic syntheses as manifested from physicochemical studies in this medium[3]. THF + H_2O mixtures are also important owing to the H-bonding between water and tetrahydrofuran.

In continuation of our earlier findings[4–7], we present here the measurement of limiting apparent molar volume, experimental slope and viscosity *B*-coefficient for some metal and ammonium sulfates at different temperatures to obtain better insight into ion-solvent, ion-ion and solvent-solvent interactions.

Results and Discussion

The experimental values of densities (ρ_0) and viscosities (η_0) of pure THF and different mass% of THF + H_2O mixtures at 298, 303, 308, 313 and 318 K are recorded in Table 1. The results reveal that η_0 of the solvent mixtures (THF + H_2O) at all the temperatures increases rapidly to a maximum at about 40 mass% of THF and thereafter decreases. Such characteristics in the viscosity vs composition curve is a manifestation of strong specific interaction[8] between unlike molecules predominated by H-bonding interaction.

The apparent molar volumes (V_ϕ) were determined from the solvent-mixture and solution densities using the equation.

$$V_\phi = \frac{M}{\rho_o} - \frac{1000(\rho - \rho_o)}{c\rho_o} \tag{1}$$

where *M* is the molecular weight of the solute, *c* the molarity of the solution and the other symbols have theri usual significance. The correction to V_ϕ due to hydrolysis of the electrolytes may be negligible, since the strong H-bonding[8] between THF and H_2O will reduce the hydrolysis of these electrolytes by free water molecules considerably.

Application of Redlich-Meyer equation[9] was not possible due to the lack of data on the compressibility and pressure variation of dielectric constant, necessary to calculate the theoretical slope S_V^*. Thus, the limiting apparent molar volumes (V_ϕ°) and experimental slopes (S_V^*) were obtained by computerized least-square methods using Masson equation[10]. Within the experimental error, our values for V_ϕ varied linearly with $c^{1/2}$ to follow the following equation.

$$V_\phi = V_\phi^\circ + S_V^* c^{1/2} \tag{2}$$

where S_V^* is a constant dependent on charge and salt type and can be related to ion-ion interactions and V_ϕ° is related to ion-solvent interactions. The values of V_ϕ° and S_V^* together with standard errors are listed in Table 2. The negative values of S_V^* for all temperatures indicate the presence of weak ion-ion interactions in case of ammonium sulfate.

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

T(K)	ρ_0 (g cm^{-3}) This work	ρ_0 (g cm^{-3}) lit.	η_0 (cp) This work	η_0 (cp) lit.
(i) 20% THF :				
298	0.98668	0.98668^a	1.49002	1.49002^c
303	0.98488	-	1.31155	-
308	0.98309	0.98309^a	1.13310	1.13310^c
313	0.98019	-	1.05991	-
318	0.97730	0.97730^a	0.89670	0.89670^c
(ii) 40% THF :				
298	0.96640	0.96640^a	1.73210	1.73210^c
303	0.96381	-	1.52760	-
308	0.96120	0.96120^a	1.32310	1.32310^c
313	0.95359	-	1.18412	-
318	0.94598	0.94598^a	1.04516	1.04516^c
(iii) 60% THF :				
298	0.94600	0.94601^a	1.49040	1.49042^c
303	0.94204	-	1.33984	-
308	0.93810	0.93810^a	1.18930	1.18931^c
313	0.93338	-	1.07421	-
318	0.92864	0.92863^a	0.95910	0.95909^c
(iv) 80% THF :				
298	0.91592	-	0.91591^a	0.92371^c
303	0.91181	-	0.85386	-
308	0.90768	0.90768^a	0.78401	0.78400^c
313	0.90251	-	0.72270	-
318	0.89732	0.89732^a	0.66141	0.66140^c
(v) 100% (pure) THF :				
298	0.88072	0.88072^a 0.8870^b	0.46300	0.46300^c 0.46000^b
303	0.87595	-	0.44536	-
308	0.87116	0.87116^a	0.42770	0.42770^b
313	0.86627	-	0.40893	-
318	0.86140	0.86140^a	0.3917	0.39017^c

^{a}Refs. 4–7. ^{b} Refs. 6,7. ^{b} Ref. 18. ^{c} Refs. 6,7.

sodium sulfate and aluminium sulfate. As expected S_V^* value decreases with rise in temperature in solvent-mixture for ammonium and aluminium sulfates which is attributed to more violent thermal agitation at higher temperature resulting in diminishing the force of ion-ion interactions (ionic dissociation)[11]. The positive and large value of S_V^* for all studied temperatures indicates the presence of strong ion-ion interaction for magnesium sulfate. The increase of S_V^* with increase of temperature in this solvent-mixture in case of sodium and magnesium sulfates suggests that more and more solute is accommodated in the void space left in the packing of large associated solvent molecules.

To examine the ion-solvent interactions, the values of V_ϕ^o can be used. Table 2 reveals that V_ϕ^o values increase with increasing temperature in case of ammonium and aluminium sulfates and decreases with increasing temperature in case of magnesium and sodium sulfates. This indicates that the solvent molecules are loosely attached to solute which expand with increase of temperature, thus resulting in higher values of V_ϕ^o at higher temperature for ammonium and aluminium sulfates, but for magnesium and sodium sulfates, more electrostrictive solvation occurs at higher temperature. Similar results were reported for some electrolytes in DMF + H_2O mixture[12].

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

$$\phi_V^o = \alpha_1 + \alpha_2 T + \alpha_3 T^2 \tag{3}$$

over the temperature range under the investigation. The coefficients α_i's are evaluated and the following equations are obtained :

$$\phi_V^o = -516083.699 + 3250.867\ T - 5.1055\ T^2 \tag{4}$$

for ammonium sulfate

$$\phi_V^o = 494125.408 - 3171.497\ T + 5.0933\ T^2 \tag{5}$$

Table 2. Limiting apparent molar volumes (V_ϕ^o) and experimental slopes (S_v*) together with standard errors of different salts in 40 mass% THF + water at different temperarures*

Salts	(V_ϕ^o) (cm^3 mol^{-1}) 303	308	313	318 K	S_v* (cm^3 dm$^{1/2}$ mol$^{-3/2}$) 303	308	313	318 K
$(NH_4)_2SO_4$	198.243 (±1.50)	855.277 (±1.90)	1257.036 (±1.22)	2199.71 (±1.60)	–461.341 (±0.96)	–1958.480 (±3.11)	–2954.390 (±4.61)	–5189.390 (±2.66)
Na_2SO_4	772.446 (±1.67)	474.990 (±2.50)	432.109 (±3.41)	395.997 (±4.10)	–1969.370 (±2.23)	–1111.680 (±3.39)	–807.784 (±2.59)	–932.239 (±1.63)
$MgSO_4$	–741.426 (±5.01)	–1056.890 (±0.90)	–1263.030 (±2.56)	–1506.240 (±6.11)	1838.357 (±4.48)	2656.686 (±3.39)	3262.604 (±2.01)	3883.211 (±1.11)
$Al_2(SO_4)_3$	931.711 (±1.91)	6239.947 (±2.39)	6461.712 (±1.42)	8893.751 (±3.61)	–2978.210 (±2.09)	–22276.500 (±1.18)	–23213.500 (±2.08)	–32754.800 (±2.05)

*Values in parenthesis are standard errors.

for sodium sulfate

$$\phi_v^o = 222426.752 - 1399.032\,T + 2.1865\,T^2 \qquad (6)$$

for magnesium sulfate

$$\phi_v^o = -9814543.783 + 63218.323\,T - 101.729\,T^2 \qquad (7)$$

for aluminium sulfate

The limiting apparent molar expansibilities, $\phi_E^o = (\delta\phi_v^o/\delta T)_p$ calculated from equations (4–7) for all the electrolytes are included in Table 3. It is evident that ϕ_E^o decreases with increase in temperature for ammonium and aluminium sulfates and is in accordance with the findings of Millero[1,13]. Table 3 also shows that ϕ_E^o increases with rise in temperature for sodium and magnesium sulfates. The increase and decrease in ϕ_E^o with the increase in temperature can be ascribed to the presence and absence of caging effect[2d], respectively.

Table 3. Limiting apparent molar expansibilities (ϕ_E^o) for various electrolytes in 40 mass% THF + water at different temperatures

Electrolyte	ϕ_E^o (cm^3 mol^{-1} K^{-1})			
	303	308	313	318 K
$(NH_4)_2SO_4$	156.934	105.879	54.824	3.769
Na_2SO_4	–84.957	–34.025	16.908	67.841
$MgSO_4$	–74.025	–52.160	–30.205	–8.431
$Al_2(SO_4)_3$	1570.549	553.259	–464.031	–1481.321

It is also observed from equations (4–7) that $(\delta^2 V_\phi^o/\delta T^2)$ for solutions of ammonium and aluminium sulfates is negative whereas it is positive for sodium and magnesium sulfates showing thereby that ammonium and aluminium sulfates behave as structure-breaker while sodium and magnesium sulfates behaves as structure-maker in this mixed solvent system keeping in view of the work of Hepler[14].

The relative viscosities of solutions for various electrolytes (ammonium, sodium, magnesium and aluminium sulfates) in 40 mass% THF + H_2O mixture at different temperatures were determined and analyzed by Jones-Dole[15] equation,

$$(\eta/\eta_0 - 1)/c^{1/2} = A + B\,c^{1/2} \qquad (8)$$

where $\eta = (Kt - L/t)P$

η_0 and η are the viscosities of 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 computerized least-squares method and are recorded in Table 4. The results reveal that the values of B-coefficient decrease with rise in temperature for sodium and magnesium sulfates whereas increase with rise in temperature for ammonium and aluminium sulfates in this solvent-mixture. This indicates that electrostrictive solvation is more at higher temperature for sodium and magnesium sulfates and in case of ammonium and aluminium sulfates the solvent molecules are loosely attached to solute which expand with rise in temperature. Similar results were reported for some metal sulfates in DMF + H_2O mixtures[16] at different temperatures.

It has been reported by a number of workers that dB/dT is a good and reasonable criterion[17] for determining the structure-making/breaking nature of any electrolyte. It is also evident from Table 4 that the values of dB/dT are negative for sodium and magnesium sulfates and positive in case of ammonium and aluminium sulfates, suggesting structure-making tendency of sodium and magnesium sulfates and structure-breaking tendency of ammonium and aluminium sulfates in this mixed solvent system. These conclusions are in excellent agreement with that drawn from $(\delta^2 V_\phi^o/\delta T^2)_p$ explained earlier.

Table 4. Values of B (cm^3 mol^{-1}) and A (cm$^{3/2}$ mol$^{-1/2}$) parameters together with standard errors for different electrolytes in 40 mass% THF + H_2O mixture at different temperatures*

Electrolyte	B values				A values			
	303	308	313	318 K	303	308	313	318 K
$(NH_4)_2SO_4$	5.294	5.676	6.114	7.497	–2.621	–2.690	–2.808	–3.343
	(±1.28)	(±1.01)	(±1.17)	(±2.01)	(±1.77)	(±2.78)	(±1.36)	(±1.56)
Na_2SO_4	6.350	5.378	5.291	5.211	–2.836	–2.519	–2.486	–2.412
	(±2.21)	(±2.81)	(±1.19)	(±2.18)	(±3.02)	(±2.81)	(±1.35)	(±1.55)
$MgSO_4$	7.175	6.333	6.123	6.003	–3.376	–3.037	–2.968	–2.955
	(±3.01)	(±2.19)	(±1.79)	(±1.88)	(±1.14)	(±0.99)	(±2.22)	(±1.91)
$Al_2(SO_4)_3$	15.326	16.510	17.408	17.945	–4.984	–5.391	–5.615	–5.765
	(±1.83)	(±0.91)	(±1.11)	(±1.99)	(±2.08)	(±3.21)	(±0.70)	(±1.89)

*Values in parenthesis are standard errors.

Experimental

Tetrahydrofuran (Merck) was kept several days over KOH, refluxed for 24 h and distilled over $LiAlH_4$. The boiling point (66°), density (0.8807 g cm^{-3}) and viscosity (0.0045 p) compared well with the literature values[18]. The specific conductance of tetrahydrofuran was *ca.* 0.81 × 10^{-6} Ω^{-1} cm^{-1} at 25°.

Ammonium sulfate, sodium sulfate, magnesium sulfate and aluminium sulfate (SD fine chemicals, A.R.) were used as such, after drying over P_2O_5. 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 density was 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. It was calibrated at 298, 308 and 318 K with double-distilled water and benzene. The pycnometer with the test solution was equilibrated in a water-bath maintained at the desired temperature (± 0.01 K) by means of 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 were reproducible to ±3 × 10^{-5} g cm^{-3}. Details have been described earlier[7]. The viscosity was measured by means of a suspended-level Ubbelohde[19] viscometer at the desired temperature (accuracy ±0.01°). The precision of the viscosity measurement was 0.05%. Details have been described earlier[4].

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NORTH BENGAL UNIVERSITY REVIEW

(Science & Technology)

Volume 12 **December 2001**

UNIVERSITY OF NORTH BENGAL
P.O. NORTH BENGAL UNIVERSITY
DT. DARJEELING
PIN - 734430

Solute-Solute and Solute-Solvent Interactions and Expansibilities of Some Electrolytes in Tetrahydrofuran + Water Mixture at Various Temperatures

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ABSTRACT :

Precise densities and viscosities for ammonium sulphate, sodium sulphate, magnesium sulphate and aluminium sulphate in 30 mass% tetrahydrofuran + water mixture are reported at 303, 308, 313 and 318K. The limiting apparent molar volume (V_ϕ^0) and Slope (S_V^*) derived from Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The experimental results for viscosity have been analyzed using the Jones-Dole equation and the obtained viscosity B-coefficient values are discussed with change in the solvent structure.

Introduction

It is well-known that the reaction plays an important role in determining the reactivity, which is reflected in thermodynamics, transport and spectral properties.[1,2]. In order to gain insight into the mechanism of such interactions, thermodynamic and transport studies involving one or more solutes in mixed solvent systems are highly useful. The volumetric and viscometric studies of electrolytes at infinite dilution in various mixed solvent systems have contributed to our knowledge about solute-solute and solute-solvent interactions. By examining the viscosity B-coefficient and V_ϕ^0 of ions as a function of size, nature, temperature and composition of the mixed solvent, it is possible to study the effect of these parameters on ion-water interactions, with the hope of obtaining a better understanding of the interactions in solutions.

As a part of a series of our earlier investigations[3-9] on the classical nature of solutes and their mutual and specific interactions with the solvent molecules, we report herein the same for some sulphate compounds in aqueous tetrahydrofuran mixture at different temperatures.

Materials and Methods

Tetrahydrofuran (Merck, India) was kept several for days over KOH; refluxed for 24 hours and distilled over $LiAlH_4$. The boiling point (66°C), density (0.8807s cm^3 and viscosity η_o= 0.0046 p) compared well with the literature values.[10] The specific conductance of tetrahydrofuran was Ca, 0.81 x 10^6 Ω^{-1}cm^{-1} at 25°C.

Ammonium sulphate, sodium sulphate, magnesium sulphate and aluminium sulphate were of A R grade (SD fine chemicals, India) and used as such, after drying over P_2O_5 in a desicator.

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 (p) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^2 and an internal diameter of the capillary of about 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 ± 0.01K of the desired temperature by means of 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 were taken into account. The density values are reproducible measurements were taken into account. The density values are reproducible to ± 3 x 10^4 g.cm^3. Details have been described earlier.[4]

The viscosities were measured by means of suspended-level Ubbelohde[11] viscometer at the desired temperature (accuracy ± 0.01°C) the precision of the viscosity measurement was 0.05%. Details have been described earlier[3] by us.

Results and Discussion

The experimental values of densities (ρ_o) and viscosities (η_o) of pure THF and different mass% THF + H_2O mixtures at 298, 303, 308, 313 and 318K are recorded in Table 1.

From the Table 1, it is seen that the viscosity (η_o) of the solvent mixtures (THF + H_2O) all the investigated temperatures increases rapidly to a maximum at about 40 mass% of THF and thereafter decreases. Such characteristics in the viscosity vs. composition curve is a manifestation of strong specific interaction[12] between unlike molecules predominated by H-bonding interaction.

The apparent molar volumes, Vϕ were determined from the solvent mixture and solution densities using the following equation

$$V_\phi = \frac{M}{c\rho_0} - \frac{1000(\rho - \rho_0 c)}{c\rho_0} \qquad (1)$$

where M is the molecular weight of the solute, c is the molarity of the solution and the other symbols have their usual significance. The correction to Vϕ due to hydrolysis of the electrolytes may be negligible, since the strong H-bonding[12] between THF and H_2O will reduce the hydrolysis of these electrolytes by free water molecules considerable.

Application of Redich-Meyer equation[13] was not possible due to the lack of data on the compressibility and pressure variation of dielectric constant, necessary to calculate the theoretical slope, S_v were obtained by computerized least square methods using Masson equation. Within the experimental error, our values for $V\phi$ varied linearly with $\sqrt{c}$ to follow the following equation.

$$V_\phi = V_\phi^o + S_v^* \sqrt{c} \qquad (2)$$

Where S_v^* is a constant dependent on charge and salt type and can be related to ion-ion interactions and $V_\square^o$ is the limiting apparent molar volume which is related to ion-solvent interactions. The values V_ϕ^o and S_v^o together with standard errors are listed in Table 2.

The experimental S_v^* values (Table 2) at various temperatures are all large and positive in 30 mass% THF + H_2O for all studied electrolytes here which indicate the presence of strong solute—solute interactions. This type of behaviour of some alkali metal chlorides and some common salts has been observed in propylene-glycol and THF - water mixtures, [8-15]. The increase of S_v* with increase of temperature for all electrolytes in this mixed solvent system suggests that more and more solute is accommodated in the void space left in the packing of large associated solvent molecules.

The V_ϕ^o values can be used with a view to interpreting the solute-solvent interactions. Table 2 shows that the V_ϕ^o values are negative and decrease with rise in temperature for all the electrolytes investigated here. This indicates the presence of electrostrictive solvation and more electrostrictive solvation occurs at higher temperature. Similar results are reported for some 1:1 electrolytes in DMF + H_2O

mixture.[16] The negative value of V_ϕ^o also indicates the presence of weak ion-solvent interactions of the investigated electrolytes in this solvent mixture system.

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

$$V_\phi^o = A_0 + A_1T + A_2T^2 \qquad (3)$$

Over the temperature range under investigation. The coefficients A_i's are determined and recorded in Table 3.

The limiting molar expansibilities, $\phi_E^o = (\delta V_\phi^o / \delta T)_p$ calculated from the equations (3) for various electrolytes at different temperatures are reported in Table 4. Table 4 reveals that the values of ϕ_E^o increase with rise of temperature, suggesting that these salts behave like common salts in this mixed solvent system. This can also be ascribed to the caging or packing effect.[17]

For determining long-range structure-making and structure-breaking capacities of electrolyte in various solvent system, following equation of Hepler[18] was used.

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

According to Hepler, structure-making solutes should have positive value and structure-breaking solutes negative value of the term of $(\delta^2 V_\phi^o/\delta T^2)_p$ respectively.

It is also observed that $(\delta^2 V_\phi^o/\delta T^2)_p$ for solutions of all electrolytes under investigation is positive showing thereby that these electrolytes behave as structure makers/promoters in this mixed system. Same results are found in some alkali metal halides in THF + H_2O mixture.[8]

The data for relative viscosities of the electrolytes studied here in 30 mass% THF + H_2O mixture at various temperatures were analyzed with the Jones-Dole[19] equation

$$(\eta/\eta_o - 1)/\sqrt{c} = A + B\sqrt{c} \qquad (5)$$

where η_o and η are the viscosities of solvent-mixture and solution respectively and c is the molar concentration. The Jones-Dole parameters A and B were calculated by computerized least squares method and their obtained values are included in Table 5.

For all the electrolytes [$(NH_4)_2SO_4$, Na_2SO_4, $MgSO_4$ and $Al_2(SO_4)_3$], the B-coefficients are found to be positive and decrease with rise of temperature (Table 5) indicating the existence of strong solute-solvent interactions and electrostrictive solvation, and this electrostrictive solvation increases with increasing temperature. Similar results are reported for some metal sulphates in DMF + H_2O mixture at various temperatures.[20]

A number of workers have reported that the first temperature derivative of B-coefficient, (dB/dT) is a better criterion[21,22] for determining the structure making/breaking nature of any electrolyte rather than simply the B-coefficient. It is evident from Table 4, that dB/dT is negative for all electrolytes studied here showing that these electrolytes behave as structure makers/promoters in this mixed solvent-mixture. These conclusions are in excellent agreement with that drawn from $(\delta^2V_\phi^o / \delta T^2)_p$ discussed earlier.[8,9]

Acknowledgement

The authors acknowledge the support of the University Grants Commission, New Delhi, under the Departmental Special Assistance Scheme, (No. 540/6/DRS/2002, SAP-1).

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Table 1 : Physical properties of pure tetrahydrofuran (THF) and different mass% of THF + H_2O mixtures at different temperatures.

		ρ_o/g.cm^3		η_o/cp	
T/K	Mass % THF	This work	lit.	This work	lit.
298	20	0.98668	0.98668[3-9]	1.49002	1.49002[4,7]
303	"	0.98488	-	1.31155	-
308	"	0.98309	0.98309[3-9]	1.13310	1.13310[4,7]
313	"	0.98019	-	1.05991	-
318	"	0.97730	0.97730[3-9]	0.89670	0.89670[4,7]
298	30	0.97833	0.97833 [3-9]	1.67977	1.67977 [4,7]
303	,,	0.97634	-	1.47326	-
308	,,	0.97434	0.97434 [3-9]	1.26674	1.26674 [4,7]
313	,,	0.97058	-	1.13165	-
318	,,	0.96681	0.96681 [3-9]	0.99656	0.99656 [4,7]
298	40	0.96640	0.96640[3-9]	1.73210	1.73210[4,7]
303	'	0.96381	-	1.52760	-
308	"	0.96120	0.96120[3-9]	1.32310	1.32310[4,7]
313	"	0.95359	-	1.18412	-
318	"	0.94598	0.94598[3-9]	1.04516	1.04516[4,7]
298	60	0.94600	0.94601[3-9]	1.49040	1.49042[4,7]
303	"	0.94204	-	1.33984	-
308	"	0.93810	0.93810[3-9]	1.18930	1.18931[4,7]
313	"	0.93338	-	1.07421	-
318	"	0.92864	0.92863[3-9]	0.95910	0.95909[4,7]
298	80	0.91592	0.91592 [3-9]	0.92237[7-11]	0.92371[4,7]
303	"	0.91181	-	0.85386	-
308	"	0.90768	0.90768[3-9]	0.78401	0.78400[4,7]
313	"	0.90251	-	0.72270	-
318	"	0.89732	0.89732[3-9]	0.66141	0.66140[4,7]
298	100(pure THF)	0.88072 0.8870[10]	0.88072[3-9]	0.46300 0.46000[10]	0.46300[4,7]
303	"	0.87595	-	0.44536	-
308	"	0.87116	0.87116[3-9]	0.42770	0.42770[10]
313	"	0.86627	-	0.40893	-
318	"	0.86140	0.86140[3-9]	0.3917	0.39017[4,7]

Table 2 : Limiting apparent molar volumes (V_ϕ^0) and Experimental slopes (S_v^*) together with standard errors of different salts in 30 mass% Tetrahydrofuron + Water at different temperatures.

Salts	(V_ϕ^0) at various temp. (cm.^{3}. mol^{-1})				S_v^* at various temp. (cm.^{3}. L$^{1/2}$ mol$^{-3/2}$)			
	303K	308K	313K	318K	303K	308K	313K	318K
$(NH_4)_2SO_4$	-317.727	-398.282	-444.678	-457.016	809.398	1045.079	1067.496	1336.469
	(±0.41)	(±1.75)	(±0.92)	(±0.05)	(±0.71)	(±0.91)	(±0.18)	(±0.63)
Na_2SO_4	-366.963	-450.454	-450.659	-466.964	1040.596	1306.241	1900.725	2124.257
	(±1.01)	(±0.32)	(±0.74)	(±0.13)	(±0.66)	(±0.92)	(±0.19)	(±0.77)
$MgSO_4$	-169.762	-213.953	-238.058	-242.095	698.095	799.572	858.725	868.047
	(±0.96)	(±1.33)	(±0.71)	(±0.54)	(±0.54)	(±0.17)	(±0.36)	(±0.47)
$Al_2(SO_4)_3$	-336.815	-414.435	-436.484	-402.811	1997.012	2429.250	2501.515	2553.862
	(±0.39)	(±0.42)	(±0.91)	(±0.61)	(±0.78)	(±0.65)	(±0.28)	(±0.19)

Table 3. Values of A_i of electrolytes in 30 mass % tetrahydrofuran (THF) + H_2O mixture.

Electrolytes	A_0	A_1	A_2
$(NH_4)_2SO_4$	68128.194	-432.292	0.68118
Na_2SO_4	160149.196	-1034.524	1.66590
$MgSO_4$	39961.653	-254.053	0.40134
$Al_2(SO_4)_3$	108280.710	-695.846	1.11344

Table 4 : Limiting apparent molar expansibilities (ϕ_E^o) for various electrolytes in 30 mass% Tetrahydrofuran + Water at different temperatures.

Electrolytes	Limiting apparent molar expansibilities ϕ_E^o (cm.^{3}.mol^{-1}.K^{-1})			
	303K	308K	313K	318K
$(NH_4)_2SO_4$	-19.263	-12.451	-5.639	1.172
Na_2SO_4	-24.988	-8.329	8.329	24.988
$MgSO_4$	-10.841	-6.827	-2.814	1.199
$Al_2(SO_4)_3$	-21.102	-9.966	1.167	12.302

Table 5. Values of B (cm^3 mol^{-1}) and A (cm$^{3/2}$ mol$^{-1/2}$) parameters together with standard errors for ammonium sulphate, sodium sulphate, magnesium sulphate and aluminium sulphate in 30 mass% THF + H_2O mixture at different temperatures.

Electrolytes	*B values of different temp*				*A values of different temp*			
	303K	308K	313K	318K	303K	308K	313K	318K
$(NH_4)_2SO_4$	7.386 (±0.92)	7.228 (±0 73)	7.115 (±0.82)	6.958 (±0.69)	-3.286 (±0.77)	-3.362 (±0.62)	-3.232 (±0.70)	-3.033 (±0.71)
Na_2SO_4	8.749 (±0.66)	8.506 (±0.27)	8.431 (±0.17)	8.286 (±0.38)	-3.730 (±0.08)	-3.383 (±0.25)	-3.769 (±0.61)	-3.501 (±0.81)
$MgSO_4$	6.255 (±0.10)	5.700 (±0.41)	5.562 (±0.51)	5.336 (±0.20)	-3.191 (±0.50)	-2.853 (±0.12)	-3.094 (±0.22)	-2.709 (±0.17)
$Al_2(SO_4)_3$	13.609 (±0.09)	13.225 (±0.88)	12.902 (±0.44)	12.649 (±0.32)	-4.490 (±0.66)	-4.465 (±0.72)	-4.396 (±0.30)	-4.432 (±0.12)

(values in parenthesis are standard errors)

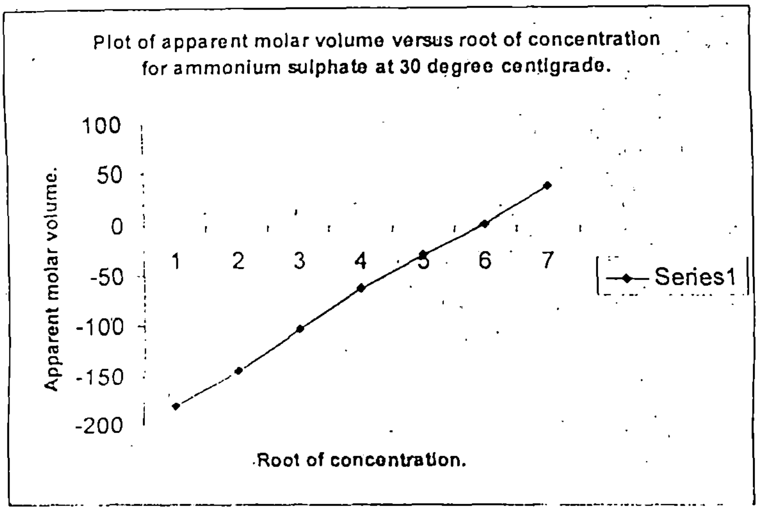
Plot of apparent molar volume versus root of concentration for ammonium sulphate at 30 degree centigrade.
100
50
0
-50
-100
-150
-200
Apparent molar volume.
1
2
3
4
5
6
7
Series1
Root of concentration.

Fig.1

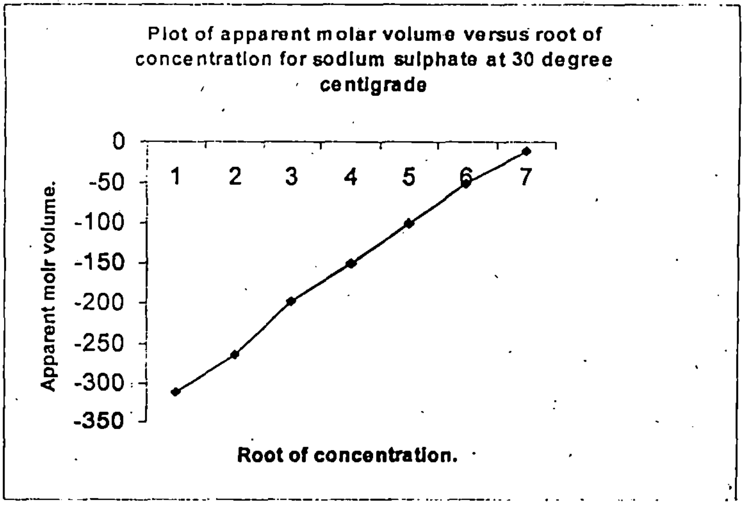
Plot of apparent molar volume versus root of concentration for sodium sulphate at 30 degree centigrade
0
-50
-100
-150
-200
-250
-300
-350
Apparent molr volume.
1
2
3
4
5
6
7
Root of concentration.

Fig. 2.

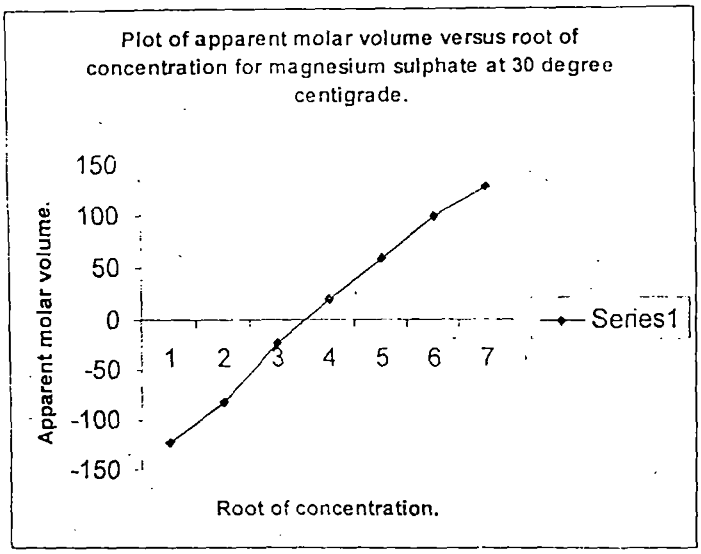
Plot of apparent molar volume versus root of concentration for magnesium sulphate at 30 degree centigrade.
Apparent molar volume.
150
100
50
0
-50
-100
-150
1
2
3
4
5
6
7
Root of concentration.
Series1

Fig. 3

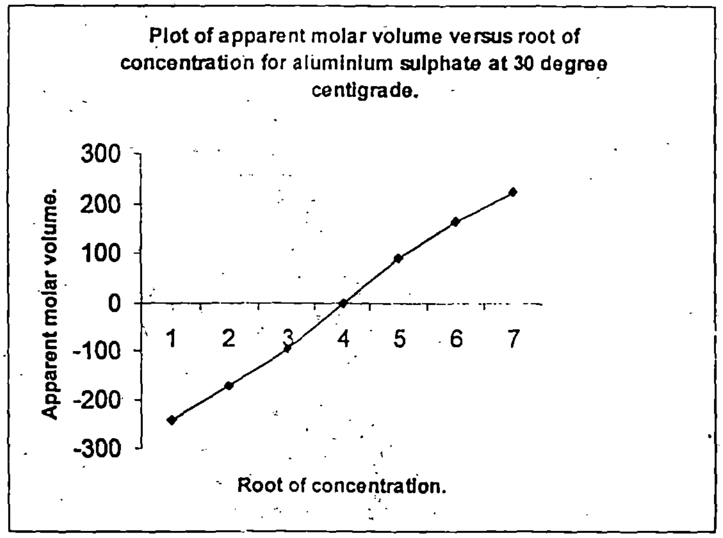
Plot of apparent molar volume versus root of concentration for aluminium sulphate at 30 degree centigrade.
Apparent molar volume.
300
200
100
0
-100
-200
-300
1
2
3
4
5
6
7
Root of concentration.

Fig.4

J.T.R. Chem. 11(2) 61-73 (2004)

Electrical conductances of tetraalkylammonium and alkali metal salts in aqueous binary mixtures of tetrahydrofuran at different temperatures

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ABSTRACT

Electrical conductance measurements are reported for tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr) and lithium bromide (LiBr) in different mass% of tetrahydrofuran (THF) [0,20,40,60,80,100] + water mixtures at 303, 313 and 323 K. The conductance data have been analysed by the Fuoss conductance-concentration equation in terms of limiting molar conductance (Λ^0), the association constant (K_A) and the distance of closest approach of ions (R). The results have been interpreted in terms of ion-ion and ion-solvent interactions.

Introduction

Extensive studies on electrical conductivities in various mixed orgnaic solvents have been peformed in recent years[1-8] to examine the nature and magnitude of ion-ion and ion-solvent interactions. Such solvent properties as the viscosity and the relative permittivity have also been taken into consideration, which help to determine the ion-association and the ion-solvent interactions.

The present study deals with the mixtures of tetrahydrofuran and water at various temperatures. Tetrahydrofuran (THF), a solvent of low permittivity (ε =7.58), has been found its probability of applications in high energy betteries[9], modern technology[10] and organic syntheses as manifested from the physico chemical studies in this medium. [11,12] Renard and Justice[13] studied the conductances of CsCl in THF + H_2O mixtres to reveal the nature of ionic assoication and mobility of ions in the mixed solvent system. In the present communication, an attempt has been made to ascertaint he complete nature of ion-solvent interactions of tetraalkylammonium and alkali metal bromide salts in THF + H_2O mitures through the measurements of their conudctances at various temperatures.

Experimental Section

Tetrahydrofuran (THF), Merck was kept several days over KOH, then refluxed for 24 h and distilled over $LiAlH_4$. Its boiling point, density and viscosity compared well with the literature values[14]. The specific conductance of THF was *ca.* 0.81×10^{-6} S.cm^{-1}.

The purities as checked by gas chromatography were found to be better than 99.8% for THF.

Tetraalkylammonium bromides and alkali metal bromide (both Fluka, purum or puriss grade) were purified as described earlier.[1,15]

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

The densities (ρ) were measured with an Ostwald-Sprengel type pyknometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pyknometer was calibrated at (303, 313 and 323) K with doubly distilled water and benzene. Details have been described earlier[16].

Conductance mesurements were carried out on a Systronic 306 conductivity bridge (accuracy +0.1%) with a dip-type immersion conductivity cell and the conductance was measured in the temperature range 303-323 K. The cell was calibrated by the method of Lind and co-workers[17] using aqueous potassium chloride solution. Measurements were made in a water bath maintained at (303$\pm$0.005, 313$\pm$0.005) and 323$\pm$0.005) K as described earlier.[18,19] Several independent solutions were prepared, and conductance measurements were performed with each of these to ensure the reproducibility of the results. Corrections were made for the specific conductances of the solvent.

The solvent properties of THF+H_2O mixtures were reported earlier[1] by us, where ε is the dielectric constant, ρ_0 the density, η_0 the viscosity and L_0 the specific conductance, W the weight percent of THF in the aqueous mixtures and X_2 the corresponding mole-fraction. Dielectric constants of the solvent mixtures were obtained by extrapolation of ε versus W % plots, the original values were taken from the work of Renard and Justice.[13]

Results and Dicussions

Molar conductance (Λ) of the salt solutions as a function of molar concentration (c) are given in Table 1 in different solvent-mixtures at different temperatures.

The conductance data have been analysed by the 1978 Fuoss conductance-concentration equation20. For a set of conductivity values (c_j, Λ_j; j = 1,..........., n), three adjustable parameters, the limiting moalr conductivity (Λ^0), the association constant (K_A) and the distance of closest approach of ions (R) are derived from the following set of equations:

Table - 1

Concentration (c), Equivalent Conductance (Λ) of some Tetraalkylammonium and Alkali Metal Bromide Salts in various (THF + H_2O) mixtures at different temperatures

c x 10^4/ mol lit^{1}	$\sqrt{c}$x10^2/ mol$^{1/2}$ lit$^{1/2}$	Λ/S cm^2 mole^{-1}	c x 10^4/ mol lit^{1}	$\sqrt{c}$x10^2/ mol$^{1/2}$ lit$^{-1/2}$	Λ/S cm^2 mole^{-1}	c x 10^4/ mol lit^{1}	$\sqrt{c}$x10^2/ mol$^{1/2}$ lit$^{-1/2}$	Λ/S cm^2 mole^{-1}
				20% mass % THF + H2O mixture				
				T = 303 K				
	Et_4NBr (M.W. = 210.17)			Pr_4NBr (M.W. = 266.27)			LiBr (M.W. = 86.85)	
22.174	4.708	101.620	22.223	4.714	98.476	22.686	4.762	75.047
44.348	6.659	92.644	44.447	6.666	90.230	45.372	6.735	69.683
88.697	9.417	81.248	88.895	9.428	79.988	90.745	9.526	59.804
133.046	11.534	72.267	133.342	11.547	72.492	136.117	11.666	55.220
177.395	13.318	63.587	177.790	13.333	66.181	181.489	13.471	50.416
221.744	14.891	56.843	222.238	14.907	58.915	226.862	15.061	44.707
226.092	16.312	50.539	266.685	16.330	54.295	272.234	16.499	39.916
310.441	17.619	45.192	311.133	17.638	50.782	317.606	17.821	34.946
354.790	18.835	40.236	355.580	18.856	44.715	362.979	19.052	31.052
399.139	19.978	34.733	400.028	20.000	39.997	408.351	20.207	30.040
				T = 313K				
21.904	4.680	111.777	21.953	4.685	104.972	22.251	4.717	78.193
43.809	6.618	105.135	43.907	6.626	98.154	44.502	6.671	71.860
87.620	9.360	93.691	87.816	9.371	85.735	89.006	9.434	62.651
131.431	11.464	85.074	131.723	11.477	78.066	133.509	11.554	57.036
175.242	13.237	78.169	175.632	13.252	70.044	178.011	13.342	54.138
219.052	14.800	71.043	219.540	14.817	64.640	222.515	14.916	48.048
262.862	16.213	66.002	263.448	16.231	57.574	267.018	16.340	45.322
306.673	17.512	60.050	307.356	17.531	53.844	311.520	17.649	41.560
350.483	18.721	54.528	351.264	18.742	48.116	356.024	18.868	36.079
394.294	19.856	51.186	395.173	19.878	44.378	400.526	20.013	32.783

T = 323 K

21.638	4.651	120.937	21.686	4.656	113.912	21.824	4.671	80.218
43.277	6.578	113.197	43.374	6.585	106.603	43.649	6.606	73.738
86.556	9.303	102.435	86.750	9.314	96.462	87.300	9.343	66.240
129.836	11.394	93.400	130.124	11.407	85.659	130.950	11.443	58.036
173.115	13.157	84.536	173.500	13.172	79.478	174.600	13.213	55.530
216.393	14.710	79.259	216.875	14.726	71.775	218.251	14.773	49.488
259.671	16.114	73.509	260.250	16.132	68.473	261.901	16.183	46.410
302.950	17.405	68.270	303.625	17.424	61.262	305.551	17.480	42.694
346.229	18.607	63.100	347.000	18.627	55.793	349.202	18.686	37.172
389.508	19.735	58.554	390.376	19.758	52.182	392.851	19.820	34.243

40 mass % THF + H_2O Mixture

T = 303 K

13.229	3.637	99.627	12.752	3.570	94.994	15.392	3.923	50.696
26.458	5.143	87.609	25.505	5.050	83.664	30.784	5.548	45.333
52.917	7.274	70.652	59.923	7.740	63.019	61.568	7.846	35.908
79.374	8.909	58.203	76.515	8.747	55.429	92.352	9.609	29.595
105.832	10.287	47.300	102.019	10.100	45.283	123.136	11.096	24.162
132.292	11.501	36.706	127.524	11.292	34.557	153.920	12.406	19.048
158.748	12.599	29.295	153.029	12.370	26.872	184.704	13.590	13.625
185.206	13.609	19.512	178.534	13.361	19.361	215.488	14.679	10.095
211.664	14.548	12.870	204.039	14.284	12.153	246.272	15.693	7.295
238.122	15.431	6.328	229.544	15.151	5.766	277.056	16.644	2.875

T = 313 K

13.068	3.615	106.477	12.597	3.549	101.301	15.097	3.885	62.262
26.137	5.112	94.421	25.195	5.019	88.863	30.194	5.494	55.304
52.274	7.230	76.772	59.195	7.693	67.694	60.388	7.770	44.643
78.410	8.855	64.072	75.586	8.694	59.759	90.582	9.517	37.257
104.547	10.225	52.952	100.780	10.038	49.779	120.776	10.989	30.048
130.686	11.432	43.491	425.976	11.224	40.971	150.970	12.287	24.426
156.821	12.523	35.240	151.172	12.295	32.443	181.165	13.459	18.909
182.958	13.526	25.623	176.367	13.280	24.367	211.359	14.538	14.268
209.095	14.460	17.802	201.563	14.197	16.775	241.553	15.541	9.448
235.232	15.337	12.290	226.758	15.058	10.622	271.747	16.484	4.674

T = 323 K

12.909	3.593	113.686	12.444	3.527	109.197	14.807	3.848	70.106
25.819	5.081	102.279	24.889	4.989	98.207	29.615	5.442	61.929
51.639	7.186	84.465	58.476	7.647	75.961	59.230	7.696	51.003
77.458	8.801	70.868	74.668	8.641	68.007	88.846	9.425	41.741
103.278	10.162	59.952	99.556	9.978	57.425	118.461	10.884	34.532
129.099	11.362	49.641	124.447	11.155	46.537	148.077	12.168	28.395
154.917	12.446	41.832	149.337	12.220	38.345	177.693	13.330	21.636
180.737	13.443	34.181	174.226	13.199	30.411	207.309	14.398	17.471
206.557	14.372	27.240	199.116	14.110	23.409	236.924	15.392	11.114
232.277	15.244	20.068	224.005	14.967	16.741	266.540	16.326	7.158

60 mass % THF + H2O Mixture

T = 303 K

6.787	2.605	103.373	6.751	2.598	96.658	8.502	2.915	48.236
13.574	3.684	89.835	13.502	3.674	85.708	17.004	4.123	41.928
27.148	5.210	72.742	27.004	5.196	69.385	34.008	5.831	34.059
40.722	6.381	60.047	40.506	6.364	56.527	51.012	7.142	30.436
54.295	7.368	48.342	54.008	7.349	45.662	68.016	8.247	24.529
67.869	8.238	38.860	67.510	8.216	36.141	85.020	9.220	20.124
81.443	9.024	29.601	81.012	9.000	26.795	102.024	10.100	18.416
95.016	9.747	21.862	94.520	9.722	20.028	119.028	10.909	14.384
108.591	10.420	12.988	108.016	10.393	11.620	136.032	11.663	9.710
122.164	11.052	7.160	121.518	11.023	5.009	153.036	12.370	7.542

T = 313 K

6.704	2.589	110.137	6.669	2.582	105.410	8.339	2.887	57.243
13.409	3.662	98.409	13.338	3.652	94.395	16.678	4.083	50.882
26.818	5.178	78.039	26.676	5.165	74.792	33.356	5.775	42.917
40.228	6.342	65.239	40.014	6.325	62.570	50.034	7.073	36.087
53.636	7.324	52.741	53.352	7.304	51.475	66.712	8.167	30.851
67.045	8.188	42.225	66.690	8.166	40.392	83.391	9.131	25.719
80.454	8.969	34.247	80.028	8.946	32.348	100.069	10.003	20.829
93.862	9.688	24.754	93.373	9.663	23.606	116.747	10.804	17.004
107.273	10.357	15.504	106.705	10.329	15.316	133.425	11.551	13.979
120.681	10.985	10.063	120.043	10.956	8.732	150.103	12.251	9.695

T = 323 K

6.623	2.573	115.521	6.588	2.567	110.673	8.179	2.859	69.243
13.246	3.639	104.430	13.176	3.629	99.962	16.358	4.044	62.348
26.492	5.147	85.051	26.352	5.133	81.012	32.716	5.719	51.769
39.739	6.304	70.147	39.528	6.287	67.509	49.075	7.005	43.909
52.985	7.279	58.009	52.704	7.259	56.053	65.433	8.089	37.789
66.231	8.138	48.504	65.881	8.116	45.455	81.793	9.043	32.355
79.477	8.915	38.525	79.056	8.891	36.411	98.151	9.907	25.661
92.722	9.629	30.327	92.239	9.604	27.925	114.510	10.700	20.906
105.971	10.294	22.339	105.409	10.267	19.105	130.868	11.439	16.853
119.216	10.918	14.806	118.586	10.889	11.878	147.227	12.133	12.848

80 mass % THF + H_2O Mixture

T = 303 K

1.480	1.216	118.162	1.669	1.291	110.258	1.594	1.262	42.007
2.961	1.720	109.834	3.338	1.827	99.059	3.187	1.785	37.009
5.922	2.433	100.396	6.676	2.583	89.060	6.374	2.524	29.892
8.884	2.980	91.481	10.014	3.164	81.427	9.561	3.092	24.778
11.845	3.441	85.446	13.352	3.654	76.215	12.748	3.570	19.777
14.807	3.847	78.890	16.689	4.085	69.518	15.936	3.991	16.398
17.768	4.215	72.854	20.028	4.475	64.934	19.123	4.372	13.544
20.729	4.552	69.261	23.366	4.833	62.483	22.309	4.723	10.044
23.691	4.867	64.188	26.704	5.167	56.031	25.497	5.049	7.147
26.652	5.162	57.873	30.042	5.481	51.594	28.684	5.355	5.521

T = 313 K

1.462	1.209	125.262	1.648	1.284	122.731	1.563	1.250	52.159
2.925	1.710	117.309	3.297	1.816	106.243	3.125	1.768	46.830
5.850	2.418	106.303	6.594	2.568	96.642	6.251	2.500	39.303
8.776	2.962	99.052	9.892	3.145	90.729	9.377	3.062	33.718
11.701	3.420	91.362	13.189	3.632	83.006	12.503	3.536	27.813
14.627	3.824	84.817	16.486	4.060	78.328	15.630	3.953	23.683
17.552	4.189	79.284	19.785	4.448	73.214	18.756	4.330	20.241
20.477	4.525	74.245	23.082	4.804	68.289	21.881	4.677	15.573
23.403	4.837	69.342	26.379	5.136	64.608	25.008	5.000	11.603
26.328	5.131	65.303	29.677	5.447	59.809	28.134	5.304	9.167

T = 323 K

1.444	1.202	133.112	1.628	1.276	130.053	1.533	1.238	60.220
2.889	1.699	125.412	3.257	1.805	124.123	3.065	1.750	54.320
5.778	2.404	112.691	6.514	2.552	105.432	6.131	2.476	44.940
8.669	2.944	104.815	9.772	3.126	96.890	9.197	3.032	38.550
11.558	3.399	97.135	13.029	3.609	90.292	12.263	3.501	32.799
14.449	3.801	90.717	16.286	4.035	85.087	15.330	3.915	27.201
17.339	4.164	84.477	19.545	4.421	78.795	18.396	4.289	22.842
20.228	4.497	79.239	22.802	4.775	75.281	21.461	4.632	19.596
23.119	4.808	74.442	26.058	5.105	70.293	24.528	4.952	14.532
26.008	5.099	71.361	29.316	5.414	66.096	27.594	5.253	11.750

$$\Lambda = P[\Lambda(1+Rx)+E_L] \qquad (1)$$

$$P = 1-\alpha(1-\gamma) \qquad (2)$$

$$\gamma = 1-K_A c\gamma^2 f^2 \qquad (3)$$

$$-\ln f = \beta\kappa/2(1+\kappa_R) \qquad (4)$$

$$\beta = e^2/DK_BT \qquad (5)$$

$$K_A = K_R/(1-\alpha) = K_R(1+K_S) \qquad (6)$$

Where Rx is the relaxation field effect, E_L is the electrophoretic countercurrent, k^{-1} is the radious of the ion atmosphere, D is the relativer permittivity of the solvent, e is the electron charge, K_B is the Boltzmann constant, λ is the fractions of solute present as unpaired ion, c is the molarity of the solution, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance. The computations were performed on a computer using the programmes suggested by Fuoss. The initial Λ^0 values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the programme is the set (c_j, Λ_j, j = 1,.....n), n, D, η, T, initial value of Λ^0, and an instruction to cover a preselected range of R values.

In practice calculations are performed by finding the values of Λ^0 and α which minimist the standard deviation

$$\sigma^2 = \sum[\Lambda_j(\text{calcd} - \Lambda_j(\text{obsd})]^2/(n-2) \qquad (7)$$

for a sequence of R values and then plotting σ against R; the best-fit R corresponds to the minimum of the σ versus R curve. First, approximate run over a fairly wide range of R values are made to locate the minimum, and then a fine scan around the minimum is made. Finally with this minimizing value of R, the corresponding Λ^0 and K_A are calculated.

The values of Λ^0, K_A, $\Lambda^0\eta^0$, σ and R obtained by this proceduce are reported in Table-2. The plots of Walden products ($\Lambda^0\eta^0$) vs mole fractions (X_1) of tetrahydrofuran at different temperatures are shown in Figures 1, 2 and 3.

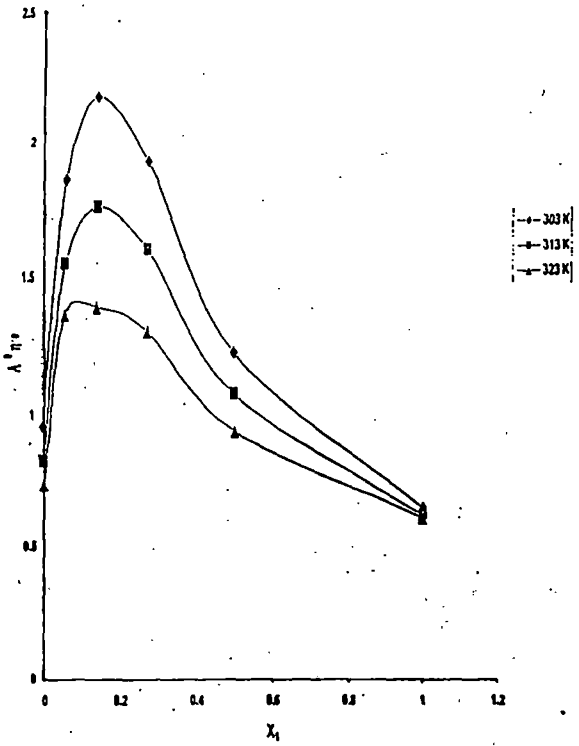

Fig. 1 : Plot of mole fraction of THF (X_1) vs Walden Product ($\Lambda^0\eta^0$) of Et_4NBr in THF + H_2O mixture at various temperatures

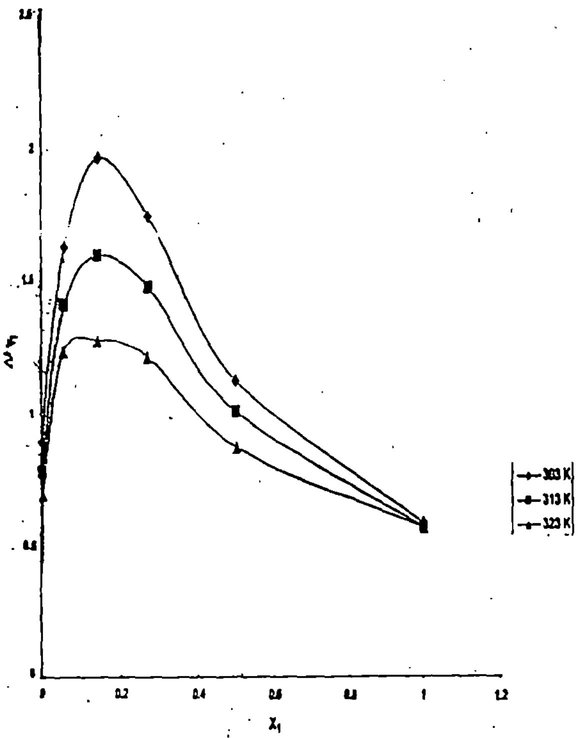

Fig. 2 : Plot of mole fraction of THF (X_1) vs Walden Product ($\Lambda^0\eta_0$) of Pr_4NBr in THF + H_2O mixture at various temperatures

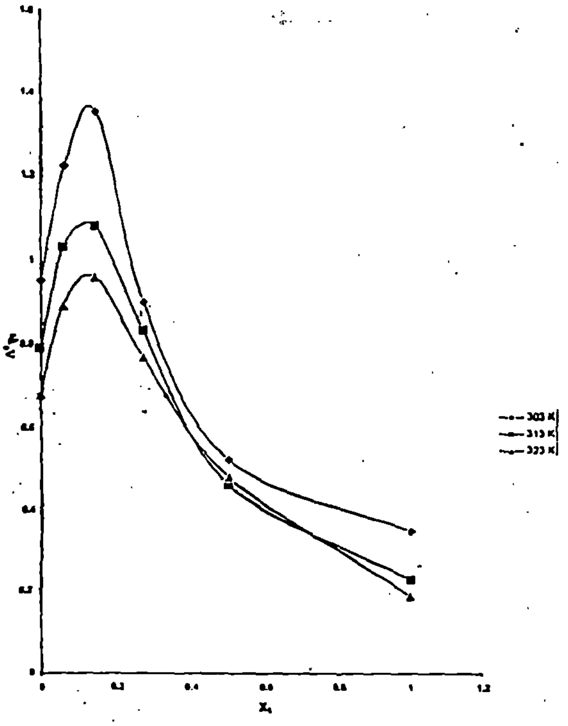

Fig. 3 : Plot of mole fraction of THF (X_1) vs Walden Product ($\Lambda^0\eta_0$) of LIBr in THF + H_2O mixture at various temperatures

The computations in these cases were carried out from arbitrarily presetting[20] of R values at R=a + d. Here a is the sum of the crystallorgraphic raddi of the ions and d the average distance corresponding to the side of a cell occupied by a solvent molecues. The distance d is given by

$$d(A) = (M/N_p)^{1/3} = 1.183(M/\rho)^{1/3} \qquad (8)$$

where M is the molecular weight of slvent and ρ is the density. for mixed solvents, M is replaced by the mole-fraction average molecular weight (Mav) which is given by

$$Mav = M_1M_2/(W_1M_2 + W_2M_1) \qquad (9)$$

where W_1 is the weight fraction of the first component of molecular weight M_1 and W_2 is the weight fraction of the second component of molecular weight M_2.

From Table2, we see that Λ^0 values for lithium bromide salt increase with rise in temperature and decrease with the addition of THF to the mixtures. In case of tetramethylammonium and tetrapropylammonium bromides, Λ^0 values increase with increase in temperature. It has also been observed that the values of Λ^0 calculated from the previous conductanc equation do not differ significantly from th

Table - 2

Derived conductance Parameters for Tetraalkylammonium and Alkali Metal Bromides in THF + H_2O at various Temperature

X_1	Λ^0	K_A	R	$\Lambda^0\eta_0$	σ
T = 303 K					
Et_4NBr					
0.000	121.62	-	14.85	0.96	-
0.059	142.15±0.05	218.70	14.91	1.86	0.05
0.143	143.21±0.12	201.61	15.21	2.18	0.12
0.273	144.56±0.03	195.11	15.61	1.93	0.03
0.500	145.12±0.08	183.27	16.09	1.23	0.08
1.000	146.86	176.22	16.89	0.65	-
Pr_4NBr					
0.000	112.64	-	14.75	0.89	-
0.059	125.04±0.04	134.42	15.02	1.63	0.04
0.143	129.26±0.06	132.63	15.17	1.97	0.06
0.273	131.12±0.07	130.73	15.50	1.75	0.07
0.500	133.05±0.011	125.83	15.98	1.13	0.011
1.000	135.78	121.76	16.79	0.60	-
LiBr					
0.000	119.85	-	5.66	0.95	
0.059	93.58±0.03	172.11	5.90	1.22	0.03
0.143	85.73±0.15	188.31	6.09	1.35	0.15
0.273	67.44±0.04	194.51	6.42	0.90	0.04
0.500	61.72±0.02	230.23	6.91	0.52	0.02
1.000	-	-	7.70	0.35	-
T = 313 K					
Et_4NBr					
0.000	128.22	-	14.86	0.83	-
0.059	147.17±0.02	104.40	14.93	1.55	0.02
0.143	148.91±0.09	98.92	15.29	1.76	0.09
0.273	149.36±0.14	92.39	15.62	1.60	0.14
0.500	150.30±0.06	85.71	16.11	1.08	0.06
1.000	151.66	74.66	16.91	0.62	-

Pr_4NBr					
0.000	120.05	-	14.76	0.78	-
0.059	133.41±0.06	131.43	15.13	1.41	0.06
0.143	135.79±0.08	128.56	15.18	1.60	0.08
0.273	137.92±0.02	123.87	15.51	1.48	0.02
0500	141.08±0.04	119.61	15.99	1.01	0.04
1.000	143.07	111.06	16.83	0.58	-
LiBr					
0.000	122.07	-	5.67	0.79	-
0.059	97.98±0.05	124.86	6.01	1.03	0.05
0.143	86.56±0.07	142.85	6.12	1.08	0.07
0.273	77.33±0.05	162.89	6.43	0.83	0.05
0.500	64.45±0.03	191.57	6.91	0.46	0.03
1.000	-	-	7.74	0.23	-
T = 323 K					
Et_4NBr					
0.000	135.52	-	14.86	0.74	
0.059	153.41±0.02	86.10	15.21	1.37	0.02
0.143	154.78±0.06	80.65	15.53	1.40	0.06
0.273	155.92±0.06	74.22	15.63	1.31	0.06
0.500	156.81±0.03	69.53	16.12	0.94	0.05
1.000	157.08	62.75	16.92	0.61	-
Pr_4NBr					
0.000	129.23	-	14.77	0.70	-
0.059	138.94±0.06	101.64	15.21	1.24	0.06
0.143	141.83±0.03	99.05	15.28	1.28	0.03
0.273	145.01±0.05	95.86	15.52	1.22	0.05
0.500	147.96±0.02	90.36	16.01	0.88	0.02
1.000	151.05	82.77	16.84	0.58	-
LiBr					
0.000	124.61	-	5.68	0.68	-
0.059	100.22±0.02	122.49	6.22	0.89	0.02
0.143	95.66±0.04	136.44	6.28	0.96	0.04
0.273	91.75±0.03	145.88	6.35	0.77	0.03
0.500	80.92±0.02	176.52	6.39	0.48	0.02
1.000	-	-	7.73	0.19	-

values of Λ^0 calculated from the 1978 Fuoss conductance concentration eqution[20]. The trend of variation of Λ^0 values in any particular temperature also indicates the actual sizes of these ions as they exist in solution. Thus, the sizes of these cations as they exist in solution follow the order.

$Et_4N^+ < Pr_4N^+ < Li^+$. This shows that Li^+ is the most solvated and Pr_4N^+ is the least one is any mole-fraction of tetrahydrofuran (THF) and in any particular temperature.

Table 2 shows that K_A values for R_4NBr salts in a given solvent-mixture decrease with increasing size of the cation in the order $Et_4N^+ > Pr_4N^+$, similar to those observed earlier[6,21], due to an apparent decrease in the ion-dipole interaction.

The variation of the Walden product shown in Table - 2 and figures 1,2 and 3 reflects the change of total solvation[22]. The value of $\Lambda^0\eta_0$ would be constant only if the effective radius of the ions were the same in different media. Since the most ions are solvated in solution the constancy of $\Lambda^0\eta_0$ is not expected. The increase of the product indicates the weak solvation of ions which attains a mazimum value at X_1=0.143. The decrease of the product indicates an increase of the hydrophobic solvation with increasing concentration of THF. The variation of $\Lambda^0\eta_0$ with X_1 is due to an electrochemical equilibrium between the cations with the solvent molecules on one hand and the selective solvation of ions on the ohter hand with the change in composition of the mixed solvents and the temperature of the solution.

On the water-rich side there exists a region, where water structure remains more or less intact as THF molecules are added interstitially into the cavities in the structure. As more and more THF is added, the cavities are progressively filled, THF-water interactions become stronger and in turn producing maximum Walden product. Further addition of THF results in progressive disruption of water structure and the ions become solvated with the other component of the solvent mixture. The effect would be more in case of a solution at a higher temperature. This charactrisitic is also a manifestation of strong specific interaction[23] between unlike molecules predominated by hydrogen bonding interaction.

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