

**STUDIES ON THE ION-SOLVENT INTERACTIONS  
OF TETRAALKYLAMMONIUM AND COMMON  
IONS IN TETRAHYDROFURAN AND ITS  
BINARY MIXTURES**

**Thesis submitted for the Degree of Doctors of Philosophy  
in Science (Chemistry) to the University of North Bengal  
2005**



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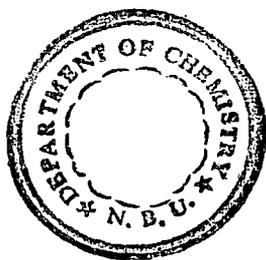
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This is to certify that Sri Rabindra Dey, M. Sc., NET (Joint CSIR-UGC National Eligibility Test) has carried out his research work under my supervision. His thesis entitled "*Studies on the Ion-Solvent Interactions of Tetraalkylammonium and Common Ions in Tetrahydrofuran and its Binary Mixtures*" is based on his original work and is being submitted for the award of Doctor of Philosophy (Science) degree in Chemistry in accordance with the rules and regulations of the University of North Bengal. He is physically fit and mentally alert to receive Ph. D. degree.



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## ACKNOWLEDGEMENT

The present work of my research was carried out by me at the Department of chemistry, University of North Bengal, Darjeeling-734430, India.

I am very much glad to express my most sincere gratitude to my respected teacher and supervisor, Dr. Mahendra Nath Roy, Reader, Department of Chemistry, University of North Bengal, Darjeeling. Throughout my research period I received from him constant guidance, valuable suggestions, constant inspiration and constructive criticism. Without his loving care and priceless supervision it could not have been possible to prepare the thesis in its present form.

I also express my deep sense of gratitude to Prof. D. K. Hazra, Department of chemistry, University of North Bengal for his invaluable assistance and continued inspiration during the course of my research work.

I am grateful to my respected father-in-law and mother-in-law for their inspiration and kind cooperation relating to my research.

I am grateful to the University authority for providing laboratory facilities. The assistance of scientific Instrumentation Centre and Computer Centre, University of North Bengal and others is acknowledged with thanks.

In connection with this thesis, I like to extend my acknowledgement to Mr. Anupam Jha, Mr. Biswajit Sinha, Mr. Ankan Choudhury, Smt. Suparna Roy Choudhury and Bhoj Bhadur Gurung for their valuable help during the course of the work.

In the long run, I would like to acknowledge my thanks to my beloved wife, Piyali for her sincere help, ceaseless inspiration and wholehearted cooperation to complete the work associated with my thesis.

I also record my thanks to the Departmental Special Assistance Scheme under the University Grants Commission New Delhi (No. 540/6/DRS/ 2002, SAP-1) for financial support.

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## List of Publications

1. Study of Ion-Solvent Interactions of Some Alkali Metal Chlorides in Tetrahydro furan + Water Mixture at Different Temperatures.  
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# 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 ( $V_\phi^\infty$ ) and slopes ( $S_\phi^*$ ) 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 ( $d^2V_\phi^\infty/dT^2$ ),  $dB/dT$ , 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.<sup>1</sup> 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.<sup>2</sup> It has been found by a number of workers<sup>3-5</sup> 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 ( $V_\phi^\infty$ ), experimental slopes ( $S_\phi^*$ ), limiting apparent molar expansibilities ( $\phi_E^\infty$ ), 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  $\text{LiAlH}_4$ .<sup>6</sup> The boiling point (66 °C), density (0.8807 g·cm<sup>-3</sup>), and viscosity ( $\eta_0 = 0.0046$  P) compared well with the literature values.<sup>7</sup> 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.<sup>8,9</sup>

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 ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> 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  $\pm 0.01$  K of the desired temperature by means of

Table 1. Properties of Pure Tetrahydrofuran (THF) and a 40 Mass % THF + H<sub>2</sub>O Solvent Mixture at Different Temperatures

T/K	mass %	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta_0/\text{cP}$	
		this work	lit.	this work	lit.
298	100 (pure THF)	0.88072	0.88072 <sup>a</sup> 0.88070 <sup>c</sup>	0.46300	0.46300 <sup>b</sup> 0.46000 <sup>c</sup>
303	100	0.87595		0.44536	
308	100	0.87116	0.87116 <sup>a</sup>	0.42770	0.42770 <sup>b</sup>
313	100	0.86627		0.40893	
318	100	0.86140	0.86140 <sup>a</sup>	0.39017	0.39017 <sup>b</sup>
298	40	0.96640	0.96640 <sup>a</sup>	1.73210	1.73210 <sup>b</sup>
303	40	0.96381		1.52760	
308	40	0.96120	0.96120 <sup>a</sup>	1.32310	1.32310 <sup>b</sup>
313	40	0.95359		1.18412	
318	40	0.94598	0.94598 <sup>a</sup>	1.04516	1.04516 <sup>b</sup>

<sup>a</sup>  $r_0$ ,<sup>9,10,22</sup> <sup>b</sup>  $h_0$ ,<sup>9,10</sup> <sup>c</sup>  $r_0$ ,  $h_0$ .<sup>7</sup>

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  $\pm 3 \times 10^{-5} \text{g}\cdot\text{cm}^{-3}$ . 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  $\pm 0.01$  °C). The precision of the viscosity measurement was 0.05%. We have previously given the details.<sup>10</sup>

The experimental values of densities ( $\rho_0$ ) and viscosities ( $\eta_0$ ) 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,  $V_\phi$ , of the solutes were calculated from the densities of the solutions by using the equation

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

**Table 2. Limiting Apparent Molar Volumes ( $V_\phi^\circ$ ) and Experimental Slopes ( $S_v^*$ ) of Different Salts in 40 Mass % THF + Water at Different Temperatures**

salt	$V_\phi^\circ$ 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 ( $\phi_E^\circ$ ) for Various Salts in 40 Mass % THF + Water at Different Temperatures**

electrolyte	limiting apparent molar expansibilities $\phi_E^\circ$ ( $\text{cm}^3 \text{mol}^{-1} \text{K}^{-1}$ )			
	303 K	308 K	313 K	318 K
LiCl	-41.656	-41.998	-39.340	-36.682
NaCl	-43.675	-43.525	-43.375	-43.225
KCl	-40.722	-47.436	-44.149	-40.863

where  $M$  is the molecular weight of the solute,  $\rho_0$  and  $\rho$  are the densities of the solvent mixture and the solution, respectively, and  $c$  is the concentration in molarity. The correction to  $V_\phi^\circ$  due to hydrolysis of salts may be negligible, because the strong H-bonding<sup>11</sup> 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 ( $V_\phi^\circ$ ) was calculated by using the equation<sup>12</sup>

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

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

The temperature dependence of  $V_\phi^\circ$  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 ( $\phi_E^\circ$ ) 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  $\phi_E^\circ$  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<sub>2</sub>O mixture at different temperatures were also determined. The data were analyzed by using the Jones-Dole<sup>13</sup> equation

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

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

where  $\eta = (Kt - At) \times \rho$ ,  $\eta_0$  and  $\eta$  are the viscosities of the solvent mixture and solution, respectively,  $A$  and  $B$  are constants,  $\rho$  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<sub>2</sub>O mixture at all of the temperatures investigated. This is an indication of strong ion-ion interactions in this solvent mixture medium.<sup>14,15</sup> This type of behavior of alkali metal chlorides and some common salts has been also observed in propylene glycol-water mixtures.<sup>16</sup> A possible explanation for the positive slopes in the 40 mass % THF + H<sub>2</sub>O 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.<sup>6</sup> The limiting apparent molar volumes  $V_\phi^\circ$  shown in Table 2 are large and negative, and these values decrease as the size of the alkali metal ion increases (from Li<sup>+</sup> to K<sup>+</sup>) 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 + H<sub>2</sub>O mixtures at different temperatures.<sup>15</sup> It is evident from Table 3 that the  $\phi_E^\circ$  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.<sup>17</sup>

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<sup>15,16,18</sup> 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.<sup>19,20</sup>

It has been reported by a number of workers that the  $(dB/dT)$  value is a better criterion<sup>21</sup> 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 <sup>-3</sup>	$\rho$ g·cm <sup>-3</sup>	$\eta$ cP	$V_{\phi}$ dm <sup>3</sup> mol <sup>-1</sup>	$B$ dm <sup>3</sup> mol <sup>-1</sup>	$A$ dm <sup>3/2</sup> mol <sup>-1/2</sup>
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	0.97442	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	0.97766	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	0.96669	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  $dB/dT$ ), suggesting a structure-promoting tendency of alkali metal chlorides. The same conclusion is

obtained by determining  $[d^2V_{\phi}/dT^2]$  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.

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

JE010009W

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# 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 ( $\phi_v^0$ ) 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<sup>1</sup>. 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 ( $\phi_v^0$ ), 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 ( $\rho_0$ ), viscosities ( $\eta_0$ ) 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  $\eta_0$  of the solvent mixture (THF + H<sub>2</sub>O) 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<sup>2</sup> between unlike molecules predominated by hydrogen bonding interaction.

The apparent molar volume ( $\phi_v$ ) 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  $\rho$  and  $\rho_0$  are the densities of the solution and solvent, respectively. The limiting apparent molar volumes ( $\phi_v^0$ ) were calculated by the Masson equation<sup>3</sup>,

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

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

Table 1. Density ( $\rho$ ), viscosity ( $\eta_0$ ), relative permittivities (*D*) and specific conductance ( $L_s$ ) for tetrahydrofuran + water at 298 K

Wt.%	<i>x</i>	<i>D</i>	$\rho_0$ g cm <sup>-3</sup>	$\eta_0$ cP	$10^6 L_s$ $\Omega^{-1} \text{cm}^{-1}$
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  $\phi_v^0$  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 ( $\phi_v^0$ ) and experimental slopes ( $S_v^0$ ) for various salts in 60% (w/w) tetrahydrofuran + water mixture at different

Salts	$\phi_v^0$ (cm <sup>3</sup> mol <sup>-1</sup> )				$S_v^0$ (L <sup>1/2</sup> mol <sup>-1/2</sup> )			
	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.

tures<sup>4</sup>. 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

Table 3. Limiting apparent molar expansibility ( $\phi_E^0$ ) for various salts in 60% (w/w) THF + water mixture at different temperature

Salts	$\phi_E^0$ [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

of these electrolytes in aqueous mixtures of THF at 298 K has been drawn from conductometric studies<sup>5</sup>. Fuoss<sup>6</sup> also found similar trends for many of the alkali metal halides in dioxane-water mixtures. The increase of  $S_v^0$  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,  $\phi_v^0$  are large and negative and this negative values increase as the size of the alkali metal ion increases (from Li<sup>+</sup> to K<sup>+</sup>) 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.

The variation of  $\phi_v^0$  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  $\phi_E^0$  increase with increase in temperature for all studied electrolytes, which can be ascribed to the presence of caging or packing effect<sup>7</sup>.

For determining structure-making and structure-breaking capacities of solutes in different solvents, the equation of Hepler<sup>8</sup> 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<sup>3/2</sup> mol<sup>-1/2</sup>) and *B* (cm<sup>3</sup> mol<sup>-1</sup>) 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 + H<sub>2</sub>O mixture (60%, w/w) have been analyzed using Jones-Dole equation<sup>9</sup>,

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

where  $\eta$  and  $\eta_0$  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<sup>10</sup> 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<sup>11</sup> 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 LiAlH<sub>4</sub> as described earlier<sup>12</sup>. The boiling point (66°), density (0.88072 g cm<sup>-3</sup>) and viscosity (0.0046 P) compared well with the literature values<sup>13</sup>. 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<sup>14</sup>.

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 ( $\rho$ ) was measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> 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<sup>12</sup>. Viscosity was measured by means of a suspended-level Ubbelohde<sup>15</sup> 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  $\pm 0.1$  s. Details have been described earlier<sup>12</sup>.

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## 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 ( $V_\phi$ ) and viscosity  $B$ -coefficients of these electrolytes are derived from these data supplemented with their densities and viscosities, respectively. The limiting apparent molar volumes ( $V_\phi^0$ ) 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  $V_\phi^0$  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<sup>1</sup>. It has been found by a number of workers<sup>2</sup> 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<sup>3</sup>. THF + H<sub>2</sub>O mixtures are also important owing to the H-bonding between water and tetrahydrofuran.

In continuation of our earlier findings<sup>4-7</sup>, 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 ( $\rho_0$ ) and viscosities ( $\eta_0$ ) of pure THF and different mass% of THF + H<sub>2</sub>O mixtures at 298, 303, 308, 313 and 318 K are recorded in Table 1. The results reveal that  $\eta_0$  of the solvent mixtures (THF + H<sub>2</sub>O) at all the temperatures increases rapidly to a maximum at about 40 mass% of THF and thereafter decreases. Such characteristics in the viscosity vs composi-

tion curve is a manifestation of strong specific interaction<sup>8</sup> between unlike molecules predominated by H-bonding interaction.

The apparent molar volumes ( $V_\phi$ ) were determined from the solvent-mixture and solution densities using the equation.

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

where  $M$  is the molecular weight of the solute,  $c$  the molarity of the solution and the other symbols have their usual significance. The correction to  $V_\phi$  due to hydrolysis of the electrolytes may be negligible, since the strong H-bonding<sup>8</sup> between THF and H<sub>2</sub>O will reduce the hydrolysis of these electrolytes by free water molecules considerably.

Application of Redlich-Meyer equation<sup>9</sup> 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 ( $V_\phi^0$ ) and experimental slopes ( $S_V^*$ ) were obtained by computerized least-square methods using Masson equation<sup>10</sup>. Within the experimental error, our values for  $V_\phi$  varied linearly with  $c^{1/2}$  to follow the following equation.

$$V_\phi = V_\phi^0 + S_V^* c^{1/2} \quad (2)$$

where  $S_V^*$  is a constant dependent on charge and salt type and can be related to ion-ion interactions and  $V_\phi^0$  is related to ion-solvent interactions. The values of  $V_\phi^0$  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<sub>2</sub>O mixtures at different temperatures

T(K)	$\rho_0$ (g cm <sup>-3</sup> )		$\eta_0$ (cp)	
	This work	lit.	This work	lit.
(i) 20% THF :				
298	0.98668	0.98668 <sup>a</sup>	1.49002	1.49002 <sup>c</sup>
303	0.98488	-	1.31155	-
308	0.98309	0.98309 <sup>a</sup>	1.13310	1.13310 <sup>c</sup>
313	0.98019	-	1.05991	-
318	0.97730	0.97730 <sup>a</sup>	0.89670	0.89670 <sup>c</sup>
(ii) 40% THF :				
298	0.96640	0.96640 <sup>a</sup>	1.73210	1.73210 <sup>c</sup>
303	0.96381	-	1.52760	-
308	0.96120	0.96120 <sup>a</sup>	1.32310	1.32310 <sup>c</sup>
313	0.95359	-	1.18412	-
318	0.94598	0.94598 <sup>a</sup>	1.04516	1.04516 <sup>c</sup>
(iii) 60% THF :				
298	0.94600	0.94601 <sup>a</sup>	1.49040	1.49042 <sup>c</sup>
303	0.94204	-	1.33984	-
308	0.93810	0.93810 <sup>a</sup>	1.18930	1.18931 <sup>c</sup>
313	0.93338	-	1.07421	-
318	0.92864	0.92863 <sup>a</sup>	0.95910	0.95909 <sup>c</sup>
(iv) 80% THF :				
298	0.91592	-	0.91591 <sup>a</sup>	0.92371 <sup>c</sup>
303	0.91181	-	0.85386	-
308	0.90768	0.90768 <sup>a</sup>	0.78401	0.78400 <sup>c</sup>
313	0.90251	-	0.72270	-
318	0.89732	0.89732 <sup>a</sup>	0.66141	0.66140 <sup>c</sup>
(v) 100% (pure) THF :				
298	0.88072	0.88072 <sup>a</sup>	0.46300	0.46300 <sup>c</sup>
		0.8870 <sup>b</sup>		0.46000 <sup>b</sup>
303	0.87595	-	0.44536	-
308	0.87116	0.87116 <sup>a</sup>	0.42770	0.42770 <sup>b</sup>
313	0.86627	-	0.40893	-
318	0.86140	0.86140 <sup>a</sup>	0.3917	0.39017 <sup>c</sup>

<sup>a</sup>Refs. 4-7. <sup>b</sup> Refs. 6,7. <sup>c</sup> Ref. 18.

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)<sup>11</sup>. 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  $V_\phi^0$  can be used. Table 2 reveals that  $V_\phi^0$  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  $V_\phi^0$  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<sub>2</sub>O mixture<sup>12</sup>.

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

$$\phi_v^0 = \alpha_1 + \alpha_2 T + \alpha_3 T^2 \quad (3)$$

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

$$\phi_v^0 = -516083.699 + 3250.867 T - 5.1055 T^2 \quad (4)$$

for ammonium sulfate

$$\phi_v^0 = 494125.408 - 3171.497 T + 5.0933 T^2 \quad (5)$$

Table 2. Limiting apparent molar volumes ( $V_\phi^0$ ) and experimental slopes ( $S_v^*$ ) together with standard errors of different salts in 40 mass% THF + water at different temperatures

Salts	$(V_\phi^0)$ (cm <sup>3</sup> mol <sup>-1</sup> )				$S_v^*$ (cm <sup>3</sup> dm <sup>1/2</sup> mol <sup>-3/2</sup> )			
	303	308	313	318 K	303	308	313	318 K
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	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 <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	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 <sub>4</sub>	-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 <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	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

$$\phi_v^0 = 222426.752 - 1399.032 T + 2.1865 T^2 \quad (6)$$

for magnesium sulfate

$$\phi_v^0 = -9814543.783 + 63218.323 T - 101.729 T^2 \quad (7)$$

for aluminium sulfate

The limiting apparent molar expansibilities,  $\phi_E^0 = (\delta\phi_v^0/\delta T)_p$  calculated from equations (4-7) for all the electrolytes are included in Table 3. It is evident that  $\phi_E^0$  decreases with increase in temperature for ammonium and aluminium sulfates and is in accordance with the findings of Millero<sup>1,13</sup>. Table 3 also shows that  $\phi_E^0$  increases with rise in temperature for sodium and magnesium sulfates. The increase and decrease in  $\phi_E^0$  with the increase in temperature can be ascribed to the presence and absence of caging effect<sup>2d</sup>, respectively.

Table 3. Limiting apparent molar expansibilities ( $\phi_E^0$ ) for various electrolytes in 40 mass% THF + water at different temperatures

Electrolyte	$\phi_E^0$ (cm <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> )			
	303	308	313	318 K
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	156.934	105.879	54.824	3.769
Na <sub>2</sub> SO <sub>4</sub>	-84.957	-34.025	16.908	67.841
MgSO <sub>4</sub>	-74.025	-52.160	-30.205	-8.431
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1570.549	553.259	-464.031	-1481.321

It is also observed from equations (4-7) that  $(\partial^2 V_p^0/\partial T^2)$  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<sup>14</sup>.

The relative viscosities of solutions for various electrolytes (ammonium, sodium, magnesium and aluminium sulfates) in 40 mass% THF + H<sub>2</sub>O mixture at different temperatures were determined and analyzed by Jones-Dole<sup>15</sup> equation,

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

$$\text{where } \eta = (Kt - Lt)P$$

$\eta_0$  and  $\eta$  are the viscosities of solvent-mixture and solution, respectively.  $A$  and  $B$  are constants,  $\rho$  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<sub>2</sub>O mixtures<sup>16</sup> at different temperatures.

It has been reported by a number of workers that  $dB/dT$  is a good and reasonable criterion<sup>17</sup> 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  $(\partial^2 V_p^0/\partial T^2)_p$  explained earlier.

Table 4. Values of  $B$  (cm<sup>3</sup> mol<sup>-1</sup>) and  $A$  (cm<sup>3/2</sup> mol<sup>-1/2</sup>) parameters together with standard errors for different electrolytes in 40 mass% THF + H<sub>2</sub>O mixture at different temperatures\*

Electrolyte	B values				A values			
	303	308	313	318 K	303	308	313	318 K
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	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 <sub>2</sub> SO <sub>4</sub>	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 <sub>4</sub>	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 <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	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  $\text{LiAlH}_4$ . The boiling point ( $66^\circ$ ), density ( $0.8807 \text{ g cm}^{-3}$ ) and viscosity ( $0.0045 \text{ p}$ ) compared well with the literature values<sup>18</sup>. The specific conductance of tetrahydrofuran was  $ca. 0.81 \times 10^{-6} \text{ } \Omega^{-1} \text{ cm}^{-1}$  at  $25^\circ$ .

Ammonium sulfate, sodium sulfate, magnesium sulfate and aluminium sulfate (SD fine chemicals, A.R.) were used as such, after drying over  $\text{P}_2\text{O}_5$ . 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  $25 \text{ cm}^3$  and an internal diameter of the capillary of  $\sim 0.1 \text{ cm}$ . 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 ( $\pm 0.01 \text{ K}$ ) 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  $\pm 3 \times 10^{-5} \text{ g cm}^{-3}$ . Details have been described earlier<sup>7</sup>. The viscosity was measured by means of a suspended-level Ubbelohde<sup>19</sup> viscometer at the desired temperature (accuracy  $\pm 0.01^\circ$ ). The precision of the viscosity measurement was 0.05%. Details have been described earlier<sup>4</sup>.

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# **NORTH BENGAL UNIVERSITY REVIEW**

( Science & Technology )

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**Volume 12**

**December 2001**

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**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 ( $V_{\phi}^{\circ}$ ) 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.<sup>1,2</sup> 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  $V_{\phi}^{\circ}$  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<sup>3-9</sup> 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  $\text{LiAlH}_4$ . The boiling point ( $66^\circ\text{C}$ ), density ( $0.8807\text{ g cm}^{-3}$ ) and viscosity ( $\eta_0 = 0.0046\text{ p}$ ) compared well with the literature values.<sup>10</sup> The specific conductance of tetrahydrofuran was  $\text{Ca. } 0.81 \times 10^6 \Omega^{-1}\text{ cm}^{-1}$  at  $25^\circ\text{C}$ .

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  $\text{P}_2\text{O}_5$  in a desiccator.

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 ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of  $25\text{ cm}^3$  and an internal diameter of the capillary of about  $0.1\text{ cm}$ . 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  $\pm 0.01\text{K}$  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 were taken into account. The density values are reproducible measurements were taken into account. The density values are reproducible to  $\pm 3 \times 10^4$  g.cm<sup>3</sup>. Details have been described earlier.<sup>4</sup>

The viscosities were measured by means of suspended-level Ubbelohde<sup>11</sup> viscometer at the desired temperature (accuracy  $\pm 0.01^\circ\text{C}$ ) the precision of the viscosity measurement was 0.05%. Details have been described earlier<sup>3</sup> by us.

### Results and Discussion

The experimental values of densities ( $\rho_0$ ) and viscosities ( $\eta_0$ ) of pure THF and different mass% THF + H<sub>2</sub>O mixtures at 298, 303, 308, 313 and 318K are recorded in Table 1.

From the Table 1, it is seen that the viscosity ( $\eta_0$ ) of the solvent mixtures (THF + H<sub>2</sub>O) 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<sup>12</sup> between unlike molecules predominated by H-bonding interaction.

The apparent molar volumes,  $V_\phi$  were determined from the solvent mixture and solution densities using the following equation

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

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  $V_\phi$  due to

hydrolysis of the electrolytes may be negligible, since the strong H-bonding<sup>12</sup> between THF and H<sub>2</sub>O will reduce the hydrolysis of these electrolytes by free water molecules considerable.

Application of Redlich-Meyer equation<sup>13</sup> 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.

$$V_\phi = V_\phi^0 + S_v^* \sqrt{c} \quad (2)$$

Where  $S_v^*$  is a constant dependent on charge and salt type and can be related to ion-ion interactions and  $V_\phi^0$  is the limiting apparent molar volume which is related to ion-solvent interactions. The values  $V_\phi^0$  and  $S_v^*$  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<sub>2</sub>O 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,<sup>8-15</sup>. 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  $V_\phi^0$  values can be used with a view to interpreting the solute-solvent interactions. Table 2 shows that the  $V_\phi^0$  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<sub>2</sub>O

mixture.<sup>16</sup> The negative value of  $V_{\phi}^{\circ}$  also indicates the presence of weak ion-solvent interactions of the investigated electrolytes in this solvent mixture system.

The variation of  $V_{\phi}^{\circ}$  with temperature of the electrolytes in this solvent-mixture follows the polynomial equation.

$$V_{\phi}^{\circ} = A_0 + A_1T + A_2T^2 \quad (3)$$

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

The limiting molar expansibilities,  $\phi_E^{\circ} = (\delta V_{\phi}^{\circ} / \delta T)_p$  calculated from the equations (3) for various electrolytes at different temperatures are reported in Table 4. Table 4 reveals that the values of  $\phi_E^{\circ}$  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.<sup>17</sup>

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

$$(\delta C_p / \delta p)_T = - (\delta^2 V_{\phi}^{\circ} / \delta T^2)_p \quad (4)$$

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

It is also observed that  $(\delta^2 V_{\phi}^{\circ} / \delta T^2)_p$  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<sub>2</sub>O mixture.<sup>8</sup>

The data for relative viscosities of the electrolytes studied here in 30 mass% THF + H<sub>2</sub>O mixture at various temperatures were analyzed with the Jones-Dole<sup>19</sup> equation

$$(\eta / \eta_0 - 1) / \sqrt{c} = A + B \sqrt{c} \quad (5)$$

where  $\eta_0$  and  $\eta$  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 [  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  ], 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 +  $\text{H}_2\text{O}$  mixture at various temperatures.<sup>20</sup>

A number of workers have reported that the first temperature derivative of  $B$ -coefficient,  $(dB/dT)$  is a better criterion<sup>21,22</sup> 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  $(\delta^2 V_\phi^0 / \delta T^2)_p$  discussed earlier.<sup>8,9</sup>

#### 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<sub>2</sub>O mixtures at different temperatures.

T/K	Mass % THF	$\rho_d/g.cm^3$		$\eta_d/cp$	
		This work	lit.	This work	lit.
298	20	0.98668	0.98668 <sup>3-9</sup>	1.49002	1.49002 <sup>4,7</sup>
303	"	0.98488	-	1.31155	-
308	"	0.98309	0.98309 <sup>3-9</sup>	1.13310	1.13310 <sup>4,7</sup>
313	"	0.98019	-	1.05991	-
318	"	0.97730	0.97730 <sup>3-9</sup>	0.89670	0.89670 <sup>4,7</sup>
298	30	0.97833	0.97833 <sup>3-9</sup>	1.67977	1.67977 <sup>4,7</sup>
303	"	0.97634	-	1.47326	-
308	"	0.97434	0.97434 <sup>3-9</sup>	1.26674	1.26674 <sup>4,7</sup>
313	"	0.97058	-	1.13165	-
318	"	0.96681	0.96681 <sup>3-9</sup>	0.99656	0.99656 <sup>4,7</sup>
298	40	0.96640	0.96640 <sup>3-9</sup>	1.73210	1.73210 <sup>4,7</sup>
303	"	0.96381	-	1.52760	-
308	"	0.96120	0.96120 <sup>3-9</sup>	1.32310	1.32310 <sup>4,7</sup>
313	"	0.95359	-	1.18412	-
318	"	0.94598	0.94598 <sup>3-9</sup>	1.04516	1.04516 <sup>4,7</sup>
298	60	0.94600	0.94601 <sup>3-9</sup>	1.49040	1.49042 <sup>4,7</sup>
303	"	0.94204	-	1.33984	-
308	"	0.93810	0.93810 <sup>3-9</sup>	1.18930	1.18931 <sup>4,7</sup>
313	"	0.93338	-	1.07421	-
318	"	0.92864	0.92863 <sup>3-9</sup>	0.95910	0.95909 <sup>4,7</sup>
298	80	0.91592	0.91592 <sup>3-9</sup>	0.92237 <sup>7-11</sup>	0.92371 <sup>4,7</sup>
303	"	0.91181	-	0.85386	-
308	"	0.90768	0.90768 <sup>3-9</sup>	0.78401	0.78400 <sup>4,7</sup>
313	"	0.90251	-	0.72270	-
318	"	0.89732	0.89732 <sup>3-9</sup>	0.66141	0.66140 <sup>4,7</sup>
298	100(pure THF)	0.88072	0.88072 <sup>3-9</sup>	0.46300	0.46300 <sup>4,7</sup>
		0.8870 <sup>10</sup>	-	0.46900 <sup>10</sup>	-
303	"	0.87595	-	0.44536	-
308	"	0.87116	0.87116 <sup>3-9</sup>	0.42770	0.42770 <sup>10</sup>
313	"	0.86627	-	0.40893	-
318	"	0.86140	0.86140 <sup>3-9</sup>	0.3917	0.39017 <sup>4,7</sup>

Table 2 : Limiting apparent molar volumes ( $V_{\phi}^{\circ}$ ) and Experimental slopes ( $S_v^*$ ) together with standard errors of different salts in 30 mass% Tetrahydrofuron + Water at different temperatures.

Salts	$(V_{\phi}^{\circ})$ at various temp. ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )				$S_v^*$ at various temp. ( $\text{cm}^3 \cdot \text{L}^{-1/2} \cdot \text{mol}^{-1/2}$ )			
	303K	308K	313K	318K	303K	308K	313K	318K
$(\text{NH}_4)_2\text{SO}_4$	-317.727 ( $\pm 0.41$ )	-398.282 ( $\pm 1.75$ )	-444.678 ( $\pm 0.92$ )	-457.016 ( $\pm 0.05$ )	809.398 ( $\pm 0.71$ )	1045.079 ( $\pm 0.91$ )	1067.496 ( $\pm 0.18$ )	1336.469 ( $\pm 0.63$ )
$\text{Na}_2\text{SO}_4$	-366.963 ( $\pm 1.01$ )	-450.454 ( $\pm 0.32$ )	-450.659 ( $\pm 0.74$ )	-466.964 ( $\pm 0.13$ )	1040.596 ( $\pm 0.66$ )	1306.741 ( $\pm 0.92$ )	1900.725 ( $\pm 0.19$ )	2124.257 ( $\pm 0.77$ )
$\text{MgSO}_4$	-169.762 ( $\pm 0.96$ )	-213.953 ( $\pm 1.33$ )	-238.058 ( $\pm 0.71$ )	-242.095 ( $\pm 0.54$ )	698.095 ( $\pm 0.54$ )	799.572 ( $\pm 0.17$ )	858.725 ( $\pm 0.36$ )	868.047 ( $\pm 0.47$ )
$\text{Al}_2(\text{SO}_4)_3$	-336.815 ( $\pm 0.39$ )	-414.435 ( $\pm 0.42$ )	-436.484 ( $\pm 0.91$ )	-402.811 ( $\pm 0.61$ )	1997.012 ( $\pm 0.78$ )	2429.250 ( $\pm 0.65$ )	2501.515 ( $\pm 0.28$ )	2553.862 ( $\pm 0.19$ )

Table 3. Values of  $A_i$  of electrolytes in 30 mass % tetrahydrofuran (THF) +  $\text{H}_2\text{O}$  mixture.

Electrolytes	$A_0$	$A_1$	$A_2$
$(\text{NH}_4)_2\text{SO}_4$	68128.194	-432.292	0.68118
$\text{Na}_2\text{SO}_4$	160149.196	-1034.524	1.66590
$\text{MgSO}_4$	39961.653	-254.053	0.40134
$\text{Al}_2(\text{SO}_4)_3$	108280.710	-695.846	1.11344

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

Electrolytes	Limiting apparent molar expansibilities $\phi_E^\circ$ ( $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ )			
	303K	308K	313K	318K
$(\text{NH}_4)_2\text{SO}_4$	-19.263	-12.451	-5.639	1.172
$\text{Na}_2\text{SO}_4$	-24.988	-8.329	8.329	24.988
$\text{MgSO}_4$	-10.841	-6.827	-2.814	1.199
$\text{Al}_2(\text{SO}_4)_3$	-21.102	-9.966	1.167	12.302

Table 5. Values of B ( $\text{cm}^3 \text{mol}^{-1}$ ) and A ( $\text{cm}^{3/2} \text{mol}^{-1/2}$ ) parameters together with standard errors for ammonium sulphate, sodium sulphate, magnesium sulphate and aluminium sulphate in 30 mass% THF +  $\text{H}_2\text{O}$  mixture at different temperatures.

Electrolytes	B values of different temp				A values of different temp			
	303K	308K	313K	318K	303K	308K	313K	318K
$(\text{NH}_4)_2\text{SO}_4$	7.386 ( $\pm 0.92$ )	7.228 ( $\pm 0.73$ )	7.115 ( $\pm 0.82$ )	6.958 ( $\pm 0.69$ )	-3.286 ( $\pm 0.77$ )	-3.362 ( $\pm 0.62$ )	-3.232 ( $\pm 0.70$ )	-3.033 ( $\pm 0.71$ )
$\text{Na}_2\text{SO}_4$	8.749 ( $\pm 0.66$ )	8.506 ( $\pm 0.27$ )	8.431 ( $\pm 0.17$ )	8.286 ( $\pm 0.38$ )	-3.730 ( $\pm 0.08$ )	-3.383 ( $\pm 0.25$ )	-3.769 ( $\pm 0.61$ )	-3.501 ( $\pm 0.81$ )
$\text{MgSO}_4$	6.255 ( $\pm 0.10$ )	5.700 ( $\pm 0.41$ )	5.562 ( $\pm 0.51$ )	5.336 ( $\pm 0.20$ )	-3.191 ( $\pm 0.50$ )	-2.853 ( $\pm 0.12$ )	-3.094 ( $\pm 0.22$ )	-2.709 ( $\pm 0.17$ )
$\text{Al}_2(\text{SO}_4)_3$	13.609 ( $\pm 0.09$ )	13.225 ( $\pm 0.88$ )	12.902 ( $\pm 0.44$ )	12.649 ( $\pm 0.32$ )	-4.490 ( $\pm 0.66$ )	-4.465 ( $\pm 0.72$ )	-4.396 ( $\pm 0.30$ )	-4.432 ( $\pm 0.12$ )

(values in parenthesis are standard errors)

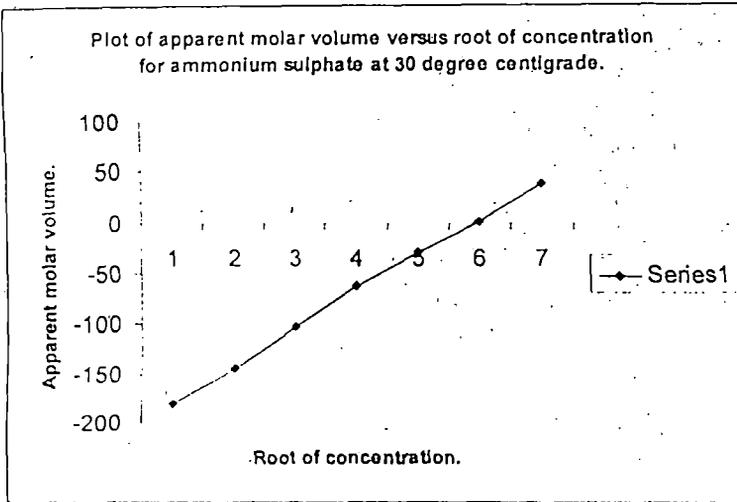


Fig.1

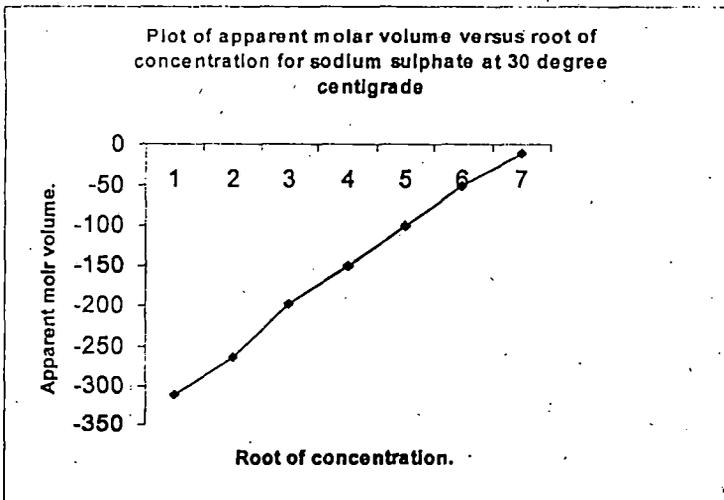


Fig. 2.

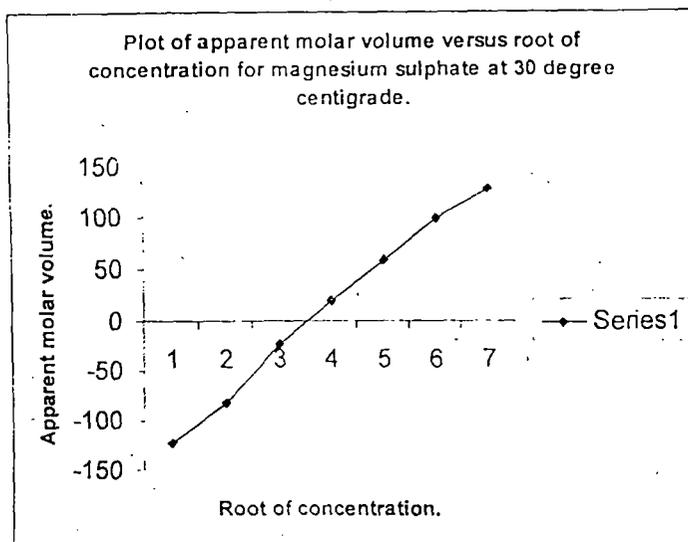


Fig. 3

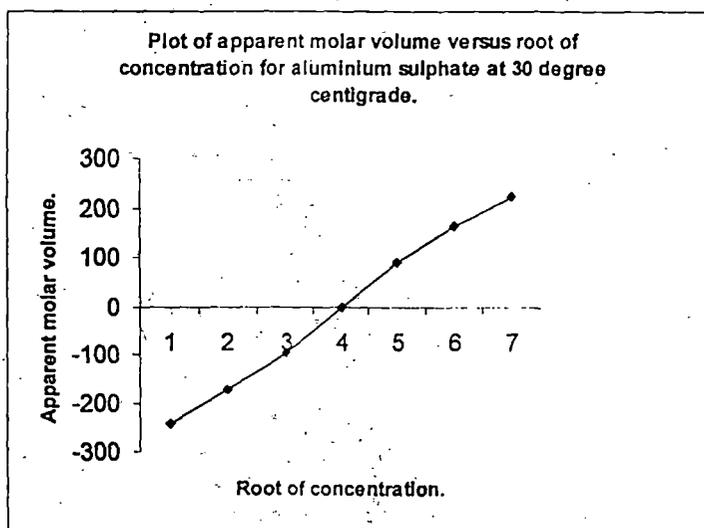


Fig.4

## 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 ( $\Lambda^0$ ), 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 organic solvents have been performed in recent years<sup>1-8</sup> 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 ( $\epsilon = 7.58$ ), has been found its probability of applications in high energy batteries<sup>9</sup>, modern technology<sup>10</sup> and organic syntheses as manifested from the physico chemical

studies in this medium.<sup>11,12</sup> Renard and Justice<sup>13</sup> studied the conductances of CsCl in THF + H<sub>2</sub>O mixtures to reveal the nature of ionic association and mobility of ions in the mixed solvent system. In the present communication, an attempt has been made to ascertain the complete nature of ion-solvent interactions of tetraalkylammonium and alkali metal bromide salts in THF + H<sub>2</sub>O mixtures through the measurements of their conductances at various temperatures.

### Experimental Section

Tetrahydrofuran (THF), Merck was kept several days over KOH, then refluxed for 24 h and distilled over LiAlH<sub>4</sub>. Its boiling point, density and viscosity compared well with the literature values<sup>14</sup>. The specific conductance of THF was ca.  $0.81 \times 10^{-6} \text{ S.cm}^{-1}$ .

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.<sup>1,15</sup>

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 the density values.

The densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (303, 313 and 323) K with doubly distilled water and benzene. Details have been described earlier<sup>16</sup>.

Conductance measurements 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<sup>17</sup> using aqueous potassium chloride solution. Measurements were made in a water bath maintained at (303±0.005, 313±0.005) and 323±0.005) K as described earlier.<sup>18,19</sup> 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<sub>2</sub>O mixtures were reported earlier<sup>1</sup> by us, where  $\epsilon$  is the dielectric constant,  $\rho_0$  the density,  $\eta_0$  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  $\epsilon$  versus  $W$  % plots, the original values were taken from the work of Renard and Justice.<sup>13</sup>

## Results and Discussions

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

The conductance data have been analysed by the 1978 Fuoss conductance-concentration equation<sup>20</sup>. For a set of conductivity values ( $c_j, \Lambda_j$ ;  $j = 1, \dots, n$ ), three adjustable parameters, the limiting molar conductivity ( $\Lambda^0$ ), 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 ( $\Lambda$ ) of some Tetraalkylammonium and Alkali Metal Bromide Salts in various (THF + H<sub>2</sub>O) mixtures at different temperatures

$c \times 10^4$ mol lit <sup>-1</sup>	$\sqrt{c} \times 10^2$ mol <sup>1/2</sup> lit <sup>-1/2</sup>	$\Lambda/S_{\text{cell}}$ mole <sup>-1</sup>	$c \times 10^4$ mol lit <sup>-1</sup>	$\sqrt{c} \times 10^2$ mol <sup>1/2</sup> lit <sup>-1/2</sup>	$\Lambda/S_{\text{cell}}$ mole <sup>-1</sup>	$c \times 10^4$ mol lit <sup>-1</sup>	$\sqrt{c} \times 10^2$ mol <sup>1/2</sup> lit <sup>-1/2</sup>	$\Lambda/S_{\text{cell}}$ mole <sup>-1</sup>
20% mass % THF + H <sub>2</sub> O mixture								
T = 303 K								
Et <sub>4</sub> NBr (M.W. = 210.17)			Pr <sub>4</sub> NBr (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<sub>2</sub>O 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	125.976	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 + H<sub>2</sub>O 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<sub>2</sub>O 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

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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

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

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

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

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

$$\beta = e^2 / DK_B T \quad (5)$$

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

Where Rx is the relaxation field effect,  $E_L$  is the electrophoretic countercurrent,  $k^{-1}$  is the radius of the ion atmosphere, D is the relative permittivity of the solvent, e is the electron charge,  $K_B$  is the Boltzmann constant,  $\lambda$  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  $\beta$  is twice the Bjerrum distance. The computations were performed on a computer using the programmes suggested by Fuoss. The initial  $\Lambda^0$  values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the programme is the set  $(c_j, \Lambda_j, j = 1, \dots, n)$ , n, D,  $\eta$ , T, initial value of  $\Lambda^0$ , and an instruction to cover a preselected range of R values.

In practice calculations are performed by finding the values of  $\Lambda^0$  and  $\alpha$  which minimize the standard deviation

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

for a sequence of R values and then plotting  $\sigma$  against R; the best-fit R corresponds to the minimum of the  $\sigma$  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  $\Lambda^0$  and  $K_A$  are calculated.

The values of  $\Lambda^0$ ,  $K_A$ ,  $\Lambda^0 \eta^0$ ,  $\sigma$  and R obtained by this procedure 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.

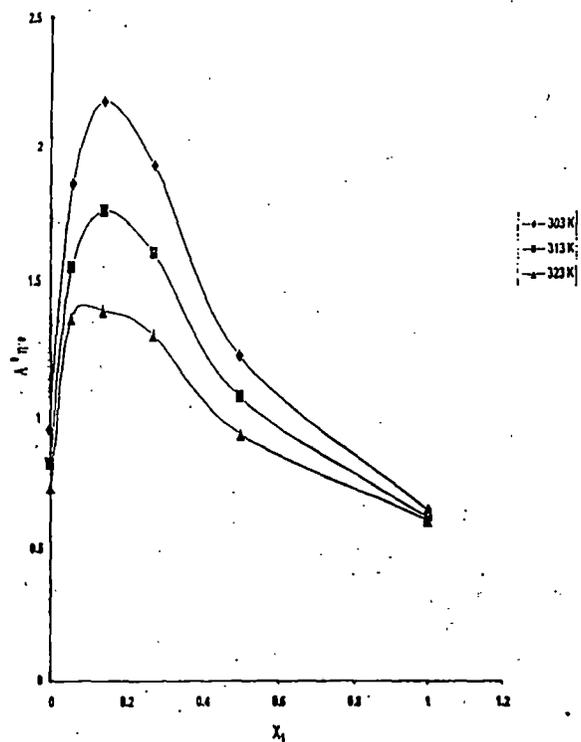


Fig. 1 : Plot of mole fraction of THF ( $X_1$ ) vs Walden Product ( $\Lambda^0 \eta^0$ ) of  $\text{Et}_4\text{NBr}$  in  $\text{THF} + \text{H}_2\text{O}$  mixture at various temperatures

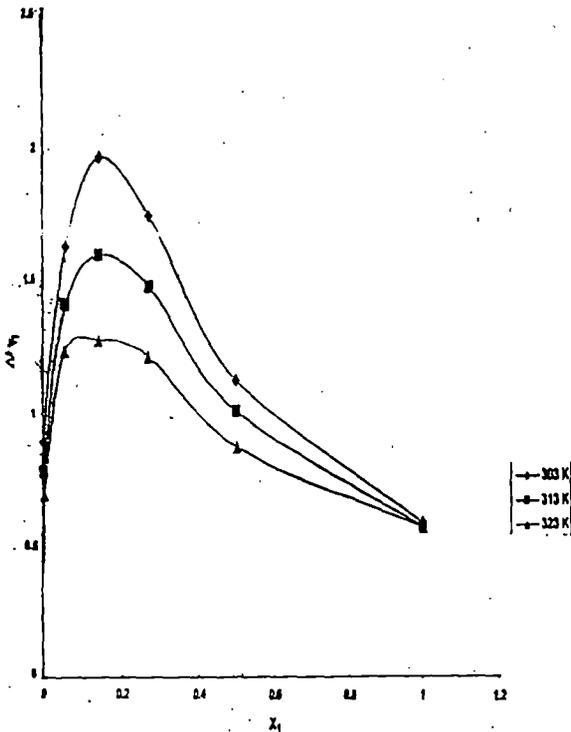


Fig. 2 : Plot of mole fraction of THF ( $X_1$ ) vs Walden Product ( $\Lambda^0\eta_0$ ) of  $\text{Pr}_4\text{NBr}$  in  $\text{THF} + \text{H}_2\text{O}$  mixture at various temperatures

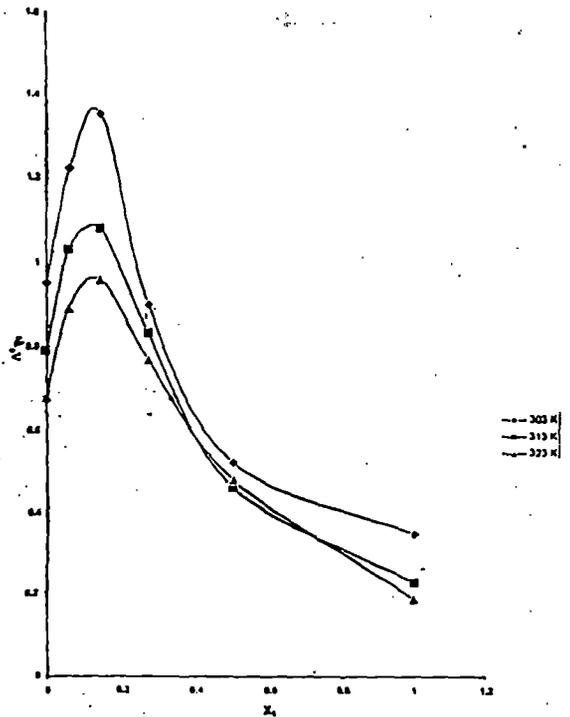


Fig. 3 : Plot of mole fraction of THF ( $X_1$ ) vs Walden Product ( $\Lambda^0\eta_0$ ) of  $\text{LiBr}$  in  $\text{THF} + \text{H}_2\text{O}$  mixture at various temperatures

The computations in these cases were carried out from arbitrarily presetting<sup>20</sup> of R values at  $R=a+d$ . Here a is the sum of the crystallographic radii of the ions and d the average distance corresponding to the side of a cell occupied by a solvent molecules. The distance d is given by

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

where M is the molecular weight of solvent and  $\rho$  is the density. for mixed solvents, M is replaced by the mole-fraction average molecular weight ( $M_{av}$ ) which is given by

$$M_{av} = M_1M_2/(W_1M_2 + W_2M_1) \quad (9)$$

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 Table 2, we see that  $\Lambda^0$  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,  $\Lambda^0$  values increase with increase in temperature. It has also been observed that the values of  $\Lambda^0$  calculated from the previous conductance equation do not differ significantly from the

Table - 2

Derived conductance Parameters for Tetraalkylammonium and Alkali Metal Bromides in THF + H<sub>2</sub>O at various Temperature

X <sub>1</sub>	$\Lambda^0$	K <sub>A</sub>	R	$\Lambda^0\eta_0$	$\sigma$
T = 303 K					
Et <sub>4</sub> NBr					
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 <sub>4</sub> NBr					
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 <sub>4</sub> NBr					
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 <sub>4</sub> NBr					
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
0.500	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 <sub>4</sub> NBr					
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 <sub>4</sub> NBr					
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  $\Lambda^0$  calculated from the 1978 Fuoss conductance concentration equation<sup>20</sup>. The trend of variation of  $\Lambda^0$  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.

$\text{Et}_4\text{N}^+ < \text{Pr}_4\text{N}^+ < \text{Li}^+$ . This shows that  $\text{Li}^+$  is the most solvated and  $\text{Pr}_4\text{N}^+$  is the least one in any mole-fraction of tetrahydrofuran (THF) and in any particular temperature.

Table 2 shows that  $K_A$  values for  $\text{R}_4\text{NBr}$  salts in a given solvent-mixture decrease with increasing size of the cation in the order  $\text{Et}_4\text{N}^+ > \text{Pr}_4\text{N}^+$ , similar to those observed earlier<sup>6,21</sup>, 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<sup>22</sup>. 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 maximum 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 other 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 characteristic is also a manifestation of strong specific interaction<sup>23</sup> between unlike molecules predominated by hydrogen bonding interaction.

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# CHAPTER – I

## **SCOPE AND OBJECT OF THE RESEARCH**

Fundamental research on non-aqueous electrolyte solutions has catalysed their wide technical applications in many fields. Non-aqueous electrolyte solutions are actually competing with other ion conductors, especially at ambient and at low temperatures, due to their high flexibility based on the choice of numerous solvents, additives, and electrolytes with widely varying properties. High-energy primary and secondary batteries, wet double-layer capacitors and supercapacitors, electrodeposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions has brought the biggest success.<sup>1-2</sup> Other fields where non-aqueous electrolyte solutions are some devices and processes for which the use of non-aqueous electrolyte solutions are broadly used include electrochromic displays and smart windows, photoelectrochemical cells, electromachining, etching, polishing, and electrosynthesis. In spite of wide technical applications, our understanding of these systems at a quantitative level is still not clear. The main reason for this is the absence of detailed information about the nature and strength of ion-molecular interactions and their influence on structural and dynamic properties of non-aqueous electrolyte solutions.

Studies of transport properties of electrolytes, along with thermodynamic and compressibility studies, give very valuable information about ion-ion and ion-solvent interactions in solutions.<sup>3</sup> The influence of these ion-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in such diverse areas as organic and inorganic synthesis,

studies of reaction mechanisms, non-aqueous battery technology and extraction.<sup>2(b),4</sup>

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become increasingly clear that the majority of the solutes is significantly modified by all solvents. Conversely, the nature of strongly structured solvents, like water, is substantially modified by the presence of solutes.<sup>5</sup>

## 1.1 CHOICE OF THE MAIN SOLVENT USED

Tetrahydrofuran(THF) has been chosen as main solvent in my research works. The study of THF, in general, is of interest because of its wide use as solvent and solubilizing agent in many industries with interests ranging from pharmaceutical to cosmetic products.

Tetrahydrofuran(THF) and its mixtures are the very important solvents widely used in various industries. THF is a good industrial solvent and figures prominently in the high energy battery technologies and has sound its application in organic syntheses as manifested from the physico-chemical studies in this medium.

Tetrahydrofuran (THF), Merck, India, was kept several days over potassium hydroxide (KOH), refluxed for 24 hours and distilled over lithium aluminium hydride ( $\text{LiAlH}_4$ ). The purified solvent had a boiling point of  $66^\circ\text{C}$ , a density of  $0.88072 \text{ g/cc}$ , a coefficient of viscosity of  $0.00460 \text{ p}$  and a specific conductance of  $\text{Ca. } 0.81 \times 10^{-6} \text{ s cm}^{-1}$  at  $25^\circ\text{C}$ .

Even though THF has drawn much focuss in recent years as solvent for electro analytical investigations, still more studies on the electrolytic behaviour in these non-aqueous medium can be explored. Therefore, we have embarked on a series of investigations on THF to study the chemical nature of the structure of ions and solvent and its mutual and specific interactions with

solvent molecules by studying the transport and thermodynamic properties of some selected compounds in THF through the measurement of conductance, viscosities, densities and the velocities of sound.

## 1.2 SCOPE OF THE WORK

The object of the present work is therefore to elucidate the nature of various interactions of some common alkali metal chloride, sulphate salts and other important salts such as resorcinol, tetraalkylammonium salts ( $\text{Bu}_4\text{NI}$ ,  $\text{Pr}_4\text{NI}$ ,  $\text{Et}_4\text{NBr}$ ,  $\text{Me}_4\text{NCl}$ ) in non-aqueous solvents having low dielectric constant such as tetrahydrofuran (THF),  $\epsilon = 7.58$  at 298.15K and 1,4 dioxane (DO),  $\epsilon = 2.209$  at 298.15K from volumetric, viscometric, conductometric and interferometric measurements. The available data have been utilized to examine the solvation phenomena of ions and ion-pairs in the non-aqueous solvents. This type of ion-pairs interaction in non-aqueous solvent media are widely applied in the high energy battery technology and the assessment of ion pairing in these systems is important because of its effect on the ionic conductivity.

Our further objective is to study the interaction between the solvent-solvent of some polar and non-polar solvent of moderate dielectric constant. These type of interactions are also widely used for cosmetic products and other organic synthesis as manifested from the physico-chemical studies in these media.

## 1.3 METHODS OF INVESTIGATIONS

The phenomenon of ion-solvent interactions and solvation is intriguing. It is desirable to attack this problem using different experimental techniques. We have, therefore, employed five important methods, namely, conductometry,

viscometry, densitometry, ultrasonic interferometry and spectrophotometry to probe the problem of solvation phenomena.

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution. The compressibility, a second derivative to Gibbs energy, is also a sensitive indicator of molecular interactions and can provide useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions.

The change in viscosity by the addition of electrolyte solutions is attributed to interionic and ion-solvent effects. The B-coefficients are also separated into ionic components by the 'reference electrolyte' method and from the temperature dependence of ionic values, a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, structure-breaking or structure-making, polarization, etc. may be given.<sup>17</sup>

The transport properties in most cases are studied using the conductance data, especially the conductance at infinite dilution. Conductance data obtained as a function of concentration can be used to study the ion-association with the help of appropriate equations.

#### **1.4A SUMMARY OF THE WORK DONE**

Tetrahydrofuran(THF) has been chosen as main solvent in my research works. The study of THF, in general, is of interest because of its wide use as solvent and solubilizing agent in many industries with interests ranging from pharmaceutical to cosmetic products.

Tetrahydrofuran(THF) and 1,4-dioxane and their mixtures are the very important solvents widely used in various industries. They are good industrial

solvent and figure prominently in the high energy modern battery technologies and have found their applications in organic syntheses as manifested from the physico-chemical studies in these media.

Even though THF and 1,4-dioxane have drawn much focus in recent years as solvents for electroanalytical investigations, still more studies on the electrolytic behaviour in these non-aqueous medium can be explored. Therefore, we have embarked on a series of investigations on THF and 1,4-dioxane to study the chemical nature of the structure of ions and solvents and their mutual and specific interactions with solvent molecules by studying the transport and thermodynamic properties of some selected compounds in THF and 1,4-dioxane through the measurements of conductances, viscosities, densities and the velocities of sound.

The present dissertation has been divided into eleven chapters.

Chapter I : This chapter involves the scope and object of the research work. This mainly contains the choice of the main solvent used and its industrial applications, scope of the work, methods of investigation and summary of the work done.

Chapter II : This chapter forms the introduction of review of the earlier works . This chapter is presenting a brief review of notable works of importance of solution chemistry, thermodynamics of ion-pair formation, division of B-coefficient into ionic values, thermodynamics of viscous flow, ion-size parameter and ionic association, Stokes' law and Walden's rule. The works are presenting the field of solute-solvent, solute-solute and solvent-solvent interactions, the discussion centres around the conductance, density, viscosity and adiabatic compressibility of different electrolytes in different solvent systems at different temperatures. Critical evaluations of different methods on the relative merits and demerits on the basis of various

assumptions employed from time to time of obtaining the single ion values and their implications have been made. The solvent properties are then discussed, stressing the importance of the work.

Chapter III : This chapter includes the experimental section which mainly contains the sources and purification of the solvents and electrolytes used and the various techniques of the experiments applied.

Chapter IV : This chapter describes the determination of the apparent and partial molar volumes and the viscosity B-coefficients of some alkali metal chlorides (LiCl, NaCl, KCl) in different mass% of THF + H<sub>2</sub>O mixtures (20, 40, 60, 80) at (303, 308, 313 and 318)K. the limiting apparent molar volumes ( $V_{\phi}^{\circ}$ ) and experimental slopes ( $S_v^*$ ) obtained by using the Masson equation have been interpreted in terms of ion-solvent and ion-ion interactions respectively. The viscosity data have been analyzed using the Jones-Dole equation and the derived parameters B and A have also been interpreted in terms of solute-solvent and solute-solute interactions respectively. The structure making and breaking capacities of alkali metal chlorides investigated here have been discussed.

Chapter V : This chapter entails the studies on the conductance of some tetraalkylammonium and alkali metal bromides in tetrahydrofuran (THF) + water mixtures (20, 40, 60, 80 mass% of THF) at (303, 313 and 318)K. The experimental data have been analyzed by the 1978 Fuoss conductance equation and the derived characteristics parameters,  $\Lambda^{\circ}$ ,  $K_A$  and R have been evaluated. The ionic Walden products have been determined and their variations with solvent composition and temperature have been discussed.

Chapter VI : This chapter describes the studies on thermodynamics and transport properties of two binary mixtures in which tetrahydrofuran (THF) plays the role of first component ( $x_1$ ) at different temperatures (303.15, 308.15, 313.15, 318.15 and 323.15 )K. From the experimental results the excess molar

volume ( $V^E$ ), the deviation of viscosity from the mole fraction average ( $\Delta\eta$ ) and Grunborg-Nissan parameter ( $d$ ) have been determined. These excess functions have been discussed on the basis of molecular interactions between the components of the mixture..

Chapter VII : This chapter includes the volumetric and viscometric studies of some mineral salts [ $\text{NH}_4\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$ ] in aqueous binary mixtures of tetrahydrofuran (THF) at different temperatures (303, 308, 313 and 318)K. Apparent molar volumes ( $V_\phi$ ) and viscosity B-coefficients of these electrolytes are derived from these data supplemented with their densities and viscosities respectively. The limiting apparent molar volume ( $V_\phi^\circ$ ) and experimental slopes ( $S_v^*$ ) obtained from the Masson equation have been discussed in terms of solute-solvent and solute-solute interactions respectively. The B-coefficient values analyzed using the Jones-Dole equation. The  $V_\phi^\circ$  values vary with temperatures as a power of series of temperature. The structure making/breaking capacities of the electrolyte studied here have been inferred from the Hepler's criterion.

Chapter VIII : This chapter entails the studies on density and viscosity of ternary liquid mixtures (n-hexane + tetrahydrofuran + benzene, n-hexane + tetrahydrofuran + isopropanol and n-hexane + isopropanol + benzene) at different temperatures (303, 313 and 323)K. Various excess thermodynamics functions viz. excess viscosity ( $\eta^E$ ), excess volume ( $V^E$ ) excess Gibbs free energy of activation of flow ( $\Delta G^{\neq E}$ ) and the values of interaction parameter  $d$  in Grunberg and Nissan equation have been calculated as a function of composition of ternary mixtures. The results have been interpreted in terms of molecular interactions existing between the components of these mixtures.

Chapter IX : In this chapter density, viscosity and ultrasonic speeds data have been reported for resorcinol in 10, 20, 30 mass% of 1,4-dioxane + water mixtures and pure 1,4-dioxane (DO) at 303.15, 313.15 and 323.15K. The

limiting apparent molar volumes ( $V_{\phi}^{\circ}$ ) and experimental slopes ( $S_v^*$ ) derived 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 and the derived parameters B and A have also been interpreted in terms of ion-solvent and ion-ion interactions respectively. The structure making/breaking capacities of resorcinol investigated here have been discussed. The compressibility obtained from the data supplemented with their ultrasonic speeds indicate the electrostriction of the solvent molecules around the ions.

Chapter X : This chapter contains the studies on electrical conductance of some ammonium halides e.g. ammonium fluoride, ammonium chloride and ammonium bromide; some tetraalkylammonium halides such as tetramethyl ammonium chloride ( $\text{Me}_4\text{NCl}$ ) and tetrabutyl ammonium Iodide ( $\text{Bu}_4\text{NI}$ ) and Sodium Iodide in different mass% (10, 20, 30) of tetrahydrofuran + water mixtures at 298.15K. The experimental data have been analyzed by the 1978 Fuoss conductance equation and the derived characteristics parameters  $\Lambda^{\circ}$ ,  $K_A$  and R have been calculated. The studies throw light on the effect of nature of the electrolytes, solvent composition on the solvation behaviour of ions in THF + water mixtures and the results have been explained in view of solute-solvent and solute-solute interactions. The ionic Walden products have also been determined and their variations with solvent composition have been discussed.

Chapter XI : The dissertation ends with some concluding remarks in this *chapter*.

## CHAPTER-II

### INTRODUCTION OF REVIEW OF THE EARLIER WORKS

#### 2.1 THE IMPORTANCE OF SOLUTION CHEMISTRY

One of the interesting facts of solution chemistry is that the exact structure of the solvent molecule in a solution is not known with certainty. The introduction of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The interactions between solute and solute, solute and solvent, and solvent and solvent molecules and the resulting ion-solvation become predominant. The assessment of ion pairing in these systems is important because of its effect on the ionic conductivity and hence the mobility of the ions in solution. This explains the spurt in research in solution chemistry to elucidate the exact nature of these interactions through experimental studies involving conductometry, viscometry, densitometry, spectroscopy, ultrasonic interferometry and other suitable methods and to interpret the experimental data collected.<sup>1-7</sup>

The behaviour of electrolytes in solution depends mainly on ion-ion and ion-solvent interactions. The former interaction, in general, is stronger than the latter. Ion-ion interaction in dilute electrolyte solutions is now theoretically well understood, but the ion-solvent interaction or ion-solvation still remains a complex process.

In the last few decades, considerable emphasis has been placed on research in the behaviour of electrolytes in non-aqueous and mixed solvents to investigate the ion-ion (solute-solute) and ion-solvent interactions under varied

conditions. Different sequences of solubility, differences in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have opened new vistas for physical chemists and interest in these organic solvents transcends traditional boundaries of inorganic, organic, physical, analytical and electrochemistry.<sup>8</sup>

In ion-solvation studies, broadly three types of approaches have been made to estimate the extent of solvation. The first is the solvational approach involving the studies of viscosity, conductance, etc., of electrolytes and the derivation of various factors associated with ionic solvation,<sup>9</sup> the second is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be elucidated,<sup>10</sup> and the third is to use spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature.<sup>11</sup>

We shall particularly dwell upon the different aspects of transport and thermodynamic properties as the present dissertation is intimately related to the studies of viscosities, conductances, ultrasonic velocities and spectroscopic properties of some important electrolytes in 2-methoxyethanol (ME), and 1,2-dimethoxyethane (DME), and in the binary mixtures of ME with N-methylacetamide (NMA) and N,N-dimethylacetamide (DMA).

## 2.2 THERMODYNAMICS OF ION-PAIR FORMATION

The standard Gibbs energy changes for the ion association process,  $\Delta G^\circ$ , can be calculated from the equation

$$\Delta G^\circ = -RT \ln K_A \quad (1)$$

The values of the standard enthalpy change,  $\Delta H^\circ$ , and the standard entropy change,  $\Delta S^\circ$ , can be evaluated from the temperature dependence of  $\Delta G^\circ$  values as follows ,

$$\Delta H^\circ = -T^2 \left( \frac{d(\Delta G^\circ / T)}{dT} \right)_p \quad (2)$$

$$\Delta S^\circ = -T^2 \left( \frac{d\Delta G^\circ}{dT} \right)_p \quad (3)$$

The  $\Delta G^\circ$  values can be fitted with the help of a polynomial of the type.

$$\Delta G^\circ = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \quad (4)$$

and the coefficients of the fits can be compiled together with the  $\sigma\%$  values of the fits.

The standard values at 298.15K are then :

$$\Delta G^\circ_{298.15} = c_0 \quad (5)$$

$$\Delta S^\circ_{298.15} = c_1 \quad (6)$$

$$\Delta H^\circ_{298.15} = c_0 + 298.15c_1 \quad (7)$$

The main factors which govern the standard entropy of ion association of electrolytes are : (i) the size and shape of the ions, (ii) charge density on the ions, (iii) electrostriction of the solvent molecules around the ions, and (iv) penetration of the solvent molecules inside the space of the ions, and the influence of these factors are discussed later.

The non-Coulombic part of the Gibbs energy,  $\Delta G^*$ , can also be calculated using the following equation,<sup>12</sup>

$$\Delta G^* = N_A W_{\pm}^* \quad (8)$$

$$K_A = (4\pi N_A / 1000) \int_a^R r^2 \exp \left[ 2q/r - W_{\pm}^*/kT \right] dr \quad (9)$$

where the symbols have their usual significance. The quantity  $2q/r$  is the Coulombic part of the interionic mean force potential and  $W_{\pm}^0$  is its non-Coulombic part.

The procedure for the evaluation of the non-Coulombic part of the entropy and enthalpy (and  $\Delta S^*$  and  $\Delta H^*$  respectively) is the same as that used for obtaining  $\Delta S^*$  and  $\Delta H^*$ .

The  $\Delta G^*$  values at different temperatures can be fitted to the polynomial

$$\Delta G^* = c_0^* + c_1^* (298.15 - T) + c_2^* (298.15 - T)^2 \quad (10)$$

and the coefficients of the fits along with the  $s\%$  values can be determined.

The values of  $\Delta G^0$ ,  $\Delta S^0$  and  $\Delta H^0$  at 298.15K are then easily obtained from the following equations.

$$\Delta G_{298.15}^* = c_0^* \quad (11)$$

$$\Delta S_{298.15}^* = c_1^* \quad (12)$$

$$\Delta H_{298.15}^* = c_0^* + 298.15c_1^* \quad (13)$$

### 2.3 VISCOSITY

Although viscosity is not a thermodynamic property, together with the partial molal volume  $V_2$ ,  $\bar{v}$  gives much information regarding the ion-solvent interactions, structures of electrolytic solutions and solvation. Jones and Dole<sup>13</sup> suggested the first quantitative empirical relation correlating the relative viscosities ( $\eta_r$ ) of the electrolytes and their molar concentrations (c):

$$\eta_r = 1 + Ac^{1/2} + Bc \quad (14)$$

The equation reduces to

$$(\eta_r - 1) / c^{1/2} = A + Bc^{1/2} \quad (15)$$

where A and B are constants specific to ion-ion and ion-solvent interactions respectively. The equation is equally applicable to aqueous and non-aqueous systems where there is no ion-association. The term  $A c^{1/2}$ , arose from the long range coulombic forces between the ions. The significance of the term has since been realized due to the development of Debye-Huckel theory<sup>14(a)</sup> of interionic attractions, Falkenhagen's theoretical calculations of 'A' using the equilibrium theory<sup>14(b),(c)</sup> and the theory of irreversible processes in electrolytes developed by Onsagar and Fuoss.<sup>14(d)</sup>

The 'A' coefficient depends on the ion-ion interactions and can be calculated using the Falkenhagen-Vernon equation<sup>14(c)</sup>

$$A_{\text{theo}} = \frac{0.2577 \Lambda^{\circ}}{\eta_0(\epsilon T)^{1/2} \lambda_+^{\circ} \lambda_-^{\circ}} \left[ 1 - 0.6863 \left( \frac{\lambda_+^{\circ} - \lambda_-^{\circ}}{\Lambda^{\circ}} \right)^2 \right] \quad (16)$$

where  $\Lambda^{\circ}$ ,  $\lambda_+^{\circ}$  and  $\lambda_-^{\circ}$  are the limiting conductances of the electrolyte, cation and anion respectively, at temperature T,  $\epsilon$  is the dielectric constant and

$\eta_0$  is the viscosity of the solvent. For most solutions this equation is valid up to 0.1M.<sup>15,16</sup>

### 2.3.1 Division of B-Coefficients into Ionic Values

In order to identify the separate contributions of cations and anions to the total solute-solvent interactions, the B-coefficients as determined by Jones-Dole's equation has to be resolved into ionic components. For this Cox and Wolfenden,<sup>17</sup> Gurney,<sup>18</sup> Sacco *et al.*,<sup>19</sup> Tuan and Fuoss,<sup>20</sup> and several authors used different approximations and assumptions for different systems. For example, Sacco *et al.*<sup>19</sup> proposed the widely used 'reference electrolyte' method. Thus, for  $\text{Ph}_4\text{PBPh}_4$  in water, we have,

$$B_{\text{BPh}_4^-} = B_{\text{PPh}_4^+} = B_{\text{Ph}_4\text{PBPh}_4} / 2 \quad (17)$$

$B_{\text{Ph}_4\text{PBPh}_4}$  is obtained from,

$$B_{\text{Ph}_4\text{PBPh}_4} = B_{\text{NaBPh}_4^+} + B_{\text{Ph}_4\text{PBr}^-} - B_{\text{NaBr}} \quad (18)$$

(since  $\text{Ph}_4\text{PBPh}_4$  is scarcely soluble in water). These values are in good agreement with those obtained by other methods.

However, according to Krumgalz<sup>21</sup> it is impossible to select any two ions for which  $l^\circ = l^\circ$  in all solvents and at proper temperatures. Also, even if the mobilities of some ions are equal at infinite dilution, they are not necessarily equal at moderate concentrations. Further, equality of ionic dimensions does not necessarily imply equality of B-coefficients of these ions, as they are likely to be solvent and ion-structure dependent.

Krumgalz proposed a method<sup>22</sup> based on the fact that the large tetraalkylammonium ions are not solvated in organic solvents. So, the ionic B-values for large  $\text{R}_4\text{N}^+$  ions (where  $\text{R} \geq \text{Bu}$ ) in organic solvents are proportional to their ionic dimensions.

$$B_{R_4NX} = a + br^3_{R_4N^+} \quad (19)$$

Where,  $a = B_x^+$  and  $b$  is a constant independent of temperature and solvent nature. Extrapolation of the plot of  $B_{R_4NX}$  ( $R > Pr$  or  $Bu$ ) against  $r^3_{R_4N^+}$  to zero cation dimension gives  $B_x^+$  directly in the proper solvent from which other ionic B-values can be calculated.

Ionic B-values can also be calculated from the following equations :

$$B_{R_4N^+} - B_{R_4^+N^+} = B_{R_4NX} - B_{R_4^+NX} \quad (20)$$

and

$$B_{R_4N^+}/B_{R_4^+N^+} = r^3_{R_4N^+}/r^3_{R_4^+N^+} \quad (21)$$

The radii of the tetraalkylammonium ions have been calculated from the accurate conductance data.<sup>23</sup>

On similar reasoning, Gill and Sharma<sup>24</sup> used  $Bu_4NBPh_4$  as the reference electrolyte and proposed the equations

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \frac{5.35}{5.00} \quad (22)$$

and

$$B_{Bu_4NBPh} = B_{Bu_4N^+} + B_{Ph_4B^-} \quad (23)$$

because the ionic radii of  $Bu_4N^+$  (5.00 Å) and of  $Ph_4B^-$  (5.35 Å) have been found to remain constant in different non-aqueous and mixed non-aqueous solvents. Lawrence and Sacco<sup>25,26</sup> used  $Bu_4NBBu_4$  and  $Ph_4PBPh_4$  as reference electrolytes because these cations and anions are symmetrically shaped and

have almost equal van der Waals volumes. Their results and the conclusions of Thomson *et al*<sup>27</sup> agreed well with the reported values.

It is obvious that most of these methods are based on certain approximations and anomalous results may arise unless proper mathematical theories are developed to calculate B-values.

### 2.3.2 Thermodynamics of Viscous Flow

Feakins *et al*<sup>28</sup> suggested the following expression

$$B = \frac{\bar{V}_1^o - \bar{V}_2^o}{1000} + \frac{\bar{V}_1^o}{1000} \left[ \frac{\Delta\mu_2^{o\#} - \Delta\mu_1^{o\#}}{RT} \right] \quad (24)$$

where  $\bar{V}_1^o$  and  $\bar{V}_2^o$  are the partial molal volumes of the solvent and solute respectively,  $\Delta\mu_1^{o\#}$  is the free energy of activation for viscous flow per mole of the solvent and  $\Delta\mu_2^{o\#}$  is the contribution per mole of solute to the free energy of activation for the viscous flow of the solution.

### 2.3.3 Effects of Shape and Size

Stokes and Mills<sup>15</sup> regarded the ions in solution as rigid spheres suspended in a continuum and proposed an equation for relative viscosity as

$$\eta/\eta_o = 1 + 2.5\phi \quad (25)$$

where  $\phi$  is the volume of the fraction occupied by the particles. However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monatomic cation). Thus, combining the above equation with Jones-Dole equation (14), we have

$$2.5\phi = Ac^{1/2} + Bc \quad (26)$$

Neglecting  $Ac^{1/2}$  in comparison with  $Bc$ , and substituting  $\phi = c\bar{V}_i$ , where  $V_i$  is the partial molal volume of the solute, we get

$$2.5 \bar{V}_i = B \quad (27)$$

Assuming that the ions behave like rigid spheres with effective radii  $R_{\pm}$ , moving in a continuum,  $B_{\pm}$  can be equated to

$$B_{\pm} = 2.5 \bar{V}_{\pm} = 2.5 \times 4/3 \pi (R_{\pm}^3 N/1000) \quad (28)$$

$R_{\pm}$  calculated using (28) should be close to crystallographic radii or corrected Stokes' radii if the ions are scarcely solvated and behave as spherical entities. But  $R_{\pm}$  values of the ions, which are higher than the crystallographic radii indicate solvation.

The number ( $n$ ) of solvent molecules bound to the ion in the primary solvation shell can be calculated by comparing the Jones-Dole equation with that of Einstein.<sup>29</sup>

$$B_{\pm} = 2.5 (V_i + n V_s) / 1000 \quad (29)$$

Where  $V_i$  is the bare ion molar volume and  $V_s$  the molar volume of the solvent. The above equation has been used by a number of workers<sup>30-33</sup> to study the nature of solvation.

## 2.4 CONDUCTANCE

Conductance measurement is one of the most accurate and widely used physical methods for investigating the electrolytic solutions.<sup>8,34,35</sup> Together with transference number determination, it provides an excellent method for obtaining single ion values. In conjunction with viscosity measurements, conductance data give much information regarding ion-ion and ion-solvent interaction.

Onsagar<sup>36</sup> was the first to successfully apply Debye-Huckel theory of interionic associations. Subsequently, Pitts,<sup>37</sup> and Fuoss and Onsagar<sup>38,39</sup> independently worked to account for both long and short range interactions. As Pitts' values different considerably from Fuoss and Onsagar's values, Fuoss and Hsia<sup>40</sup> modified the original Fuoss-Onsagar equation. The modified Fuoss-Onsagar equation is of the form<sup>35</sup>

$$\Lambda = \Lambda^{\circ} - \frac{\sigma \Lambda^{\circ} c^{1/2}}{(1+\kappa a)(1+\kappa a/z^{1/2})} - \frac{\beta c^{1/2}}{(1+\kappa a)} + G(\kappa a) \quad (30)$$

where  $G(\kappa a)$  is a complicated function of the variable. The simplified form

$$\Lambda = \Lambda^{\circ} - S c^{1/2} + E c \ln c + J_1 c - J_2 c^{1/2} \quad (31)$$

is generally employed in the analysis of experimental results. Fuoss and Accascina<sup>38</sup> made further correction of equation (31) taking into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation is

$$\Lambda = \Lambda^{\circ} - S c^{1/2} + E c \ln c + J_1 c - J_2 c^{1/2} - B \Lambda^{\circ} c \quad (32)$$

In most cases, however,  $J_2$  is made zero, but this leads to ; a systematic deviation of the experimental data from the theoretical equations.

### 2.4.1 Ion-Association

The plot  $\Lambda$  versus  $c^{1/2}$  (limiting Onsagar equation) is used to determine the dissociation or association of electrolytes. If  $\Lambda^{\circ}_{(\text{expt})} > \Lambda^{\circ}_{(\text{theo})}$ , the electrolyte may be regarded as completely dissociated but if  $\Lambda^{\circ}_{(\text{expt})} < \Lambda^{\circ}_{(\text{theo})}$ , the electrolytes may be regarded as associated. The difference between  $\Lambda^{\circ}_{(\text{expt})}$  and  $\Lambda^{\circ}_{(\text{theo})}$ , would be considerable with increasing association.<sup>41</sup>

For strongly associated electrolytes, association constants  $K_A$  and  $\Lambda^0$  were determined using the Fuoss-Kraus equation<sup>42</sup> or Shedlovsky's equation,<sup>43</sup>

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda^0} + \frac{K_A}{(\Lambda^0)^2} \times \frac{c\gamma_{\pm}^3 \Lambda}{T(z)} \quad (33)$$

Where  $T(z) = F(z)$  (Fuoss-Kraus) and  $I/T(z) = S(z)$  (Shedlovsky)

$$F(z) = 1 - z(1 - z((1 - z(1 - \dots))^{-1/2})^{-1/2})^{-1/2} \quad (34)$$

$$\text{and } S(z) = 1 + z + z^2/2 + z^3/8 + \dots \quad (35)$$

The plot of  $T(z) / \Lambda$  against  $c\gamma_{\pm}^2 \Lambda / T(z)$  should be a straight line having an intercept of  $1/\Lambda^0$  and a slope of  $K_A / (\Lambda^0)^2$ . When  $K_A$  is large, there will be considerable uncertainty in the values of  $\Lambda^0$  and  $K_A$  determined from the equation (33).

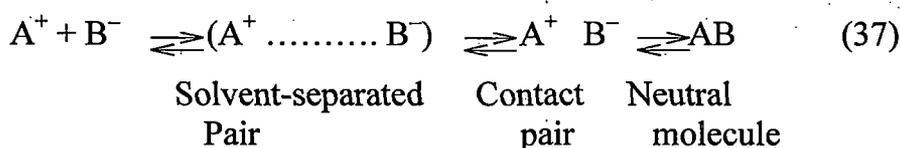
The Fuoss-Hsia conductance equation for associated electrolytes is given as

$$\Lambda = \Lambda^0 - S(\alpha c)^{1/2} + E(\alpha c) \ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{1/2} - K_A \Lambda \gamma_{\pm}^2(\alpha c) \quad (36)$$

This equation was modified by Justice.<sup>44</sup>

#### 2.4.2 Ion-Size Parameter and Ionic Association

In 1978, Fuoss put forward a new conductance equation,<sup>45</sup> replacing the one he had formulated three years earlier. He classified the ions of electrolytic solutions into three categories: (i) those which find an ion of opposite charge in the first shell of the nearest neighbours (contact pairs) with  $r_{ij} = a$ ; (ii) those with overlapping Gurney co-spheres (solvent separated pairs); and (iii) those which find no other unpaired ion in a surrounding sphere of radius  $R$ , where  $R$  is the diameter of the co-sphere (unpaired ions). Thermal motion and forces establish a steady state, represented by the equilibria



From this equation Fuoss derived an expression for the association constant or conductometric pairing constant.

$$K_A = K_R (1 + K_s) \quad (38)$$

Where,  $K_R$  describes the formation and separation of solvent-separated pairs by diffusion, in and out of the spheres of diameter  $R$  around the cations (calculated using the continuum theory),  $K_s$  is a constant describing the specific short range ion-solvent and ion-ion interactions by which contact pairs form and dissociate.

The details of the calculations are presented in the 1978 paper. The shortcomings of the previous papers have been rectified in the present set of equations that are more general than the previous ones and can be used in higher concentration regions (0.1 n in aqueous solutions).

For a given set of conductivity values ( $c_j, \Lambda_j, j = 1, \dots, n$ ) three adjustable parameters, the limiting molar conductivity ( $\Lambda^0$ ), association constant ( $K_A$ ), and the co-sphere diameter ( $R$ ), are derived from the following set of equations :

$$\Lambda = p[\Lambda^0(1 + R_x) + E_L] \quad (39)$$

$$p = 1 - \alpha(1 - \gamma) \quad (40)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (41)$$

$$-\ln f = \beta k / 2(1 + kR) \quad (42)$$

$$\beta = e^2 / Dk_B T \quad (43)$$

$$K_A = K_R / (1 - \alpha) = K_R(1 + K_s) \quad (44)$$

Where  $R_x$  is the relaxation field effect,  $E_L$  is the electrophoretic countercurrent,  $k^{-1}$  is the radius of the ion atmosphere,  $D$  is the dielectric constant of the solvent,  $e$  is the electron charge,  $k_B$  is the Boltzmann constant,  $\gamma$  is the fraction of solute present as unpaired ion,  $c$  is the molarity of the solution,  $f$  is the activity coefficient,  $T$  is the temperature in absolute scale, and  $b$  is twice the Bjerrum distance. The computations can be performed on a computer using the programme suggested by Fuoss.

### 2.4.3 Limiting Ionic Equivalent Conductances

The limiting equivalent conductance ( $\Lambda^0$ ) can be divided into ionic components using the experimentally determined transport number of ions ( $t_{\pm}$ ) as follows

$$\lambda_+^0 = t_+ \Lambda^0 \text{ and } \lambda_-^0 = t_- \Lambda^0 \quad (45)$$

However, accurate transference number determinations are limited to only a few solvents. Hence, various attempts were made to develop indirect methods to obtain the limiting ionic equivalent conductance, in ionic solvents for which experimental transference numbers are not yet available. These methods have been well described by Walden,<sup>46</sup> Fuoss,<sup>47</sup> and Gill.<sup>48</sup>

Krumgalz,<sup>49</sup> suggested a new method based on the fact, confirmed by NMR studies that the large tetraalkyl(aryl) onium ions are not solvated in organic solvents, in the kinetic sense, due to the extremely weak electrostatic interactions between the solvent molecules and the large ions with low surface charge density.

From the consideration of the motion of a solvated ion in an electrostatic field as a whole, it is possible to calculate the radius of the moving particle by the Stokes equation

$$r_s = |Z| F^2 / (A \pi N \eta_0 \lambda_{\pm}^0) \quad (46)$$

Where  $A$  is a coefficient varying from 6 (in the case of perfect sticking) to 4 (in the case of perfect slipping). Since the  $r_s$  values, the real dimensions of the non-solvated tetraalkyl (aryl) onium ions, must be constant, we have

$$\lambda_{\pm}^{\circ} \eta_0 = \text{constant} \quad (47)$$

This relation has been tested using the  $\lambda_{\pm}^{\circ}$  values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the  $\text{I-Am}_4\text{B}^-$ ,  $\text{Ph}_4\text{As}^+$  and  $\text{Ph}_4\text{B}^-$  ions and for tetraalkylammonium cations starting from  $\text{Et}_4\text{N}^+$ . The relation can also be well utilized to determine  $\lambda_{\pm}^{\circ}$  values of ions in other organic solvents from the determined  $\Lambda^{\circ}$  values.

We have used  $\text{Bu}_4\text{NBPh}_4$  as the 'reference electrolyte', but instead of equal division, we divided the  $\Lambda^{\circ}$  values using a method similar to that proposed by Krungalz<sup>21</sup> for division of B-values.

$$\frac{\lambda^{\circ}(\text{Bu}_4\text{N}^+)}{\lambda^{\circ}(\text{Ph}_4\text{B}^-)} = \frac{r(\text{Ph}_4\text{B}^-)}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} = 1.07 \quad (48)$$

The  $r$  values have been taken from the works of Gill *et al.*<sup>48</sup>

The values calculated by this method seem to be correct in different organic and mixed organic solvents. However, in aqueous binary mixtures, the solvation pattern may be different and the validity of this equation may be questioned.

Recently, Gill *et al.*<sup>50</sup> proposed the following equation

$$\frac{\lambda^{\circ}(\text{Bu}_4\text{N}^+)}{\lambda^{\circ}(\text{Ph}_4\text{B}^-)} = \frac{5.35 - (0.0103\epsilon_0 + r_y)}{5.00 - (0.0103\epsilon_0 + r_y)} \quad (49)$$

and the ratio is close to 1.07 as used by us.

#### 2.4.4 Solvation Number

An ion has an electric field or force around it which fades out into a negligible value after a short distance ( $\sim 10\text{\AA}$ ). In other words there is an effective volume within which its influence operates. The solvent molecules within this volume may be said to be interacting with the ion, resulting in the solvation of the ion. These interactions result in the orientation of the solvent molecules towards the ion. The number of solvent molecules that are involved in the solvation of the ion is called solvation number. If the solvent is water, this is called hydration number.<sup>51</sup>

Depending upon the distance from the ion, we can classify two solvation regions : primary and secondary solvation regions. Here we are concerned with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their own translational freedom and remain with a the ion, tightly bound, as it moves around, or the number of solvent molecules which are aligned in the force field of the ion.

If the limiting conductance of the ion I of charge  $Z_i$  is known, the effective radius of the solvated ion can be determined from Stokes' law. The volume of the solvation shell is given by the equation.

$$V_s^s = \frac{4}{3} \pi (r_s^3 - r_c^3) \quad (50)$$

Where  $r_c$  is the crystallographic radius of the ion. The solvation number  $n_s$  would then be obtained from

$$n_s^s = V_s / \bar{V}_o \quad (51)$$

Assuming Stokes' relation to hold good, the ionic solvated volume can be obtained, because of the packing effects,<sup>52</sup> from

$$V_s^o = 4.35 r_s^3 \quad (52)$$

Where  $V_s^\circ$  is expressed in mol/mole and  $r_s$  in angstroms. However, this method is not applicable to ions of medium size though a number of empirical<sup>53</sup> and theoretical corrections<sup>54,55</sup> have been suggested in order to apply it to most of the ions.

#### 2.4.5 Stokes' Law and Walden's Rule

The limiting conductance  $\lambda_i^\circ$  of a spherical ion of radius  $R_i$  moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

$$\lambda_i^\circ = 0.819 |Z_i| / \eta_i R_i \quad (53)$$

If the radius  $R_i$  is assumed to be the same in every organic solvent, as would be the case of bulky organic ions, we get

$$\lambda_i^\circ \eta_o = 0.819 |Z_i| / R_i = \text{constant} \quad (54)$$

This is known as the Walden rule.<sup>56</sup> The effective radii obtained using this equation can be used to estimate the solvation numbers. However, Stokes' radii failed to give the effective size of the solvated ions for small ions.

#### 2.4.6 Recent Conductivity Equations

From 1992 to 1995, Blum, Turq and co-workers<sup>57-59</sup> have developed a mean spherical approximation (MSA) version of conductivity equations. Their theory starts from the same continuity and hydrodynamics equations used in the more classical treatments; however, an important difference consists in the use of the MSA expressions for the equilibrium and structural properties of the electrolyte solutions. Although the differences in the derivation of the classical and MSA conductivity theories seem relatively small, it has been claimed that the performance of the MSA equation is good over a much wider concentration

range than that covered by the classical equations. However, no thorough study of the performance of the new equations at the level of the experimental uncertainty of conductivity measurement is yet available in the literature, with the exception of a very recent study by Bianchi *et al.*<sup>60(a)</sup> They compared the results obtained using the old and new equations in order to evaluate their capacity to describe the conductivity of different electrolyte solution. Their investigation too is limited to only three aqueous salt solutions and the picture is consistent showing a better performance for the classical equations as far as the system electrolytes are concerned.

In 2000, A Chandra and B. Bagchi<sup>60(b)</sup> have evolved a new microscopic approach to ionic conductance and viscosity based on mode coupling theory. Their study gives microscopic expressions of conductance and viscosity in terms of static and dynamic structure factors of the charge and number densities of the electrolyte solution. They claim that their new equation is applicable at low as well as at high concentrations and it describes the cross over from low to high concentration smoothly. Debye, Huckel, Onsagar and Falkenhagen expressions can be derived from this self-consistent theory at the limiting, very low ion concentration. For conductance the agreement seems to be satisfactory up to 1 M concentration.

## 2.5 APPARENT AND PARTIAL MOLAR VOLUMES

Fundamental properties such as enthalpy, entropy and Gibbs energy represent the macroscopic state of the system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these properties in terms of molecular phenomena is generally difficult. Sometimes, higher derivatives of these properties can be interpreted more effectively in terms of molecular phenomena is generally difficult. Sometimes,

higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions. For example, the partial molar volume, the pressure derivative of partial molal Gibbs energy, is a useful parameter for interpreting solute-solvent interactions. Various concepts regarding molecular processes in solutions such as, electrostriction,<sup>61</sup> hydrophobic hydration,<sup>62</sup> micellization<sup>63</sup> and cosphere overlap during solute-solute interactions<sup>18,64</sup> have to a large extent been derived and interpreted from the partial molar volume data of many compounds.

The apparent molar volumes,  $\phi_v$ , of the solutes can be calculated using the following equation

$$\phi_v = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \quad (55)$$

where  $M$  is the molecular weight of the solute,  $\rho_0$  and  $\rho$  are the densities of the solvent and solution respectively and  $c$  is the molarity of the solution. The partial molar volume,  $\bar{V}_2$  can be obtained from the equation

$$\bar{V}_2 = \phi_v + \frac{1000 - \phi_v}{2000 + c^{3/2}(d\phi_v/dc^{1/2})} c^{1/2} \frac{d\phi_v}{dc^{1/2}} \quad (56)$$

Masson<sup>65</sup> found that  $\phi_v$  varies with the square root of the molar concentration by the linear equation

$$\phi_v = \phi_v^0 + S_v^0 \sqrt{c} \quad (57)$$

where  $\phi_v^0$  is the apparent molar volume at infinite dilution (equal to the partial molar volume at infinite dilution) and  $S_v^0$  is the experimental slope. Redlich and Meyer<sup>66</sup> have shown that an equation of the form of (57) cannot be any more than a limiting law where for a given solvent and temperature, the slope  $S_v^0$  should depend only upon the valence type. They suggested the equation

Most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods developed for aqueous solutions. For sometime, the method of Conway *et al*<sup>70</sup>

Most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods developed for aqueous solutions. For sometime, the method of Conway *et al*<sup>70</sup> was widely used. They plotted the limiting partial molar volume,  $\bar{V}_{R_4NX}^0$  for a series of homologous tetraalkylammonium chlorides, bromides and iodides with a halide ion in common, as a function of the formula weight of the cation,  $M_{R_4N^+}$ , and obtained straight-line graphs for each series. Their results were claimed to fit the equation.

$$\bar{V}_{R_4NX}^0 = \bar{V}_{X^-}^0 + bM_{R_4N^+} \quad (63)$$

and the extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions,  $V_{X^-}^0$ . Uosaki *et al*<sup>71</sup> and later Krungalz<sup>72</sup> applied the same method to non-aqueous electrolyte solutions in a wide temperature range. In our laboratory too we have used this method for the division of partial molar volumes into the ionic components in 2-methoxyethanol.<sup>73</sup>

## 2.6 ULTRASONIC VELOCITY

In the last two decades there have been a number of studies on the ultrasonic velocities and isentropic compressibilities of liquids, solutions and liquid mixtures<sup>74</sup> because these data provide useful information about molecular interactions, association and dissociation. Various parameters like molar isentropic and isothermal compressibilities, apparent molal compressibility, isentropic compressibility, deviation in isentropic compressibility from ideality, etc. can very well be evaluated and studied from

$$\phi_v = \phi_v^0 + S_v \sqrt{c} + b_v c \quad (58)$$

where  $S_v = Kw^{3/2}$ , is the theoretical slope based on molar concentration, including the valence factor where

$$w = 0.5 \sum v_i Z_i^2 \quad (59)$$

and

$$K = N^2 e^3 (8p / 1000 \epsilon^3 RT)^{1/2} (\delta \ln \epsilon / \delta P)_T - \beta/3 \quad (60)$$

In equation (60),  $\beta$  is the compressibility of the solvent and the other terms have their usual significance.

The Redlich-Meyer's extrapolation equation<sup>66</sup> adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies<sup>67</sup> on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation. Thus, for poly-valent electrolytes, the more complete Owen-Brinkley equation<sup>68</sup> can be used to aid in the extrapolation to infinite dilution and to adequately represent the concentration dependency of  $\phi_v$ . The Owen-Brinkley equation<sup>68</sup> which includes the ion-size parameter,  $a$  (cm), is given by

$$\phi_v = \phi_v^0 + S_v \tau (\kappa a) \sqrt{c} + 0.5 W_v \theta (\kappa a) c + 0.5 K_v c \quad (61)$$

where the symbols have their usual significance. However, this equation is not widely used for non-aqueous solutions.

Recently, the Pitzer formalism has been used by Pogue and Atkinson<sup>69</sup> to fit the apparent molal volume data. The Pitzer equation for the apparent molar volume of a single salt  $Mv_M Xv_X$  is

$$\phi_v = \phi_v^0 + v \left[ Z_M Z_X \left| A_v / 2b \ln(1 + b\sqrt{I}) + 2v_M v_X RT [mB_{MX}^V + m^2 (v_M v_X)^{1/2} C_{MX}^V] \right. \right] \quad (62)$$

where the symbols have their usual significance.

### Ionic Limiting Partial Molar Volumes

the measurement of ultrasonic speeds in solutions. Isentropic compressibilities play a vital role in characterization of binary liquid mixtures.

### 2.6.1 Apparent Molal Isentropic Compressibility

The apparent molal isentropic compressibility, the second derivative of the Gibbs energy, is also a sensitive indicator of molecular interactions and can provide useful information about these, particularly in cases where partial molal volume data alone fail to provide an unequivocal interpretation of the interactions.<sup>75-78</sup> The isentropic compressibility ( $\kappa_s$ ) values are calculated using the Laplace equation

$$\kappa_s = 1/(u^2\rho) \quad (64)$$

where 'u' is the sound velocity in solution and  $\rho$  is the solution density.

The apparent molal isentropic compressibility ( $\kappa_\phi$ ) of the liquid solution is calculated using the relation.

$$\kappa_\phi = [(1000/m\rho\rho_o) (\kappa_s\rho_o - \kappa_s^o\rho)] + \kappa_s M/\rho_o \quad (65)$$

where  $m$  is the molality of the solution;  $\kappa_s^o$  and  $\kappa_s$  are the compressibility coefficients of the solvent and solution respectively.

Plotting of  $\kappa_\phi$  against the square-root of the molal concentration of the solutes and extrapolation to zero molal concentration gives the limiting apparent molal isentropic compressibility ( $\kappa_\phi^o$ ) according to the equation.<sup>75,78</sup>

$$\kappa_\phi = \kappa_\phi^o + S_k \sqrt{m} \quad (66)$$

where  $S_k$  is the experimental slope.

The limiting molal isentropic compressibility ( $\kappa_\phi^o$ ) and the experimental slope ( $S_k$ ) can be interpreted in terms of solute-solvent and solute-solute interactions, respectively. It is well established that the solutes causing electrostriction lead to a decrease in the compressibility of the solution.<sup>79,80</sup>

This is reflected by the negative values  $\kappa_{\phi}^{\circ}$  of electrolyte solutions. Hydrophobic solutes often show negative compressibilities due to the ordering induced by them in the water structure.<sup>63,79</sup> The compressibility of hydrogen-bonded structure, however, varies depending on the nature of H-bonds involved,<sup>79</sup> the poor fit of the solute molecules<sup>81</sup> as well as the possibility of flexible H-bond formation causing a more compressible environment (and hence a positive  $\kappa_{\phi}^{\circ}$  value) in the aqueous medium. Positive  $\kappa_{\phi}^{\circ}$  values have been reported in aqueous non-electrolytes<sup>82</sup> and non-electrolyte-non-electrolyte solution.

## 2.7 SOME RECENT TRENDS IN SOLVATION MODELS

The last decade (1990-2000) witnessed some interesting trends in development of some solvation models and computer software. Based on a vast collection of experimental free energy of solvation data, C.J.Cramer, D.G.Truhlar and co-workers from the University of Minnesota, USA, constructed a series of solvation models (SMI-SM5 series) to predict and calculate the free energy of solvation of a chemical compound.<sup>84-88</sup> These models are applicable to virtually any substance composed of H, C, N, O, F, P, S, Cl, Br and/or I. The only input data required are molecular formula, geometry, refractive index, surface tension, Abraham's  $a$  (acidity parameter) and  $b$  (basicity parameter) values, and, in the latest models, the dielectric constants. Many of these parameters for a number of compounds are available in the internet at <http://comp.chem.umn.edu/solvation>.<sup>89</sup>

The advantage of models like SM5 series is that they can be used to predict the free energy of self-solvation to better than 1 Kcal/mol. They can also be used to predict the vapour pressure at 298.15K with useful accuracy. They are especially useful when other methods are not available. One can also analyse factors like, electrostatics, dispersion, hydrogen bonding, etc., using

these tools. They are also relatively inexpensive and available in easy to use computer codes.

A Galindo *et al.*<sup>90,91</sup> have developed Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to model the thermodynamics and phase equilibria of electrolyte aqueous solutions. The water molecules are modeled as hard spheres with four short range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modeled as two hard spheres of different diameter to describe the anion and cation. The Debye-Huckel and mean spherical approximations are used to describe the interactions.

Good agreement with experimental data is found for a number of aqueous electrolyte solutions. The relative permittivity takes values very close to unity, especially in the case in which the mean spherical approximation is used, indicating a good description of the solvent. E.Bosch *et al.*<sup>92</sup> of the University of Barcelona, Spain, have compared several Preferential Solvation Models especially for describing the polarity of dipolar hydrogen bond acceptor-cosolvent mixtures.

## 2.8 Viscous Antagonism and Synergy

Tetrahydrofuran(THF) is a good industrial solvent. It figures prominently in the high energy battery industry and has found its application in organic syntheses as manifested from the physico-chemical studies in this medium.<sup>93,94</sup>

Alcohols are very widely used in industry, including the manufacture of pharmaceuticals and cosmetic products, in enology and as an energy source.

Rheology is the branch of science that studies material deformation and flow, and is increasingly applied to analyse the viscous behavior of many pharmaceutical products,<sup>95-104</sup> and to establish their stability and even

bioavailability since it has been firmly established that viscosity influences drug absorption rate in the body.<sup>105-106</sup>

The present investigation quantifies the viscous antagonism established in two ternary mixture studied here at different temperatures. Since these systems exhibit volume contraction, an analysis has also been made of the density of the mixtures at various temperatures.

The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics or industrial products, etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the products.

Viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component considered separately. In contraposition to viscous antagonism, viscous synergy is the term used in application to the interaction between the components of a system that causes the total viscosity of the latter to be greater than the sum of the viscosities of each component considered separately.

In turn, if the total viscosity of the system is equal to the sum of the viscosities of each component considered separately the system is said to lack interaction.<sup>107-108</sup>

The method most widely used to analyse the antagonic and synergic behaviour of various solvent-mixtures is that developed by Kaletune-Gencor and Peleg<sup>109</sup> allowing quantification of antagonic interactions taking place in mixtures involving variable proportions of the constituent components. The method compares the viscosity of the system, determined experimentally,  $\eta_{\text{exp}}$ , with the viscosity expected in the absence of interaction  $\eta_{\text{mix}}$ , defined as :

$$\eta_{\text{mix}} = X_A \eta_A + X_B \eta_B \quad (121)$$

where  $X_A$ ,  $X_B$  are the fraction by weight of the system A and B, and  $\eta_A$  and  $\eta_B$  are the viscosities measured experimentally, of the systems A and B respectively. Accordingly, when  $\eta_{\text{exp}} < \eta_{\text{mix}}$ , the system is considered to exhibit viscous synergy.

This procedure is used when Newtonian fluids are involved, since in Non-Newtonian systems shear rate must be taken into account, and other antagonism indices defined in consequence.<sup>110</sup> In order to secure more comparable viscous antagonism results, the so-called antonic index ( $I_h$ ), introduced by Howell,<sup>111</sup> is also taken into account :

$$I_\eta = (\eta_{\text{mix}} - \eta_{\text{exp}})/\eta_{\text{mix}} = f \eta/\eta_{\text{mix}} \quad (122)$$

The method used to analyse volume contraction and dilatation is similar to that applied to viscosity, i.e., density of the mixture is determined experimentally,  $\rho_{\text{exp}}$  and a calculation is made of its theoretical value,  $\rho_{\text{mix}}$ , in the supposition that volume contraction exists, based on the following expression :

$$\rho_{\text{mix}} = X_A \rho_A + X_B \rho_B \quad (123)$$

where  $X_A$ ,  $X_B$  are the fraction by weight of the system A and B and  $\rho_A$  and  $\rho_B$  are the densities, measured experimentally of the systems A and B respectively. Accordingly, when  $\rho_{\text{exp}} > \rho_{\text{mix}}$ , volume

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## CHAPTER III

### EXPERIMENTAL SECTION

#### 3.1 CHEMICALS USED : THEIR SOURCES AND PURIFICATION

##### Solvents -

Tetrahydrofuran (THF) [Merck, India] was kept for several days over KOH, refluxed for 24 hours and distilled over  $\text{LiAlH}_4$ .<sup>1</sup> The boiling point ( $66^\circ\text{C}$ ), density ( $0.8807 \text{ g.cm}^3$ ) and viscosity ( $0.0046 \text{ p}$ ) compared well with the literature values<sup>7</sup>. The specific conductance of THF was  $\sim 0.81 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  at  $25^\circ\text{C}$ .

Water was first deionized and then distilled from an all glass distilling set using alkaline  $\text{KMnO}_4$  solution.<sup>2</sup> The double distilled water was then finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from  $\text{CO}_2$  and other impurities. The triply distilled (TD) water had specific conductance less than  $1 \times 10^{-6} \text{ Ohm}^{-1} \text{ cm}^{-1}$ .

1,4 dioxane (DO), Merck, India, was kept several days over Potassium hydroxide (KOH).<sup>3</sup> This was followed by refluxing over excess of sodium for 12 hours. Finally, the dioxane is distilled from sodium. The pure compound had a boiling point of  $101.5^\circ\text{C}$ , a density of  $1.0292 \text{ g cm}^3$  at  $298.15\text{K}$ , a coefficient of viscosity  $0.012235 \text{ p}$  at  $298.15\text{K}$ .

Normal hexane, benzene and isopropanol were purified according to the standard procedures and then distilled very carefully. After distillation of one solvent the instruments were properly washed by water and then acetone and dried completely. After distillation, the purities were checked by density determination dilatometrically at  $303.15 \pm 0.1\text{K}$ . The density and viscosity of normal hexane, benzene and isopropanol were recorded as  $0.64968 \text{ g cm}^{-3}$ ,

0.00445 p ;  $0.86865 \text{ g cm}^{-3}$ ,  $0.00564 \text{ p}$  and  $0.78542 \text{ g cm}^{-3}$ ,  $0.01768 \text{ p}$  respectively.

## Electrolytes

Alkali metal chlorides<sup>4,5</sup> (Fluka) viz. LiCl, NaCl, KCl were of Purum or Puriss grade and were used as such after drying over CaO for 48 hours and were used without further purification.

Sulfate salts viz.  $\text{NH}_4\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  (SD fine chemicals, A.R.) were used as such, after drying over  $\text{P}_2\text{O}_5$  for 96 hours in vacuo at 423K.

Resorcinol (A.R.) were also used after drying in desiccator at least 24 hours. The compound was dried and stored in a vacuum condition and was purified by the reported procedure<sup>3</sup>.

Ammonium halides ( $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ ,  $\text{NH}_4\text{F}$ ) and Sodium Iodide, NaI (Fluka, Purum) were dried in desiccator at least 48 hours over CaO.

"Tetraalkylammonium salt ( $\text{Bu}_4\text{NI}$ ,  $\text{Pr}_4\text{NI}$ ,  $\text{Et}_4\text{NBr}$ ,  $\text{Me}_4\text{NCl}$ ) were of Purum or Puriss grade (Fluka) were used as such after drying in desiccator for 48 hours and were purified as described earlier.<sup>7</sup>

## 3.2 EXPERIMENTAL TECHNIQUES

### 3.2.1 Density Measurements

Densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of  $25 \text{ cm}^3$  and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 25, 35 and  $45^\circ\text{C}$  with doubly distilled water. The precision of the density measurements was  $\pm 3 \times 10^{-5} \text{ g cm}^{-3}$

The measurements were carried out in a thermostatic water bath maintained with an accuracy of  $\pm 0.01^\circ\text{C}$  of the desired temperature.<sup>8</sup> A 60 W heating element and a toluene-mercury thermo-regulator were used to maintain the temperature of the experimental thermostat which was placed in a hot-cum-cold thermostat. The temperature of the hot-cum-cold thermostat was preset at the desired temperature using a contact thermometer and relay system. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.<sup>9</sup>

### 3.2.2 Viscosity Measurements

The kinematic viscosities were measured by means of a suspended-level Ubbelohde<sup>10</sup> viscometer with a flow time of about 539s for distilled water at  $25^\circ\text{C}$ . The time of efflux was measured with a stop watch capable of recording 0.1s. The viscometer was always kept in a vertical position in a water thermostat. The viscometer needed no correction for kinetic energy. The kinematic viscosity ( $\nu$ ) and the absolute viscosity ( $\eta$ ) are given by the following equations :

$$\nu = ct - k/t \quad (1)$$

$$\eta = \nu\rho \quad (2)$$

where,  $t$  is the efflux time,  $\rho$  is the density and  $c$  and  $k$  are the characteristic constants of the viscometer. The values of the constants  $c$  and  $k$ , determined by using water and benzene as the calibration liquids at  $25$ ,  $35$ , and  $45^\circ\text{C}$ , were found to be  $1.648 \times 10^{-5} \text{ cm}^2\text{s}^2$  and  $-0.02331647 \text{ cm}^2$  respectively. The precision of the viscosity measurements was  $\pm 0.05\%$ . In all cases, the experiments were performed in at least five replicates and the results were averaged.

Relative viscosities ( $\eta_r$ ) were obtained using the equation :

$$\eta_r = \eta/\eta_o = \rho_t/\rho_o t_o \quad (3)$$

Where,  $\eta$ ,  $\eta_0$ ,  $\rho$ ,  $\rho_0$  and  $t$ ,  $t_0$  are the absolute viscosities, densities and flow times for the solution and solvent respectively.

The measurements were carried out in a thermostatic water bath maintained with an accuracy  $\pm 0.01^\circ\text{C}$  of the desired temperature as described earlier.

### 3.2.3 Conductance Measurements

Conductance measurements were carried out on a Philips Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant  $1.14\text{ cm}^{-1}$  and having an accuracy of 0.1%. The instrument was standardized using standard KCl solutions. The cell was calibrated by the method of Lind and co-workers.<sup>11</sup> The Conductivity cell was sealed to the side of a  $500\text{ cm}^3$  conical flask closed by a ground glass fitted with a side arm through which dry and pure nitrogen gas was passed to prevent admission of air into the cell when solvent or solution was added. The measurements were made in an oil bath maintained at the required temperatures  $\pm 0.005^\circ\text{C}$  by means of a mercury in glass thermo regulator.

Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities measured as described above. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent at all temperatures.

### 3.2.4 Ultrasonic Velocity Measurements

Sound velocities were measured, with an accuracy of 0.3%, using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi) operating at 4 MHz, which was calibrated with water, methanol, and

benzene at each temperature. The temperature stability was maintained within  $\pm 0.01^\circ\text{C}$  by circulating thermostated water around the cell by a circulating pump. The thermostatic bath was maintained with an accuracy of  $\pm 0.01^\circ\text{C}$  of the desired temperature, as described earlier.

The principle used in the measurement of the sound velocity ( $u$ ) is based on the accurate determination of the wavelength ( $\lambda$ ) in the medium. Ultrasonic waves of known frequency ( $\gamma$ ) are produced by a quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes maximum. If the distance is now increased or decreased and the variation is exactly one half wavelength ( $\lambda/2$ ) or integral multiple of it, anode current again becomes maximum. From the knowledge of the wavelength ( $\lambda$ ), the velocity ( $u$ ) can be obtained by the relation :

$$\text{Velocity}(u) = \text{Wavelength}(\lambda) \times \text{Frequency}(\gamma) \quad (4)$$

Isentropic compressibility ( $\kappa_s$ ) can then be calculated by the following formula :

$$\kappa_s = 1/(u^2\rho) \quad (5)$$

where  $\rho$  is the density of the experimental liquid.

The ultrasonic interferometer consists of the following two parts : (i) the high frequency generator, and (ii) the measuring cell. The measuring cell is connected to the output terminal of the high frequency generator through a shielded cable. The cell is filled with the experimental liquid before switching on the generator. The ultrasonic waves move normal from the quartz crystal till

they are reflected back from the movable plate and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal.

The micrometer is slowly moved till the anode current on the high frequency generator shows a maximum. A number of maximum readings of anode current are passed on and their number (n) is counted. The total distance ( $\rho$ ) thus moved by the micrometer gives the value of wavelength ( $\lambda$ ) with the following relation :

$$\rho = n \times \lambda/2 \quad (6)$$

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## **CHAPTER IV**

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

#### **4.1. INTRODUCTION**

It is well known that the reaction medium plays an important role in determining reactivity which is reflected in thermodynamic, transport and spectral properties.<sup>1-2</sup> 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. Studies on the apparent molar volume of electrolytes and 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.<sup>3</sup> It has been found by a number of workers<sup>4-6</sup> that the addition of electrolyte could break or make the structure of a liquid. Since the 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 continuation of our earlier works,<sup>7-12</sup> on the volumetric, viscometric and conductometric behaviour of solutions of some alkali metal halides and some tetraalkylammonium halides in pure tetrahydrofuran and aqueous binary mixtures of tetrahydrofuran at different temperatures, we report herein the volumetric and viscometric measurements on aqueous binary mixtures of tetrahydrofuran solutions of lithium, sodium and potassium chloride at different

temperatures in order to unravel the nature of various types of interactions prevailing in these electrolyte solutions.

## 4.2. Materials and Methods

Tetrahydrofuran (Merck, India) was kept several days over KOH, refluxed for 24 hours and distilled over  $\text{LiAlH}_4$ . The boiling point ( $66^\circ\text{C}$ ), density ( $0.88072\text{g/cm}^3$ ) and viscosity ( $\eta = 0.0046\text{P}$ ) compared well with the literature values.<sup>13</sup> The specific conductance of tetrahydrofuran was  $\text{Ca.}0.81 \times 10^6\text{S (cm}^{-1}\text{)}$  at  $25^\circ\text{C}$ .

Alkali metal chlorides (Fluka) were purum or puriss grade and purified as described earlier.<sup>14</sup>

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 ( $\rho$ ) were measured with an Ostwald-Sprengel type Pycnometer having a bulb volume of  $2.5\text{cm}^3$  and an internal diameter of the capillary of about  $0.1\text{cm}$ . 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  $\pm 0.01\text{K}$  of the desired temperature by means of a mercury in glass thermoregulator, and the absolute temperature is 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. As average of triplicate measurements were taken into account. The density values are reproducible to  $\pm 3 \times 10^{-5}\text{g cm}^{-3}$ . Details have been described earlier.<sup>8</sup>

The viscosities were measured by means of suspended-level-Ubbelohde<sup>15</sup> viscometer at the desired temperature (accuracy  $\pm 0.01\text{K}$ ). The precision of the viscosity measurement was 0.05%. Details have been described earlier.<sup>8-11</sup>

The experimental values of densities ( $\rho$ ) and viscosities ( $\eta$ ) of pure tetrahydrofuran in 20, 40, 60 and 80 mass % tetrahydrofuran + water mixtures at 298, 303, 308, 313 and 318K are given in Table 1. The molar concentration ( $c$ ), Densities ( $\rho$ ), Viscosities ( $\eta$ ) Apparent molar volumes ( $V_\phi$ ) and values of  $(\eta/\eta-1)/\sqrt{c}$  of different investigated electrolytes in different mass % of THF + H<sub>2</sub>O mixtures at various temperatures are recorded in Table 6.

### 4.3 Results and Discussion

From the Figure 1 and Table 1, we see that viscosity ( $\eta$ ) of the solvent mixture (THF + H<sub>2</sub>O) at all the investigated temperatures increases rapidly to a maximum about 0.143 mole-fraction or 40 mass % of THF and thereafter decreases. Such characteristics in the viscosity vs. composition curve is a manifestation of strong specific interactions<sup>16</sup> between unlike molecules predominated by hydrogen bonding interaction.

The apparent molar volumes (AMV),  $V_\phi$ , were calculated from the solvent and solution densities using the following equation.

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

Where  $c$  is the molarity of the solution and the other symbols have their usual significance. The correction to  $V_\phi$  due to hydrolysis of electrolytes may be negligible, since the strong hydrogen bonding<sup>16</sup> between the THF and H<sub>2</sub>O

will reduce the hydrolysis of these electrolytes by free water molecules considerably.

Application of the Redlich-Meyer equation<sup>17</sup> 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,  $S_v^*$ . Thus, the limiting apparent molar volumes,  $V_\phi$  and experimental slopes,  $S_v^*$  were obtained by computerized least square methods using Masson equation<sup>17</sup>. Within the experimental error, our value for  $V_\phi$  varied linearly with  $\sqrt{c}$  to follow the following equation. The plots of  $V_\phi$  vs  $\sqrt{c}$  for different salts at the different temperatures are shown in Figure No. 1.

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

Where  $S_v^*$  is a constant dependent on charge and salt type and can be related to ion-ion interactions and  $V_\phi$  is the limiting apparent molar volumes which is related to ion-solvent interactions. The  $V_\phi$  values with the experimental slopes ( $S_v^*$ ) in 20, 40, 60 and 80 mass % THF at different temperatures (303, 308, 313 and 318K) are recorded in Table 2.

The experimental  $S_v^*$  values shown in Figure 2 and 3 and Table 2 at different temperatures in different solvent mixtures (THF + H<sub>2</sub>O) are positive indicating the presence of ion-ion interactions. As expected  $S_v^*$  value increases with rise in temperature in 20, 40, 60 and 80 mass % THF for all electrolytes, which is attributed to accommodation of more and more solute in the void space left in the packing of associated solvent molecules resulting increasing the force of ion-ion interactions (ionic association)<sup>19</sup> and this increases on addition to tetrahydrofuran. This type of behaviour of some common and tetraalkylammonium perchlorate salts is also found in DMF + H<sub>2</sub>O mixtures.<sup>20-21</sup> Table 2 also shows that the  $S_v^*$  values (ion-ion interaction)

increase as the size of the cation increases as well as with the addition of tetrahydrofuran. Exactly the same conclusion regarding the ion-association behaviour of these electrolytes in aqueous mixtures of THF at 298 and 303K has been drawn from conductometric studies.<sup>7</sup> Fuoss and other workers have also found similar trends for many of the alkali metal halides in dioxan-water mixtures.<sup>22</sup>

The limiting apparent molar volumes ( $V_\phi^0$ ) shown in Table 2 and Figure 4 are large and negative for all electrolytes over the entire solvent mixtures investigated and these values decrease as the size of the alkali metal ions increases (from Li to K), with increasing amount of THF in the solvent mixtures (from 20 to 80 mass %THF) and with increasing temperature (from 303 to 318K). This indicates that there is a large amount of electrostriction occurring in these solutions and this electrostrictive solvation is more at large metal ion, higher mass % of THF and higher temperature. Similar results are reported for some 1:1 electrolytes in aqueous DMF mixtures.<sup>23</sup>

The variation of  $V_\phi$  with temperature of the electrolytes in solvent mixtures follows the polynomial

$$V_\phi = a + a_1T + a_2T^2 \quad (3)$$

Over the temperature range under investigation where T is the temperature in degree Kelvin.

The apparent molar expansibilities ( $\phi_E$ ) can be obtained by differentiating equation (3) with respect to temperature.

$$\phi_E = (\delta V_\phi / \delta T)_p = a_1 + 2a_2T \quad (4)$$

The  $\phi_E$  values of the studied electrolytes in different solvent mixtures at different temperatures are determined and recorded in Table 3.

Table 3 shows that the values of  $\phi_E$  increase with increasing temperature for all studied salts and this positive increase of  $\phi_E$  with temperature can be ascribed to the presence of caging or packing effect.

Structure-making/structure breaking capacity of the solute in different solvent media can be interpreted by using following equation of Hepler.<sup>25</sup>

$$(\delta\phi_E/\delta T) = (\delta^2V_\phi/\delta T^2)_p \quad (5)$$

The values of  $(\delta^2V_\phi/\delta T^2)_p$  are summarised in Table 4. According to Hepler, structure making solutes should have positive value and structure breaking solutes negative values of the term  $(\delta^2V_\phi/\delta T^2)_p$  respectively. It has been observed from Table 4 that  $(\delta^2V_\phi/\delta T^2)_p$  for all studied electrolytes are positive in all mass percentages of THF suggesting thereby that these electrolytes (LiCl, NaCl and KCl) behave as structure-makers in these solvent-mixtures.

The viscosity data of solutions for various electrolytes (LiCl, NaCl and KCl) in 20, 40, 60 and 80 mass % THF + H<sub>2</sub>O mixtures have been analysed using the Jones-Dole<sup>26</sup> equation. The plots of  $(\eta/\eta_0 - 1)/\sqrt{c}$  vs  $\sqrt{c}$  for different salts at the different temperatures are shown in Figure No. 2.

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{c} \quad (6)$$

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

and,  $\eta$  and  $\eta_1$  are the viscosities of solvent-mixture and solution respectively. A and B are constant,  $\rho$  is the density of the solution, t is the flow time in second of solution and K and L are constants for a particular viscometer. Within the experimental error, our value for  $(\eta/\eta_0 - 1)/\sqrt{c}$  varied

linearly with  $\sqrt{c}$ . The values of A and B are estimated by computerized least squares method and these values are recorded in Table 5.

It is found from Table 5 and Figures 5 and 6 that the values of B-coefficients for all investigated electrolytes are positive and these values decrease from lithium chloride to potassium chloride (except 20 mass % of THF) with increasing temperature and increase with increasing mass % of THF. This indicates that these electrolytes (LiCl, NaCl and KCl) act as structure-maker in all studied THF + water mixtures and the structure making tendencies of the electrolytes are in order: Li-salt > Na-salt > K-salt in 40, 60 and 80 mass % of THF and K-salt > Na-salt > Li-salt in 20 mass % of THF and the structure making tendencies increase in addition of THF to the mixture for all electrolytes. A similar trend was reported by other workers<sup>27</sup> in case of viscosities of perchlorates of lithium and sodium in propionic acid + ethanol mixtures.

It has been reported by a number of workers that  $dB/dT$  is a better criterion<sup>28-29</sup> for determining the structure-making or structure-breaking nature of any electrolyte rather than simply the B-coefficient. Table 5 shows that the values of B are positive and decrease with increasing temperature (negative  $dB/dT$  value) suggesting structure-making tendencies of all the studied electrolytes in studied solvent mixtures. These conclusions are in excellent agreement with that drawn from  $(\delta^2 V_\phi^0 / \delta T^2)_p$  discussed earlier.

## Acknowledgement

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

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**Table 1**

**Physical properties of pure tetrahydrofuran (THF) and different mass % of  
THF + H<sub>2</sub>O mixtures at different temperatures**

T/K	Mass % THF	$\rho_0/\text{g.cm}^{-3}$		$\eta_{sp}/\text{cp}$	
		This work	Lit.	This work	Lit.
298	20	0.98688	0.98668 <sup>6-11</sup>	1.49002	1.49002 <sup>8-11</sup>
303	20	0.98488	-	1.31155	-
308	20	0.98309	0.98309 <sup>7-11</sup>	1.13310	1.13310 <sup>8-11</sup>
313	20	0.98019	-	1.05991	-
318	20	0.97730	0.97730 <sup>7-11</sup>	0.89670	0.89670 <sup>8-11</sup>
298	40	0.96640	0.96640 <sup>7-11</sup>	1.73210	1.73210 <sup>8-11</sup>
303	40	0.96381	-	1.52760	-
308	40	0.96120	0.96120 <sup>7-11</sup>	1.32310	1.32310 <sup>8-11</sup>
313	40	0.95359	-	1.18412	-
318	40	0.94598	0.94598 <sup>7-11</sup>	1.04516	1.04516 <sup>8-11</sup>
298	60	0.94600	0.94601 <sup>7-11</sup>	1.49040	1.49042 <sup>8-11</sup>
303	60	0.94204	-	1.33984	-
308	60	0.93810	0.93811 <sup>7-11</sup>	1.18930	1.18931 <sup>8-11</sup>
313	60	0.93338	-	1.07421	-
318	60	0.92864	0.92863 <sup>7-11</sup>	0.95910	0.95909 <sup>8-11</sup>
298	80	0.91592	0.91591 <sup>7-11</sup>	0.92370	0.92371 <sup>8-11</sup>
303	80	0.91181	-	0.85386	-
308	80	0.90768	0.90768 <sup>7-11</sup>	0.78401	0.78400 <sup>8-11</sup>
313	80	0.90251	-	0.72270	-
318	80	0.89732	0.89732 <sup>7-11</sup>	0.66141	0.66140 <sup>8-11</sup>
298	100 (Pure THF)	0.88072	0.88082 <sup>7-11</sup> 0.88700 <sup>13</sup>	0.46300	0.46300 <sup>8-11</sup> 0.46000
303	100	0.87595	-	0.44536	-
308	100	0.87116	0.87116 <sup>7-11</sup>	0.42770	0.42770 <sup>8-11</sup>
313	100	0.86627	-	0.40893	-
318	100	0.86140	0.86140 <sup>7-11</sup>	0.39017	0.39017 <sup>8-11</sup>

**Table 2**  
**Limiting apparent molar volumes ( $V_{\phi}^0$ ) and experimental slopes ( $S_v^*$ ) of**  
**electrolytes in THF + water at different temperatures**

Mass %	$V_{\phi}^0/(\text{cm}^3\text{mol}^{-1})$				$S_v^*/(\text{cm}^3\text{dm}^{1/2}\text{mol}^{-3/2})$			
	303K	308K	313K	318K	303K	308K	313K	318K
<b>THF</b>								
<b>Lithium chloride</b>								
20	-9.71 (± 0.50)	-14.33 (± 0.19)	-18.22 (± 0.22)	-21.96 (± 0.90)	36.23 (± 0.85)	37.91 (± 0.02)	41.93 (± 0.06)	44.97 (± 0.52)
40	-191.75 (± 0.71)	-240.50 (± 1.21)	-443.85 (± 0.09)	-633.91 (± 0.11)	388.19 (± 0.91)	525.75 (± 0.01)	971.60 (± 0.96)	1355.92 (± 0.12)
60	-268.19 (± 0.01)	-311.53 (± 0.01)	-480.48 (± 0.02)	-641.19 (± 0.01)	759.86 (± 0.01)	875.09 (± 0.01)	1301.10 (± 0.02)	1678.60 (± 0.01)
80	-290.85 (± 0.68)	-313.14 (± 0.98)	-482.18 (± 0.44)	-650.75 (± 0.54)	1057.64 (± 0.33)	1147.82 (± 0.75)	1818.11 (± 0.88)	2433.65 (± 0.06)
<b>Sodium chloride</b>								
20	-15.70 (± 0.42)	-18.78 (± 0.66)	-23.59 (± 0.48)	-27.64 (± 0.23)	44.41 (± 0.44)	50.10 (± 0.13)	59.01 (± 0.54)	63.62 (± 0.12)
40	-224.46 (± 0.33)	-285.36 (± 0.71)	-502.61 (± 0.62)	-719.11 (± 0.41)	466.51 (± 0.91)	650.98 (± 0.15)	1039.87 (± 0.97)	1620.59 (± 0.66)
60	-346.80 (± 0.02)	-371.25 (± 0.01)	-554.39 (± 0.01)	-727.15 (± 0.02)	1112.94 (± 0.02)	1144.79 (± 0.01)	1700.39 (± 0.01)	2264.46 (± 0.01)
80	-1116.14 (± 0.93)	-1136.69 (± 0.79)	-1156.07 (± 0.71)	-1180.61 (± 0.03)	7647.51 (± 0.75)	7788.11 (± 0.62)	7801.98 (± 0.96)	7843.33 (± 0.48)
<b>Potassium chloride</b>								
20	-22.41 (± 0.85)	-38.93 (± 0.91)	-47.74 (± 0.39)	-55.62 (± 0.28)	92.28 (± 0.47)	108.33 (± 0.57)	112.85 (± 0.48)	119.62 (± 0.27)
40	-464.25 (± 0.63)	-542.19 (± 0.04)	-770.16 (± 0.73)	-982.70 (± 0.91)	1024.51 (± 0.17)	1234.66 (± 0.98)	1753.64 (± 0.67)	2243.32 (± 0.01)
60	-528.19 (± 0.02)	-561.24 (± 0.01)	-782.68 (± 0.02)	-990.20 (± 0.01)	1747.01 (± 0.01)	1835.35 (± 0.01)	2541.66 (± 0.01)	3260.97 (± 0.01)
80	-1652.97 (± 0.16)	-1702.72 (± 0.89)	-1750.68 (± 0.78)	-1940.25 (± 0.43)	11940.83 (± 0.43)	12075.11 (± 0.02)	12297.58 (± 0.41)	12542.35 (± 0.76)

**Table 3**  
 $\phi_E^{01}(\text{cm}^3 \text{mol}^{-1} \text{K}^{-1})$  for the electrolytes in different mass % of THF + water  
at different temperatures

Mass % THF	303K	308K	313K	318K
<b>Lithium Chloride</b>				
20	-0.822	-0.792	-0.762	-0.731
40	-44.656	-41.998	-39.340	-36.682
60	-36.264	-34.614	-32.965	-31.315
80	-33.944	-33.849	-33.755	-33.662
<b>Sodium Chloride</b>				
20	-1.190	-1.038	-0.885	-0.733
40	-43.675	-43.525	-43.375	-43.225
60	-39.737	-37.663	-35.589	-33.516
80	-4.229	-3.996	-3.762	-3.528
<b>Potassium chloride</b>				
20	-2.024	-1.846	-1.669	-1.492
40	-50.722	-47.436	44.149	-40.863
60	-48.467	-45.682	-42.896	-40.111
80	-10.125	-9.767	-9.409	-9.051

**Table 4**  
The term  $(\delta^2 V_\phi^0 / \delta T^2)(\text{cm}^3 \text{mol}^{-1} \text{K}^{-2})$  for electrolytes in THF + water mixture

Electrolytes	Mass % THF			
	20	40	60	80
Lithium Chloride	$6.04 \times 10^{-3}$	$530.00 \times 10^{-3}$	$330.00 \times 10^{-3}$	$18.80 \times 10^{-3}$
Sodium Chloride	$30.44 \times 10^{-3}$	$30.04 \times 10^{-3}$	$414.82 \times 10^{-3}$	$46.80 \times 10^{-3}$
Potassium Chloride	$35.48 \times 10^{-3}$	$675.24 \times 10^{-3}$	$557.00 \times 10^{-3}$	$71.60 \times 10^{-3}$

**Table 5**  
Values of B and A of studied electrolytes in THF + water at a different  
temperatures

Mass % THF	B/( $\text{cm}^3 \text{mol}^{-1}$ )				A/( $\text{cm}^{3/2} \text{mol}^{-3/2}$ )			
	303K	308K	313K	318K	303K	308K	313K	318K
<b>Lithium Chloride</b>								

20	0.938	0.918	0.819	0.789	-1.121	-0.979	-0.973	-0.938
40	7.205	6.419	6.376	6.170	-3.512	-3.119	-3.067	-2.964
60	7.570	7.567	6.909	6.714	-3.189	-3.168	-2.956	-2.603
80	17.077	16.814	16.205	15.591	-4.871	-4.871	-4.632	-4.349
<b>Sodium Chloride</b>								
20	1.809	1.588	1.378	1.169	-1.744	-1.566	-1.430	-1.348
40	6.281	6.261	6.223	5.308	-3.108	-2.957	-2.869	-2.523
60	7.393	7.139	6.749	6.178	-3.147	-2.980	-2.842	-2.577
80	16.789	15.354	15.191	15.063	-4.524	-4.209	-3.939	-3.875
<b>Potassium chloride</b>								
20	2.271	1.849	1.683	1.672	-2.113	-1.683	-1.586	-1.525
40	4.665	4.434	4.364	4.299	-2.411	-2.314	-2.184	-2.105
60	5.881	4.945	4.939	4.904	-2.189	-2.131	-2.116	-2.073
80	14.746	14.635	14.488	13.915	-4.177	-4.140	-3.924	-3.785

Table 6

**Molar Concentrations (C), Densities ( $\rho$ ), Viscosities ( $\eta$ ), Apparent molar Volumes ( $V_\phi$ ) and Values of  $(\eta/\eta_0 - 1)/\sqrt{c}$  of LiCl, NaCl and KCl in different mass % of THF + H<sub>2</sub>O mixtures at different temperatures**

**20 mass % THF + H<sub>2</sub>O Mixture**

$c/\text{mol dm}^{-3}$	$\sqrt{c}/(\text{mol dm}^{-3})^{1/2}$	$\rho/\text{g.cm}^{-3}$	$\eta/\text{cp}$	$V_\phi/\text{cm}^3\text{mol}^{-1}$	$(\eta/\eta_0 - 1)/\sqrt{c}$
<b>T = 303K</b>					
<b>LiCl</b>					
0.02504	0.15824	0.98603	0.83282	-3.67831	-2.30669
0.07512	0.27408	0.98810	0.84969	-0.43290	-1.28483
0.18781	0.43337	0.99195	0.86422	5.89452	-0.78701
0.32554	0.57056	0.99509	0.89222	11.21151	-0.56036
0.45073	0.67136	0.99734	0.90144	14.98470	-0.46575
0.60099	0.77523	0.99914	0.92356	18.94530	-0.38159
0.80133	0.89517	1.00149	0.95123	21.99563	-0.30690
<b>NaCl</b>					
0.02422	0.15562	0.98646	0.83219	-7.0090	-2.34861
0.08478	0.29117	0.99009	0.84664	-3.0089	-1.21741
0.16956	0.41177	0.99462	0.86106	1.0425	-0.83415
0.31490	0.56115	1.00111	0.87781	7.0068	-0.58933
0.43602	0.66031	1.00418	0.89623	14.4052	-0.47956
0.58136	0.76246	1.00799	0.91107	18.9665	-0.40047
0.77514	0.88042	1.01187	0.93182	23.9876	-0.32885

**KCl**

0.02025	0.14230	0.98661	0.80926	-10.7649	-2.69131
0.06075	0.24647	0.98925	0.81695	2.7348	-1.53004
0.16200	0.40249	0.98947	0.81677	13.9876	-0.93728
0.26325	0.51307	0.99858	0.82001	22.8542	-0.73046
0.36450	0.60373	0.99914	0.82098	35.9876	-0.61954
0.48602	0.69715	1.00101	0.84613	42.0098	-0.50901
0.64802	0.80499	1.00521	0.88491	51.0987	-0.40409

**T = 308K**

**LiCl**

0.02490	0.15779	0.98434	0.80489	-8.0094	-1.83571
0.07501	0.27387	0.98649	0.81825	-3.0099	-1.01459
0.18775	0.43330	0.99093	0.83541	-0.6220	-0.60632
0.32541	0.57044	0.99476	0.86401	6.8439	-0.41631
0.45067	0.67131	0.99727	0.87751	11.0986	-0.33601
0.60089	0.77517	0.99940	0.89094	15.5070	-0.27570
0.80126	0.89513	1.00130	0.91051	19.9979	-0.21945

**NaCl**

0.02405	0.15508	0.98475	0.75886	-10.9876	-2.12973
0.08465	0.29094	0.98845	0.76498	-4.9458	-1.11665
0.16925	0.41140	0.99248	0.77123	2.9912	-0.77628
0.31439	0.56070	0.99872	0.78879	8.8909	-0.54193
0.43582	0.66016	1.00256	0.79894	13.9876	-0.44672
0.58100	0.76223	1.00562	0.80642	20.0056	-0.37824
0.77482	0.88023	1.00934	0.82394	24.9899	-0.30996

**KCl**

0.02019	0.14209	0.98509	0.79819	-25.3233	-2.08015
0.06043	0.24582	0.98886	0.79019	-12.9332	-1.23110
0.16190	0.40236	0.99421	0.78253	5.9844	-0.76893
0.26301	0.51284	0.99766	0.77845	19.4827	-0.61030
0.36401	0.60333	1.00025	0.78253	27.8799	-0.51280
0.48589	0.69705	1.00215	0.75983	35.9213	-0.47259
0.64795	0.80495	1.00219	0.74762	45.8444	-0.42263

**T = 313K**

**LiCl**

0.02456	0.15671	0.98152	0.68266	-12.0056	-2.27124
0.07489	0.27366	0.98373	0.70365	-4.9459	-1.22824
0.18763	0.43316	0.98848	0.71472	-1.8432	-0.75186
0.32521	0.57027	0.99249	0.73314	4.6550	-0.54062+-
0.45069	0.67133	0.99449	0.74552	10.8634	0.44183
0.60035	0.77482	0.99681	0.75589	15.0089	-0.37019
0.80114	0.89506	0.99924	0.77855	18.9876	-0.29657

**NaCl**

0.02396	0.15479	0.98192	0.67104	-13.9877	-2.37024
0.08435	0.29043	0.98578	0.67476	-7.9865	-1.25117
0.16906	0.41116	0.98959	0.67963	2.9256	-0.87261
0.31441	0.56045	0.99612	0.68751	7.9090	-0.62690
0.43536	0.65981	0.99944	0.69460	14.5224	-0.52236
0.58095	0.76220	1.00111	0.70137	22.8956	-0.44381
0.77436	0.87997	1.00420	0.70894	27.9898	-0.37629

**KCl**

0.02012	0.14184	0.98249	0.67592	-35.0098	-2.55418
0.06032	0.24560	0.98563	0.68165	-15.9321	-1.45309
0.16180	0.40224	0.99273	0.69075	-2.9867	-0.86588
0.26298	0.51279	0.99714	0.69276	10.3209	-0.67551
0.36388	0.60322	0.99948	0.69489	21.9823	-0.57091
0.48521	0.69657	1.00146	0.70570	31.3332	-0.47976
0.64702	0.80437	1.00236	0.72619	41.0988	-0.39143

**T = 318K**

**LiCl**

0.02434	0.15601	0.97868	0.62700	-15.0399	-1.92788
0.07469	0.27329	0.98115	0.64062	-9.3420	-1.04497
0.18749	0.43300	0.98592	0.64705	-3.6754	-0.64297
0.32510	0.57017	0.98981	0.65580	3.9988	-0.47117
0.45015	0.67093	0.99204	0.66549	9.8763	-0.38431
0.60016	0.77469	0.99557	0.67659	12.2183	-0.31685
0.80105	0.89501	0.99725	0.68719	17.8965	-0.26105

**NaCl**

0.02375	0.15411	0.97909	0.55672	-17.4591	-2.46022
0.08413	0.29005	0.98291	0.55979	-8.4598	-1.29537
0.16892	0.41099	0.98734	0.56645	-1.0456	-0.89611
0.31400	0.56035	0.99381	0.57511	5.9934	-0.64002
0.43512	0.65963	0.99720	0.58092	13.0001	-0.53387
0.58089	0.76216	0.99931	0.58835	20.9999	-0.45118
0.77410	0.87982	0.99991	0.59771	29.9088	-0.37897

**KCl**

0.02001	0.14145	0.97968	0.62683	-40.0035	-2.12767
0.06003	0.24501	0.98312	0.63324	-22.9867	-1.19917
0.16120	0.40149	0.99072	0.63710	-8.9219	-0.72107
0.26205	0.51190	0.99606	0.63791	3.0001	-0.56378
0.36259	0.60215	0.99796	0.63894	17.9898	-0.47737
0.48395	0.69566	0.99925	0.64372	29.8769	-0.40554
0.64611	0.80380	1.00085	0.65083	38.9865	-0.34112

**40 mass % THF + H<sub>2</sub>O Mixture**

$c/\text{mol dm}^{-3}$	$\sqrt{c}/(\text{mol dm}^{-3})^{1/2}$	$\rho/\text{g.cm}^{-3}$	$\eta/\text{cp}$	$V_b/\text{cm}^3\text{mol}^{-1}$	$(\eta/\eta_0 - 1)/\sqrt{c}$
<b>T = 303K</b>					
<b>LiCl</b>					
0.01313	0.11458	0.96575	0.99243	-145.66	-3.05754
0.04595	0.21435	0.97219	1.00110	-110.11	-1.60792
0.08535	0.29214	0.97404	1.02710	-80.58	-1.12151
0.13131	0.36236	0.97482	1.03799	-43.13	-0.88450
0.18383	0.42875	0.97670	1.06218	-28.82	-0.71060
<b>NaCl</b>					
0.01398	0.11823	0.96677	1.06336	-160.05	-2.57042
0.04896	0.22126	0.97332	1.03639	-141.22	-1.45329
0.08393	0.28970	0.97579	1.05111	-87.62	-1.07670
0.12589	0.35480	0.97756	1.05706	-52.82	-0.86816
0.17485	0.41815	0.97876	1.07656	-28.19	-0.70611
<b>KCl</b>					
0.04821	0.21956	0.98263	1.05443	-240.01	-1.41076
0.07231	0.26890	0.98290	1.06487	-196.84	-1.12648

0.09642	0.31051	0.98330	1.08155	-132.52	-0.94036
0.12052	0.34715	0.98517	1.09379	-106.70	-0.81803
0.14462	0.38028	0.98592	1.10480	-81.37	-0.72781

**T = 308K**

**LiCl**

0.01305	0.11423	0.96394	0.90829	-175.11	-2.74458
0.04886	0.21375	0.96786	0.91471	-107.52	-1.44403
0.08369	0.29163	0.97067	0.92137	-71.78	-1.04114
0.12543	0.36175	0.97157	0.92823	-38.33	-0.82499
0.14462	0.42799	0.97325	0.93587	-24.37	-0.68382

**NaCl**

0.01395	0.11811	0.96477	0.96952	-205.02	-2.26260
0.04569	0.22104	0.97142	0.94613	-156.94	-1.28897
0.08505	0.28929	0.97303	0.95573	-86.29	-0.95979
0.13087	0.35416	0.97393	0.96265	-44.85	-0.76922
0.18318	0.41737	0.97512	0.97992	-22.36	-0.62145

**KCl**

0.04800	0.21908	0.97846	0.89552	-293.53	-1.47510
0.07208	0.26847	0.97990	0.91118	-195.14	-1.15964
0.09610	0.31000	0.98013	0.92732	-128.86	-0.96493
0.12028	0.34681	0.98322	0.93389	-113.54	-0.84820
0.14445	0.38006	0.98480	0.94827	-92.67	-0.74540

**T = 313K**

**LiCl**

0.01300	0.11401	0.95838	0.81882	-340.51	-2.70589
0.04563	0.21361	0.96646	0.83169	-251.30	-1.39333
0.08479	0.29118	0.96770	0.84274	-130.12	-2.51304
0.13040	0.36110	0.96813	0.86306	-72.52	-0.75086
0.18281	0.42756	0.97131	0.89269	-57.19	-0.57562

**NaCl**

0.01394	0.11806	0.96390	0.84957	-375.55	-2.39310
0.04884	0.22099	0.97103	0.85564	-313.25	-1.25528
0.08357	0.28908	0.97158	0.89418	-164.52	-0.84702
0.12536	0.35406	0.97346	0.90996	-104.95	-0.65393

0.17394      0.41706      0.97366      0.94027      -59.71      -0.49377

**KCl**

0.04791      0.21888      0.97666      0.83841      -426.72      -1.33385  
0.07186      0.26806      0.97690      0.85276      -262.02      -1.04393  
0.09597      0.30979      0.97881      0.87157      -198.50      -0.85203  
0.11990      0.34626      0.98019      0.88391      -155.00      -0.73219  
0.14423      0.37977      0.98331      0.89991      -137.96      -0.63200

**T = 318K**

**LiCl**

0.01299      0.11397      0.95230      0.73823      -475.66      -2.57671  
0.04555      0.21342      0.96472      0.74545      -390.28      -1.34364  
0.08454      0.29075      0.96489      0.76479      -191.72      -0.92263  
0.13005      0.36062      0.96547      0.76495      -113.61      -0.74344  
0.18248      0.42717      0.96957      0.79444      -91.86      -0.56157

**NaCl**

0.01380      0.11747      0.95396      0.76986      -540.561      -2.24231  
0.04862      0.22049      0.96669      0.79606      -388.62      -1.08094  
0.08316      0.28837      0.96692      0.79824      -204.62      -0.81926  
0.12477      0.35322      0.96883      0.80578      -131.84      -0.64842  
0.17318      0.41614      0.96912      0.82426      -81.34      -0.50789

**KCl**

0.04779      0.21860      0.97417      0.73289      -544.48      -1.36677  
0.07167      0.26771      0.97424      0.75281      -338.04      -1.04485  
0.09559      0.30917      0.97490      0.79315      -241.05      -0.77989  
0.11963      0.34587      0.97794      0.82595      -203.61      -0.60640  
0.14382      0.37923      0.98051      0.86532      -175.02      -0.45373

**60 mass % THF + H<sub>2</sub>O Mixture**

$c/\text{mol dm}^{-3}$	$\sqrt{c}/(\text{mol dm}^{-3})^{1/2}$	$\rho/\text{g.cm}^{-3}$	$\eta/\text{cp}$	$V_f/\text{cm}^3\text{mol}^{-1}$	$(\eta/\eta_0 - 1)/\sqrt{c}$
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**T = 303K**

**LiCl**

0.01062	0.10309	0.94443	0.98701	-194.414	-2.55438
0.03542	0.18821	0.94775	0.93673	-123.089	-1.59852
0.06376	0.25252	0.94897	0.95249	-70.383	-1.14485

0.09565	0.30927	0.94864	0.95533	-28.356	-0.92791
0.12399	0.35212	0.94833	1.06147	-8.871	-0.59003

**NaCl**

0.00770	0.08775	0.94416	1.04839	-231.002	-2.47890
0.02569	0.16031	0.94787	0.92462	-178.988	-1.93312
0.04629	0.21517	0.94885	0.85612	-91.795	-1.67785
0.06940	0.26344	0.94941	0.94032	-49.159	-1.13188
0.09000	0.30000	0.94919	0.97000	-22.309	-0.92009

**KCl**

0.01099	0.10488	0.94646	1.12404	-348.418	-1.53567
0.03139	0.17720	0.95110	1.05098	-227.396	-1.21664
0.04980	0.22316	0.95146	1.08079	-121.819	-0.86638
0.07009	0.26476	0.95081	1.11921	-53.707	-0.62195
0.09229	0.30380	0.95011	1.17972	-13.678	-0.39337

**T = 308K**

**LiCl**

0.01059	0.10292	0.94076	0.87800	-223.319	-2.53667
0.03531	0.18792	0.94481	0.83395	-157.347	-1.58997
0.06356	0.25211	0.94502	0.85579	-71.011	-1.11231
0.09532	0.30874	0.94553	0.85428	-37.898	-0.91239
0.12361	0.35159	0.94510	0.94588	-15.213	-0.58213

**NaCl**

0.00764	0.08740	0.94046	0.94433	-267.446	-2.35667
0.02552	0.15975	0.94420	0.83572	-192.673	-1.86103
0.04597	0.21440	0.94648	0.82581	-132.082	-1.42551
0.06902	0.26271	0.94610	0.85336	-61.298	-1.07518
0.08970	0.29949	0.94593	0.87827	-30.786	-0.87321

**KCl**

0.01094	0.10459	0.94273	0.99843	-372.286	-1.53446
0.03120	0.17663	0.94752	0.90669	-242.520	-1.34532
0.04964	0.22280	0.94838	0.89815	-141.453	-1.09876
0.06984	0.26427	0.94760	0.93828	-65.532	-0.79865
0.09188	0.30311	0.94650	0.98061	-18.003	-0.57890

**T = 313K**

**LiCl**

0.01058	0.10290	0.93738	0.78791	-360.010	-2.59002
0.03526	0.18780	0.94357	0.76914	-262.894	-1.51218
0.06351	0.25202	0.94454	0.79297	-142.988	-1.03885
0.09521	0.30857	0.94446	0.79904	-78.800	-0.83014
0.12341	0.35130	0.94229	0.80716	-32.009	-0.70767

**NaCl**

0.00763	0.08735	0.93667	0.86454	-399.987	-2.23451
0.02549	0.15965	0.94179	0.75730	-291.001	-1.84787
0.04592	0.21428	0.94425	0.77112	-191.098	-1.31673
0.06894	0.26256	0.94439	0.78045	-108.596	-1.04153
0.08960	0.29933	0.93685	0.79620	-41.460	-0.86461

**KCl**

0.01092	0.10449	0.93929	0.90348	-499.999	-1.52098
0.03114	0.17646	0.94665	0.82229	-376.806	-1.32899
0.04945	0.22237	0.94635	0.81408	-201.231	-1.08897
0.06963	0.26387	0.94471	0.85029	-94.455	-0.78997
0.09178	0.30295	0.94202	0.89056	-20.991	-0.56432

**T = 318K**

**LiCl**

0.01055	0.10273	0.93355	0.76194	-455.897	-2.00098
0.03518	0.18757	0.94127	0.71301	-341.210	-1.36789
0.06336	0.25173	0.94494	0.72867	-231.533	-0.95438
0.09508	0.30836	0.94316	0.74756	-118.788	-0.71526
0.12324	0.35106	0.93897	0.82781	-44.626	-0.38992

**NaCl**

0.00759	0.08712	0.93273	0.79197	-518.003	-2.00012
0.02541	0.15940	0.93917	0.69908	-383.561	-1.70074
0.04588	0.21419	0.94167	0.71436	-242.998	-1.19135
0.06875	0.26220	0.94120	0.73003	-133.935	-0.91090
0.08919	0.29864	0.93749	0.73839	-44.001	-0.77056

**KCl**

0.01086	0.10421	0.93578	0.80916	-628.009	-1.50009
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0.03098	0.17601	0.94461	0.74132	-475.056	-1.29008
0.04914	0.22167	0.94352	0.74222	-246.002	-1.02009
0.06928	0.26321	0.94106	0.76612	-99.022	-0.76442
0.09117	0.30194	0.93741	0.79786	-23.323	-0.55678

**80 mass % THF + H<sub>2</sub>O Mixture**

$c/\text{mol dm}^{-3}$	$\sqrt{c}/(\text{mol dm}^{-3})^{1/2}$	$\rho/\text{g.cm}^{-3}$	$\eta/\text{cp}$	$V_{\phi}/\text{cm}^3\text{mol}^{-1}$	$(\eta/\eta_0 - 1)/\sqrt{c}$
<b>T = 303K</b>					
<b>LiCl</b>					
0.01336	0.11558	0.91436	0.56809	-163.096	-2.89560
0.02895	0.17015	0.91630	0.51565	-123.964	-2.32789
0.03563	0.18876	0.91621	0.57825	-89.056	-1.71000
0.04899	0.22134	0.91616	0.64385	-50.934	-1.11119
0.06681	0.25848	0.91573	0.73048	-17.893	-0.55898
<b>NaCl</b>					
0.00161	0.04012	0.91308	0.72284	-801.235	-3.82458
0.00376	0.06132	0.91431	0.84244	-667.092	-3.55437
0.00699	0.08361	0.91529	0.83507	-482.345	-3.14679
0.00968	0.09839	0.91542	0.61990	-345.961	-2.78478
0.01291	0.11362	0.91524	0.60187	-227.967	-2.59734
0.01721	0.13119	0.91489	0.58896	-132.453	-2.36480
<b>KCl</b>					
0.00107	0.03271	0.91311	0.75248	-1256.170	-3.62976
0.00249	0.04989	0.91433	0.70680	-1032.230	-3.45209
0.00605	0.07778	0.91691	0.63998	-842.934	-3.22189
0.00641	0.08006	0.91617	0.64878	-664.322	-2.99999
0.00854	0.09241	0.91635	0.63915	-501.342	-2.72111
0.01139	0.10672	0.91534	0.62067	-371.895	-2.55900

**T = 308K**

<b>LiCl</b>					
0.01333	0.11545	0.91037	0.53238	-175.778	-2.77999
0.02889	0.16998	0.91238	0.47955	-132.532	-2.28453
0.03556	0.18859	0.91239	0.53707	-99.111	-1.67009
0.04891	0.22117	0.91206	0.60133	-52.001	-1.05352
0.06665	0.25817	0.91165	0.68688	-18.996	-0.47983
<b>NaCl</b>					
0.00160	0.04009	0.90898	0.67153	-832.099	-3.57834
0.00375	0.06127	0.91014	0.62948	-653.337	-3.21678

0.00697	0.08353	0.91121	0.58693	-493.786	-3.00930
0.00966	0.09831	0.91142	0.57231	-362.983	-2.74659
0.01289	0.11354	0.91114	0.56719	-231.723	-2.43567
0.01719	0.13111	0.91001	0.56173	-135.231	-2.16234

**KCl**

0.00106	0.03268	0.90901	0.69259	-1301.240	-3.56789
0.00248	0.04985	0.91028	0.65020	-1072.885	-3.42367
0.00604	0.07772	0.91304	0.58793	-896.934	-3.21789
0.00639	0.07999	0.91221	0.59525	-699.299	-3.00987
0.00850	0.09223	0.91246	0.58737	-537.417	-2.71932
0.01135	0.10655	0.91365	0.57692	-407.357	-2.47895

**T = 313K**

**LiCl**

0.01324	0.11507	0.90624	0.50768	-265.988	-2.58554
0.02874	0.16954	0.90880	0.45558	-195.866	-2.18009
0.03541	0.18818	0.90829	0.49762	-133.991	-1.65498
0.04868	0.22065	0.90752	0.69033	-67.096	-0.92009
0.06634	0.25756	0.90645	0.64638	-18.954	-0.41000

**NaCl**

0.00159	0.03987	0.90382	0.62738	-848.893	-3.30789
0.00373	0.06107	0.90499	0.58990	-672.238	-3.00872
0.00694	0.08330	0.90619	0.55874	-523.871	-2.72345
0.00961	0.09803	0.90631	0.54863	-373.913	-2.45698
0.01282	0.11322	0.90633	0.54067	-266.235	-2.22457
0.01709	0.13072	0.90575	0.54098	-145.783	-1.92346

**KCl**

0.00105	0.03240	0.90385	0.64262	-1332.890	-3.41986
0.00246	0.04959	0.90518	0.60839	-1123.880	-3.18934
0.00600	0.07746	0.90794	0.55482	-921.342	-2.99876
0.00636	0.07975	0.90730	0.56560	-752.240	-2.72567
0.00845	0.09192	0.90750	0.55543	-572.376	-2.51789
0.01127	0.10616	0.90766	0.54188	-423.872	-2.35672

**T = 318K**

**LiCl**

0.01316	0.11473	0.90219	0.47397	-365.934	-2.47010
0.02864	0.16925	0.90586	0.43864	-285.342	-1.99001

Study of Ion-Solvent Interactions of Some Alkali  
Metal .....at Different Temperatures

0.03529	0.18785	0.90451	0.49616	-180.077	-1.33000
0.04852	0.22027	0.90358	0.54928	-96.541	-0.76959
0.06611	0.25713	0.90254	0.59542	-40.765	-0.38800

**NaCl**

0.00159	0.03987	0.89855	0.57661	-863.932	-3.21567
0.00371	0.06091	0.89987	0.54117	-701.743	-2.98456
0.00690	0.08306	0.90114	0.51339	-553.342	-2.69423
0.00955	0.09772	0.90129	0.50520	-399.024	-2.41678
0.01275	0.11292	0.90130	0.50010	-282.749	-2.15976
0.01701	0.13042	0.90084	0.49970	-165.912	-1.87456

**KCl**

0.00104	0.03225	0.89880	0.59104	-1506.240	-3.29879
0.00245	0.04950	0.90035	0.55995	-1298.240	-3.09898
0.00598	0.07733	0.90371	0.51557	-1107.756	-2.85123
0.00634	0.07962	0.90310	0.52180	-933.277	-2.65101
0.00842	0.09176	0.90446	0.51224	-765.237	-2.45782
0.01123	0.10597	0.90376	0.50151	-556.923	-2.28123

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Figure 1 : Plot of Apparent Molar Volume ( $V_\phi$ ) vs square root of concentration ( $c^{1/2}$ ) for various salts in different mass% of THF + water mixtures at different temperatures

- = LiCl
- = NaCl
- △ = KCl

20 mass % THF + H<sub>2</sub>O mixture

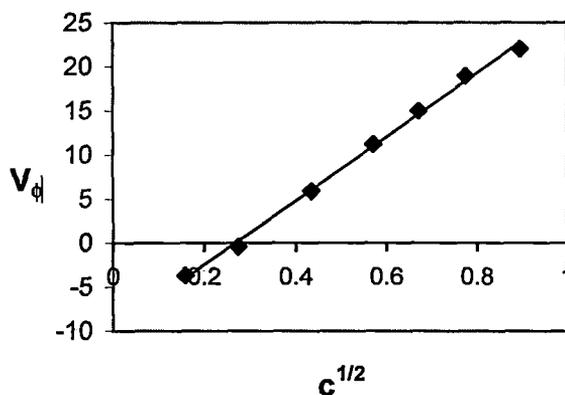


Fig.1(a) at 303K

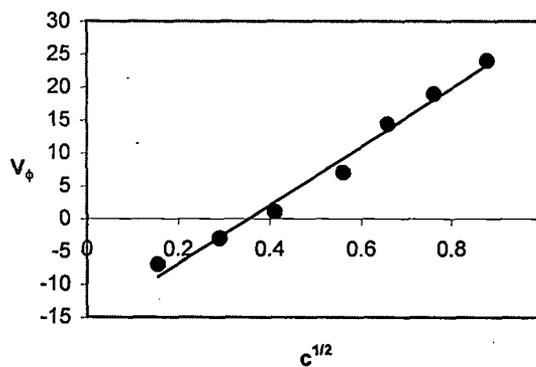


Fig.1(b) at 303K

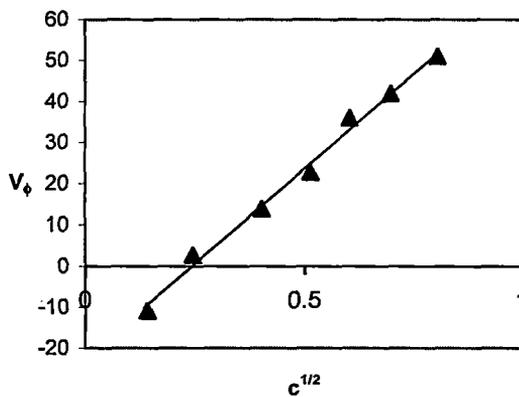


Fig.1(c) at 303K

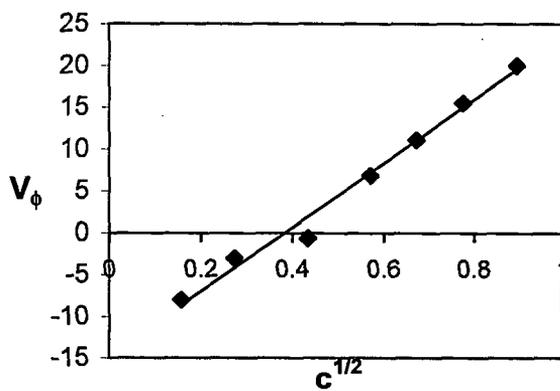


Fig.1(d) at 308K

□ = LiCl  
○ = NaCl  
△ = KCl

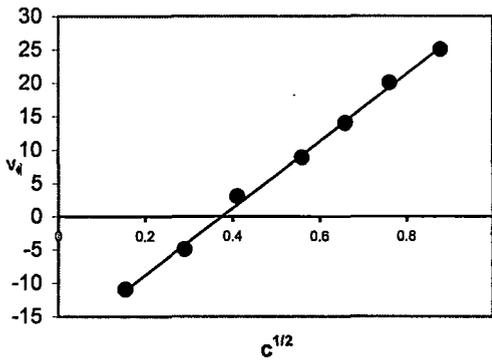


Fig.1(e) at 308K

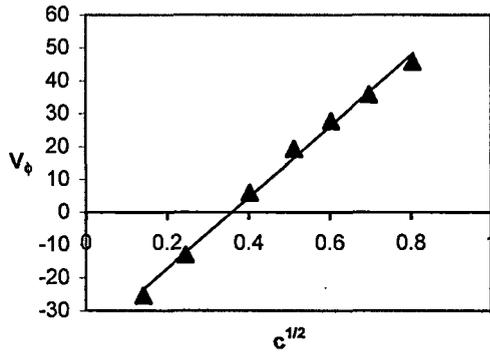


Fig.1(f) at 308K

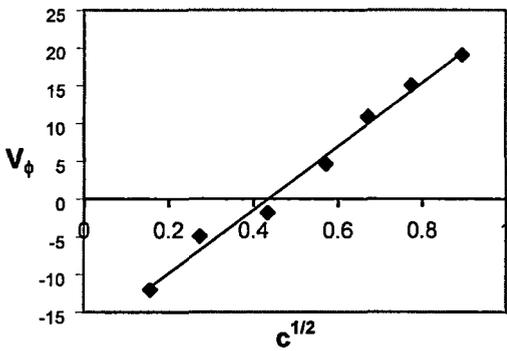


Fig.1(g) at 313K

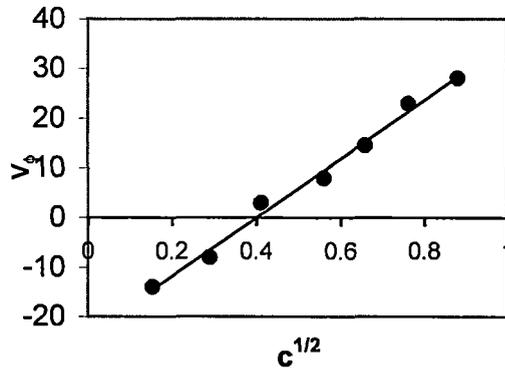


Fig.1(h) at 313K

□ = LiCl  
 ○ = NaCl  
 △ = KCl

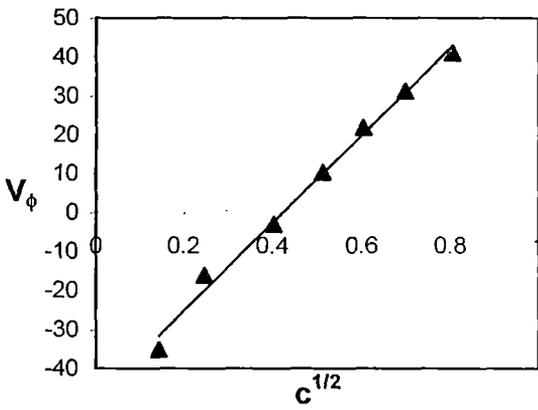


Fig.1(i) at 313K

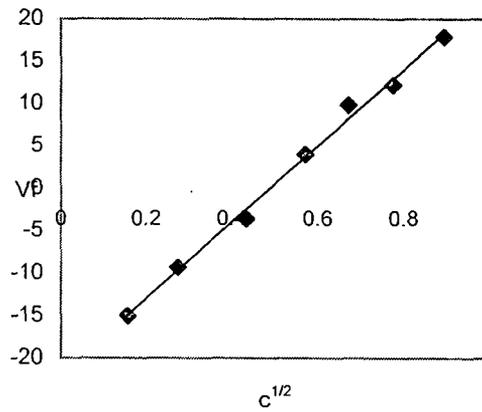


Fig.1(i) at 318K

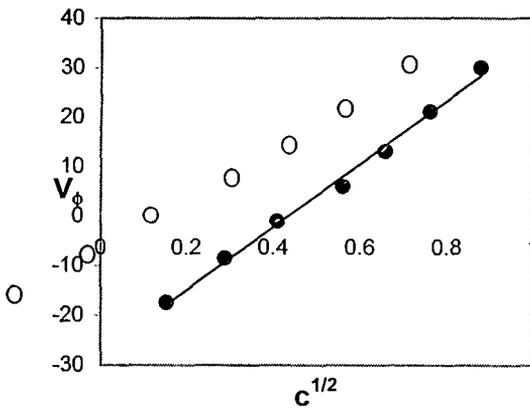


Fig.1(k) at 318K

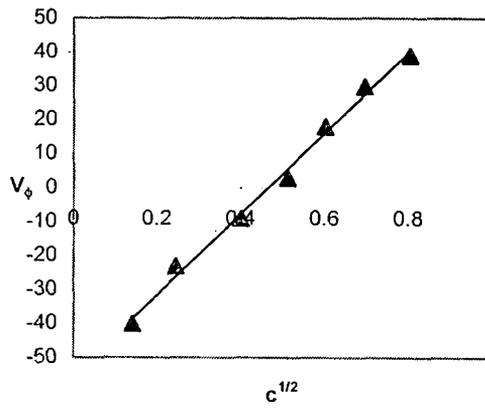


Fig.1(l) at 318K

- = LiCl
- = NaCl
- △ = KCl

40 mass% THF + H<sub>2</sub>O mixture

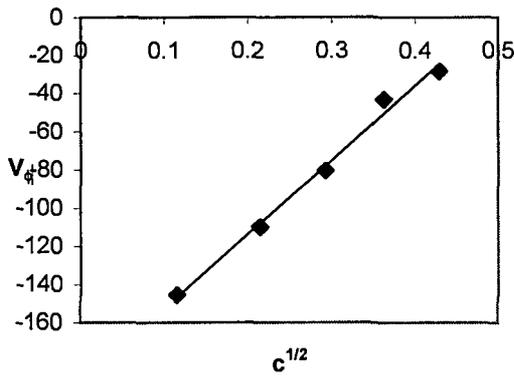


Fig.1(a) at 303K

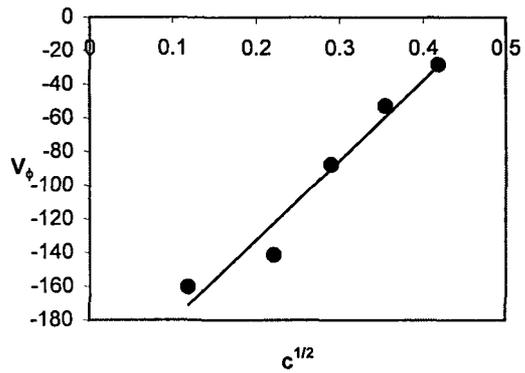


Fig.1(b) at 303K

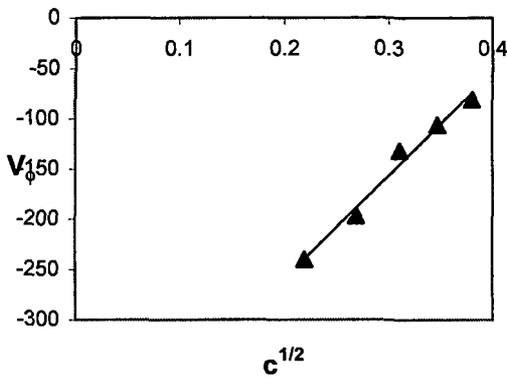


Fig.1(c) at 303K

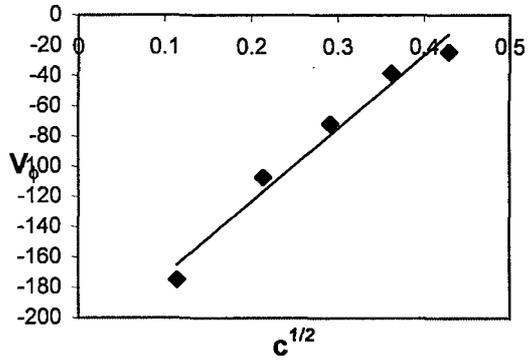


Fig.1(d) at 308K

□ = LiCl  
○ = NaCl  
△ = KCl

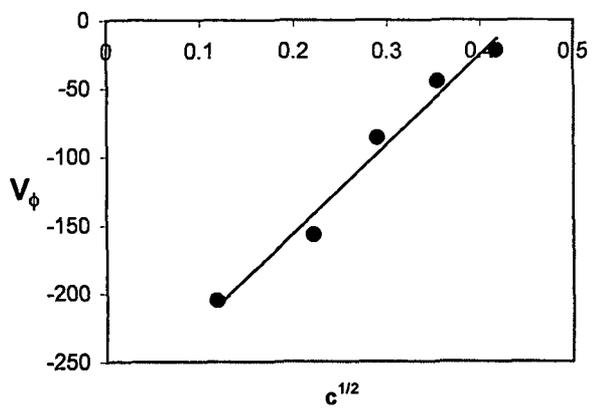


Fig.1(e) at 308K

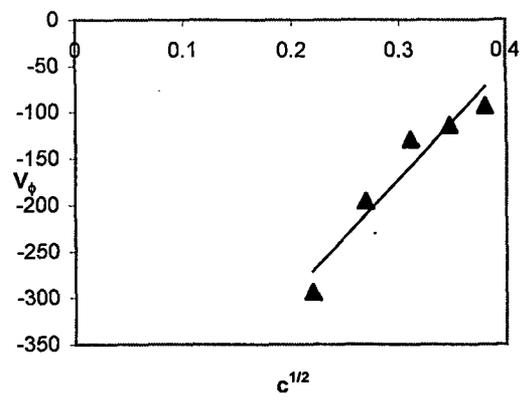


Fig.1(f) at 308K

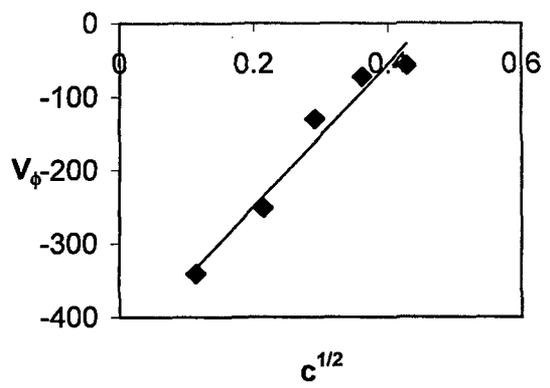


Fig.1(g) at 313K

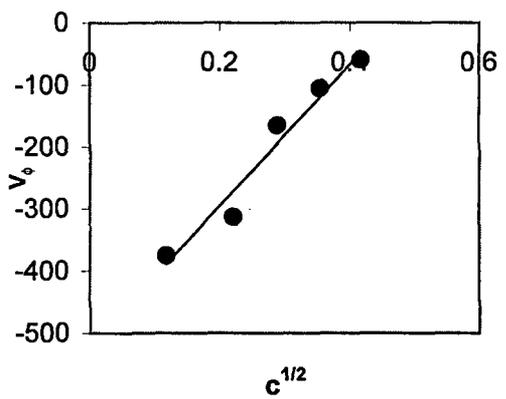


Fig.1(h) at 313K

□ = LiCl  
 ○ = NaCl  
 △ = KCl

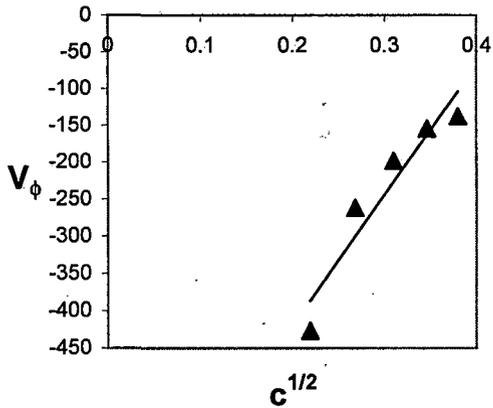


Fig. 1(i) at 313K

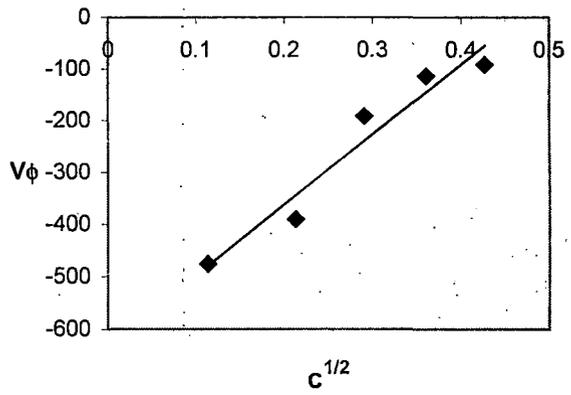


Fig. 1(i) at 318K

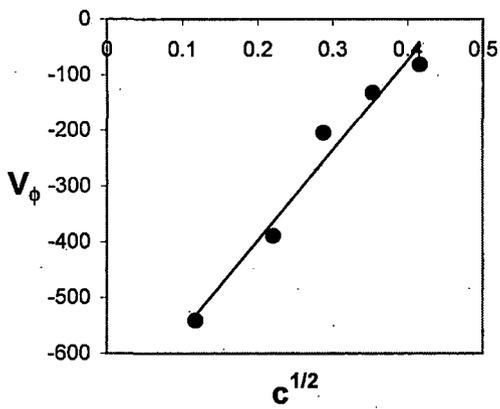


Fig. 1(k) at 318K

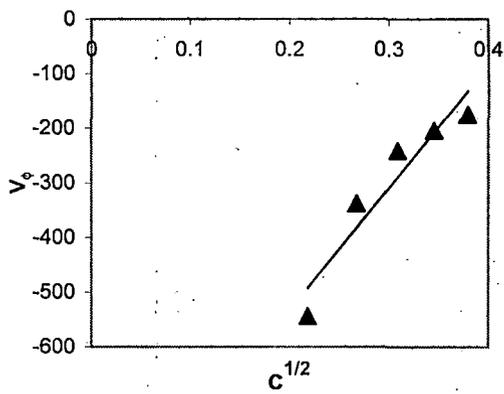


Fig. 1(l) at 318K

- = LiCl
- = NaCl
- △ = KCl

60 mass% THF + H<sub>2</sub>O mixture

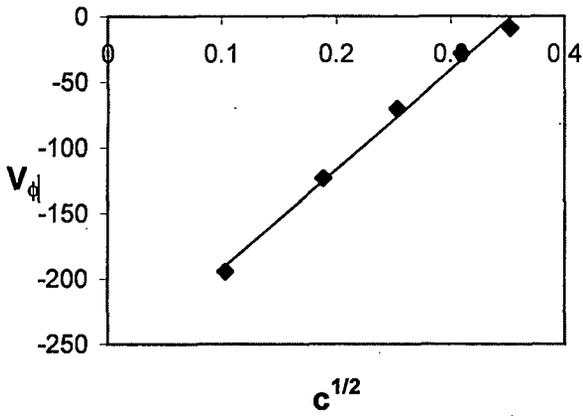


Fig.1(a) at 303K

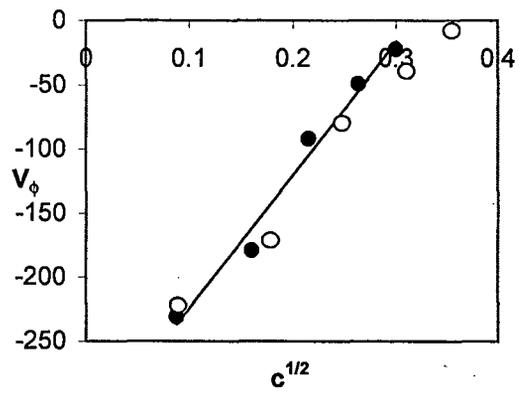


Fig.1(b) at 303K

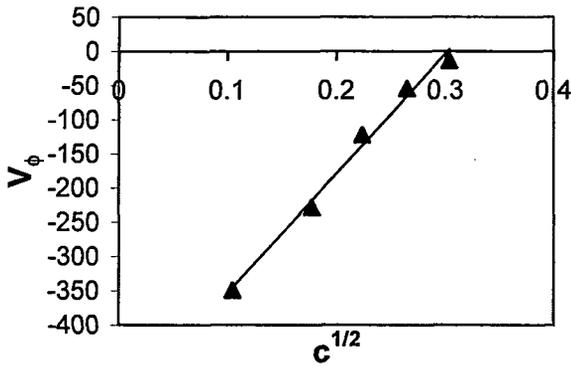


Fig.1(c) at 303K

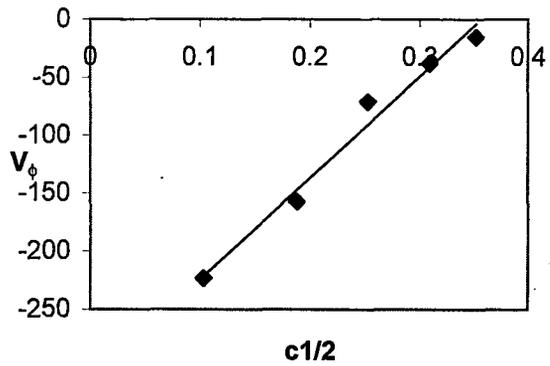


Fig.1(d) at 308K

□ = LiCl  
○ = NaCl  
△ = KCl

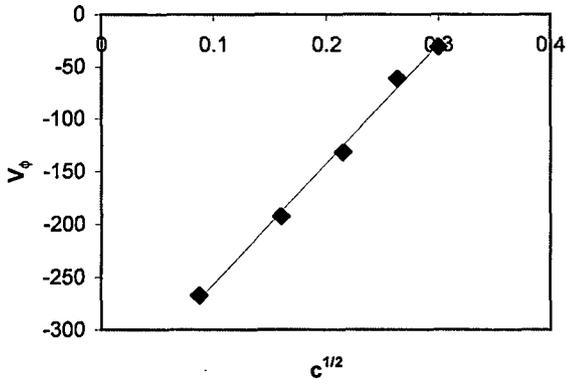


Fig.1(e) at 308K

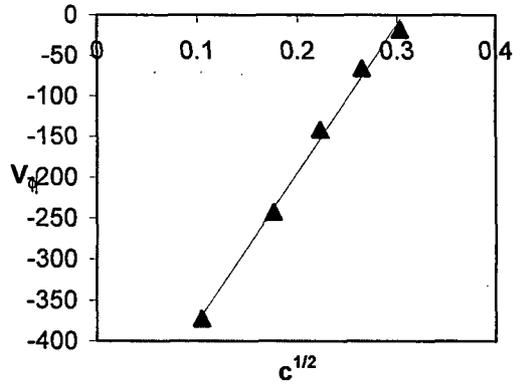


Fig.1(f) at 308K

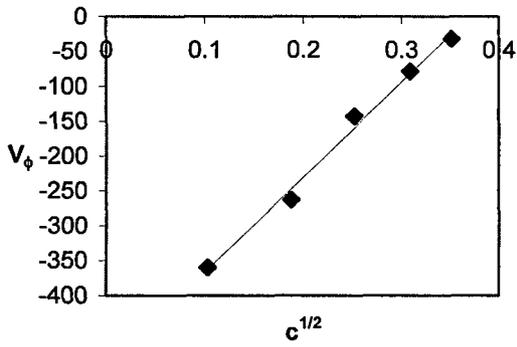


Fig.1(a) at 313K

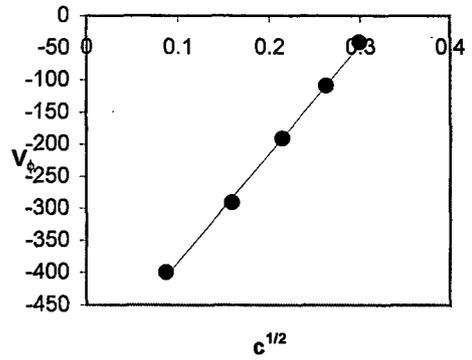


Fig.1(h) at 313K

□ = LiCl  
 ○ = NaCl  
 △ = KCl

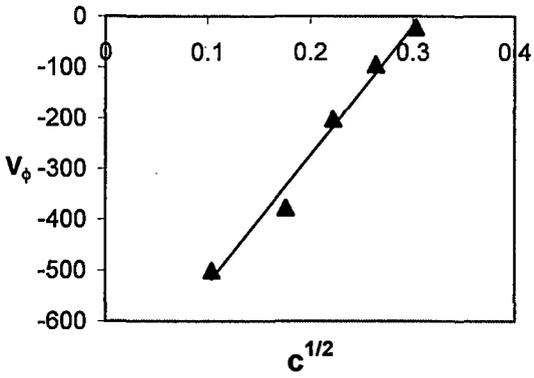


Fig.1(h) at 313K

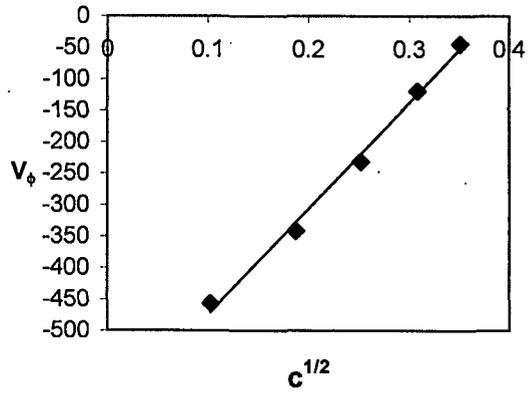


Fig.1(i) at 318K

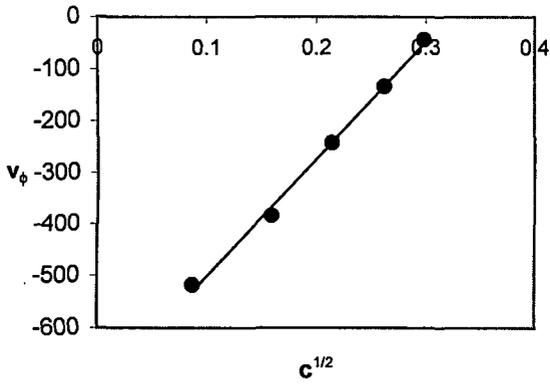


Fig.1(j) at 318K

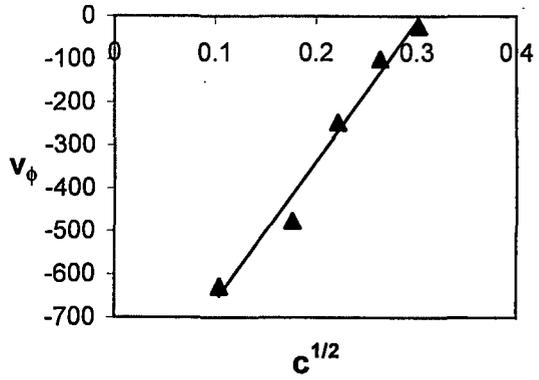


Fig.1(k) at 318K

80 mass% THF + H<sub>2</sub>O mixture

- = LiCl
- = NaCl
- △ = KCl
- 303K

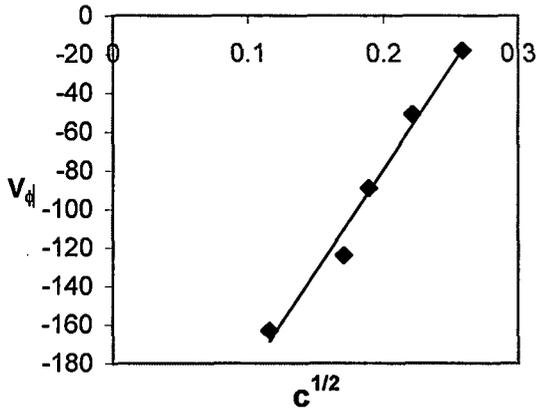


Fig.1(a) at 303K

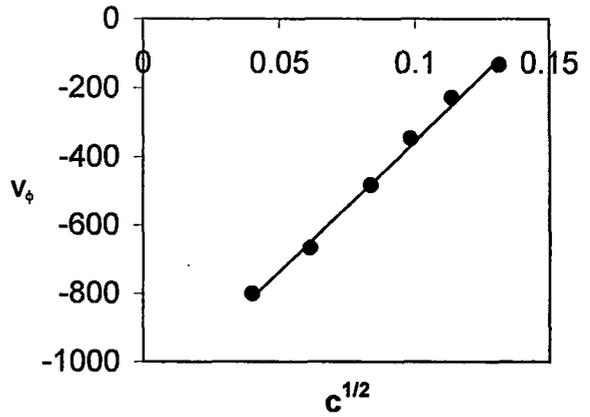


Fig.1(b) at 303K

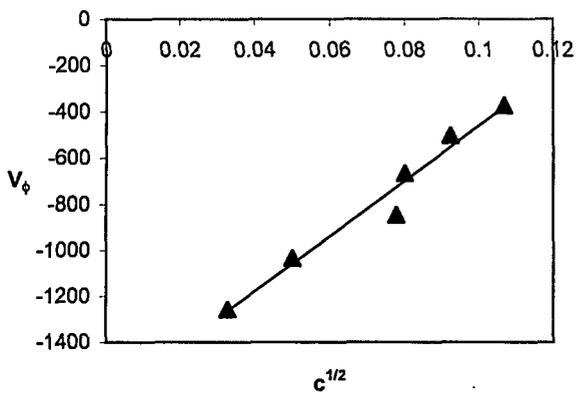


Fig.1(c) at 303K

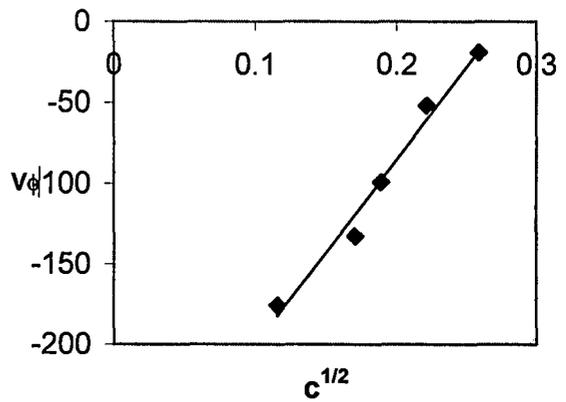


Fig.1(d) at 308K

□ = LiCl  
○ = NaCl  
△ = KCl

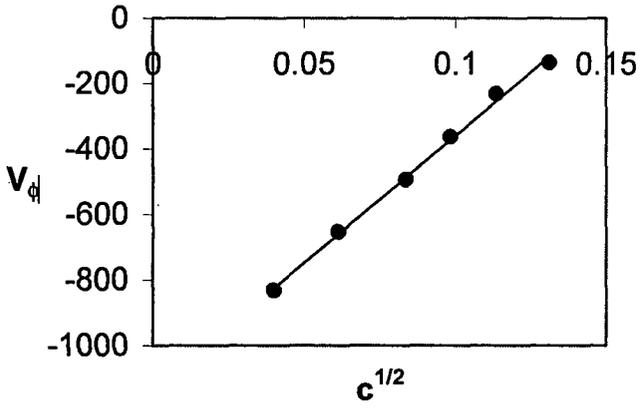


Fig.1(e) at 308K

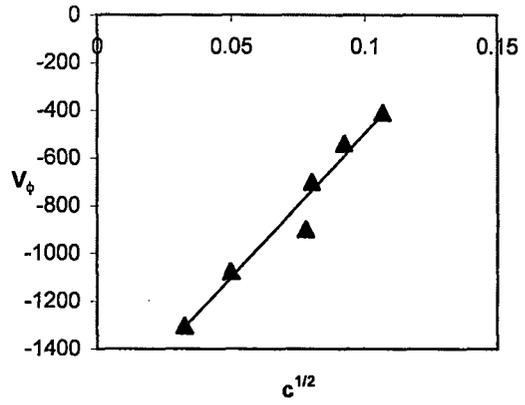


Fig.1(f) at 308K

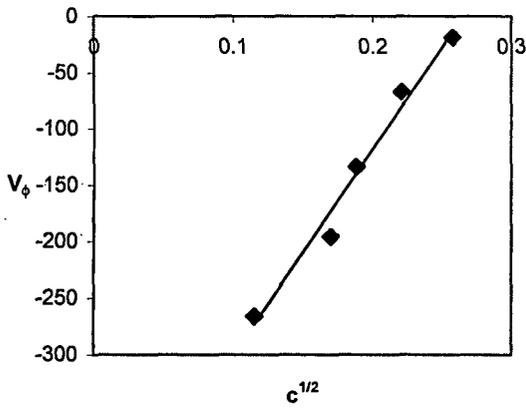


Fig.1(g) at 313K

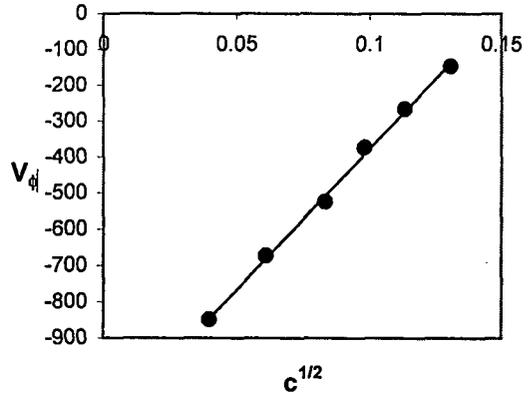


Fig.1(h) at 313K

□ = LiCl  
○ = NaCl  
△ = KCl

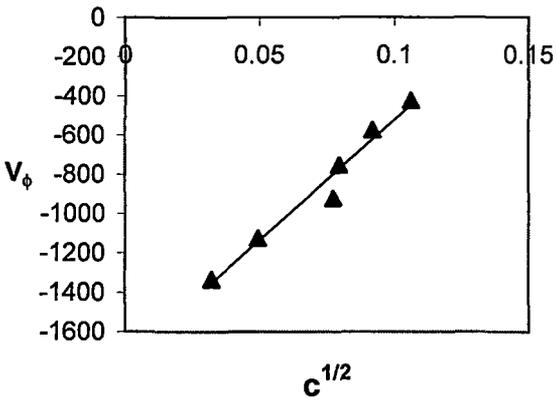


Fig.1(h) at 313K

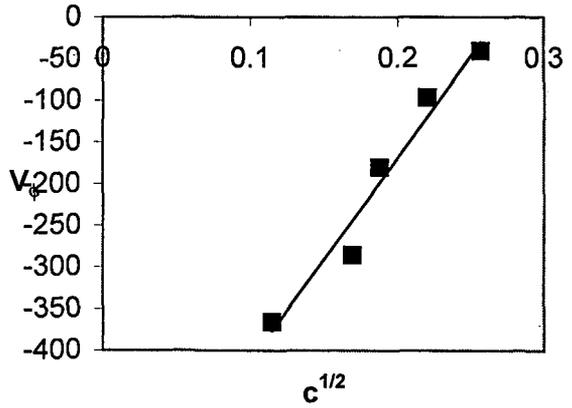


Fig.1(i) at 318K

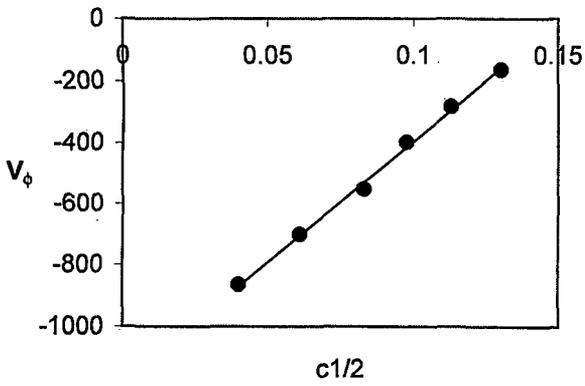


Fig.1(j) at 318K

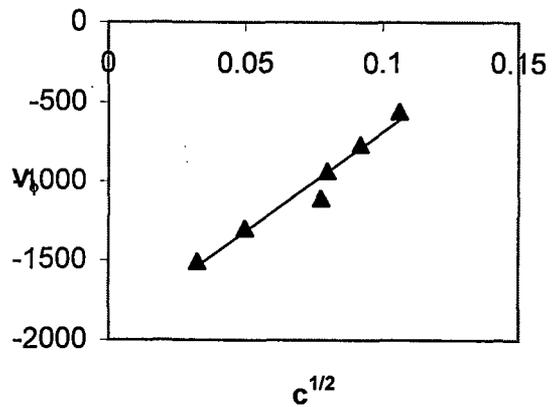


Fig.1(k) at 318K

Figure 2: Plot of  $(\eta/\eta_0-1)/c^{1/2}$  vs square root of concentration ( $c^{1/2}$ ) for various salts in different mass % of THF + water mixtures at different temperatures.

20 mass % THF + water mixture

□ = LiCl  
○ = NaCl  
△ = KCl

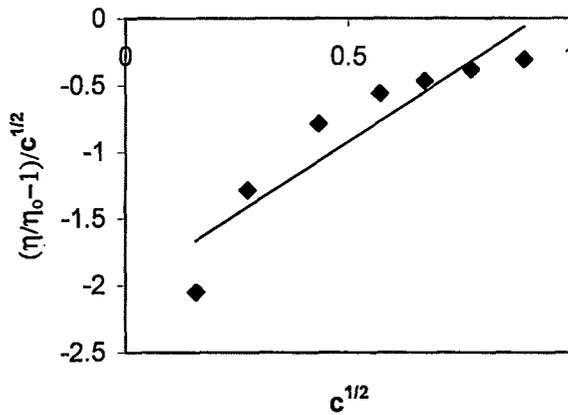


Fig.2(a) at 303K

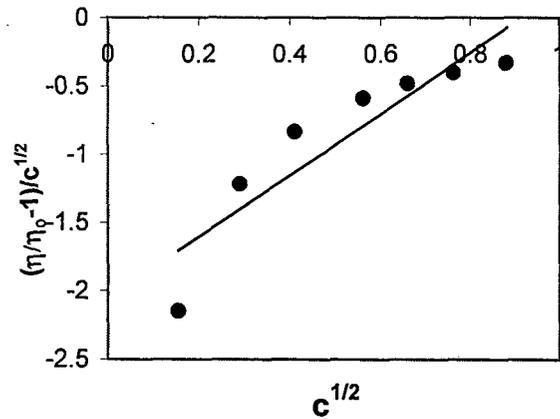


Fig.2(b) at 303K

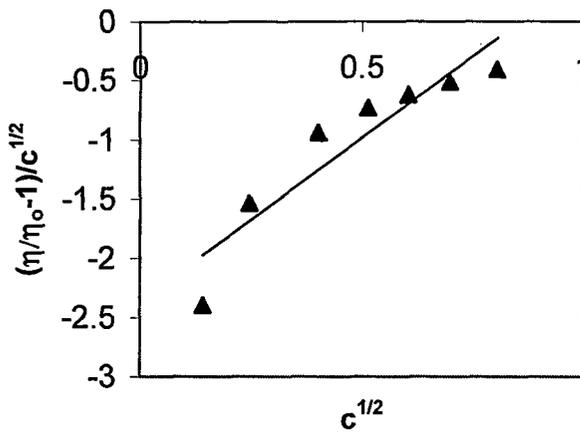


Fig.2(c) at 303K

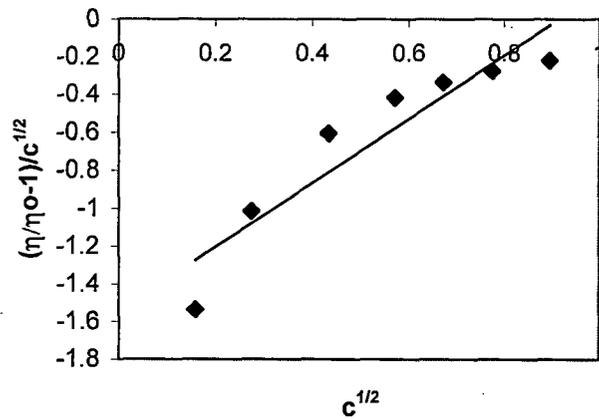


Fig.2(d) at 308K

- = LiCl
- = NaCl
- △ = KCl

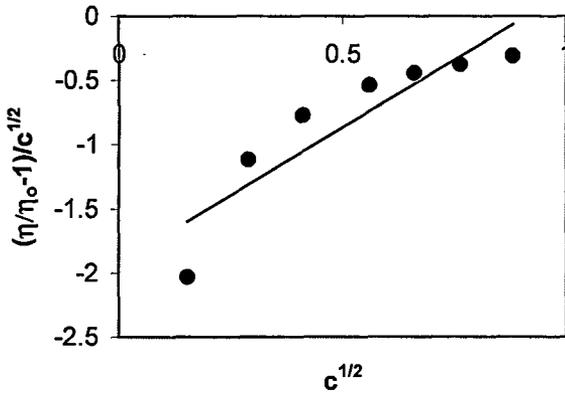


Fig.2(e) at 308K

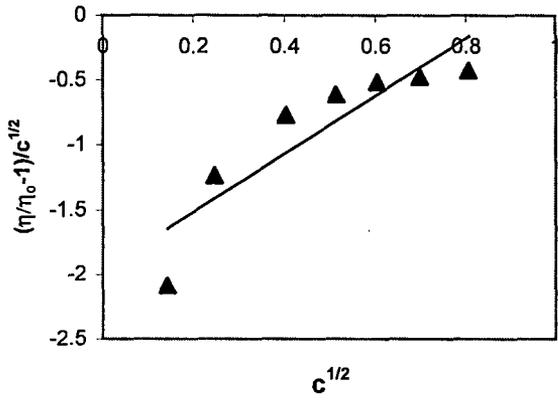


Fig. 2(f) at 308K

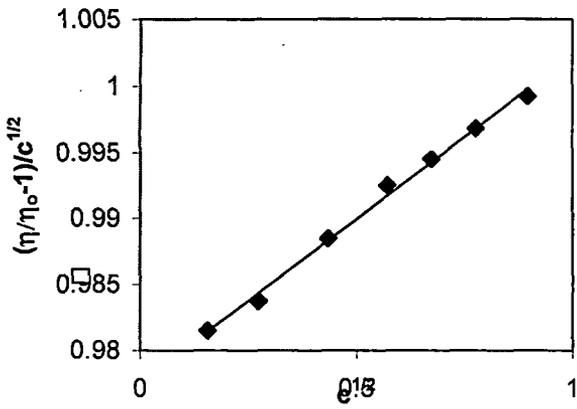


Fig.2(g) at 313K

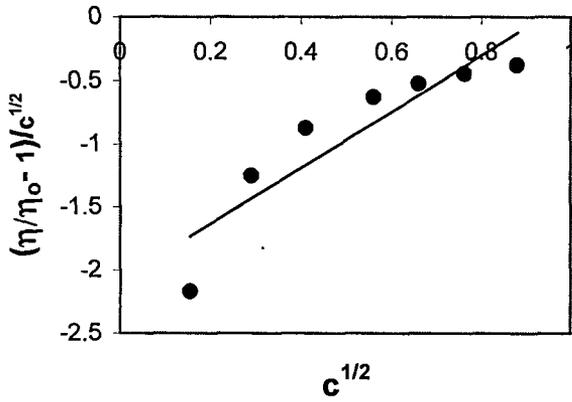


Fig.2(h) at 313K

□ = LiCl  
 ○ = NaCl  
 △ = KCl

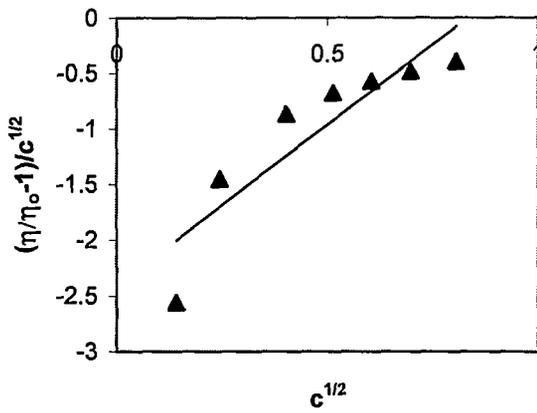


Fig.2(i) at 313K

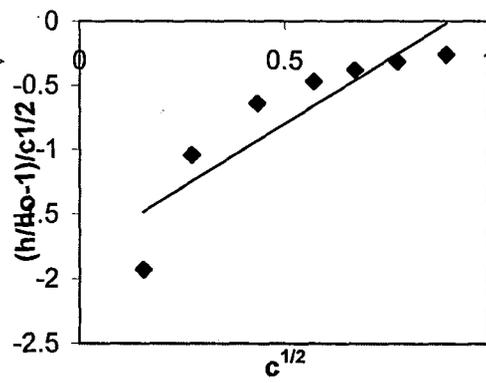


Fig.2(j) at 318K

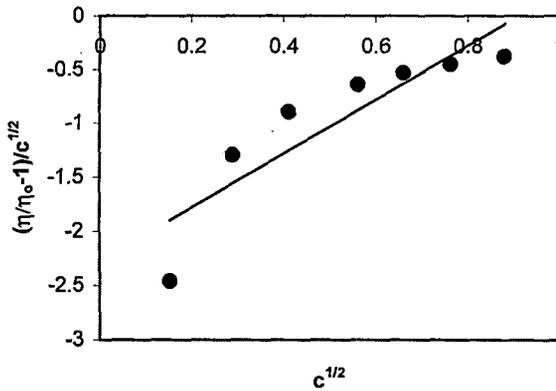


Fig.2(k) at 318K

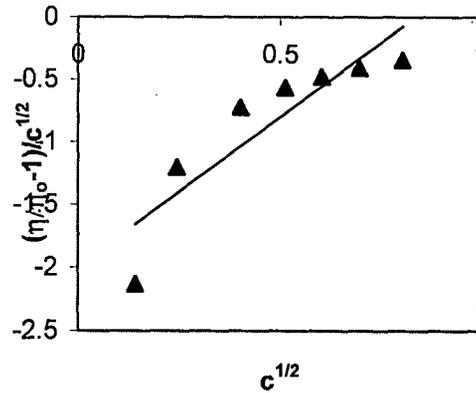


Fig.2(l) at 318K

- = LiCl
- = NaCl
- △ = KCl

40 mass% THF + Water mixture

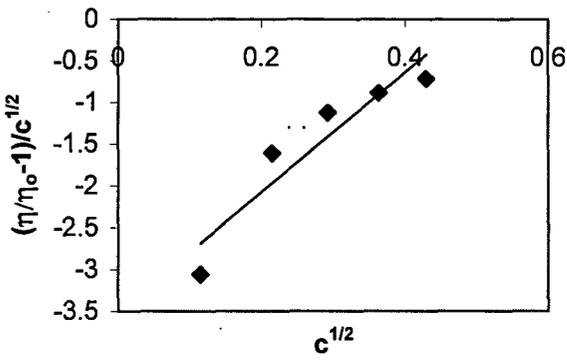


Fig.2(a) at 303K

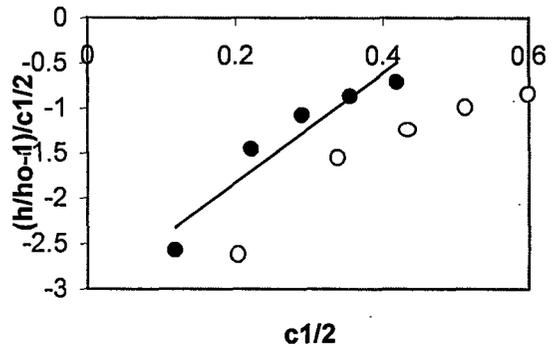


Fig.2(b) at 303K

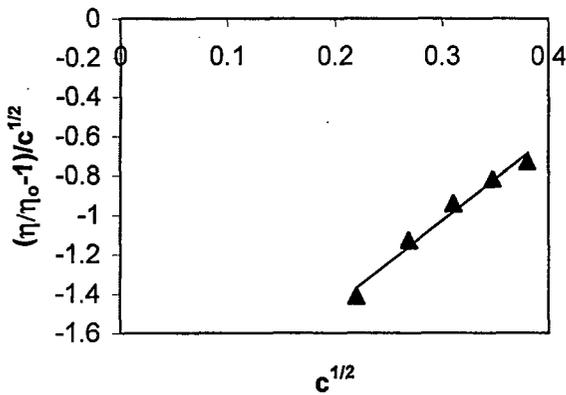


Fig.2(c) at 303K

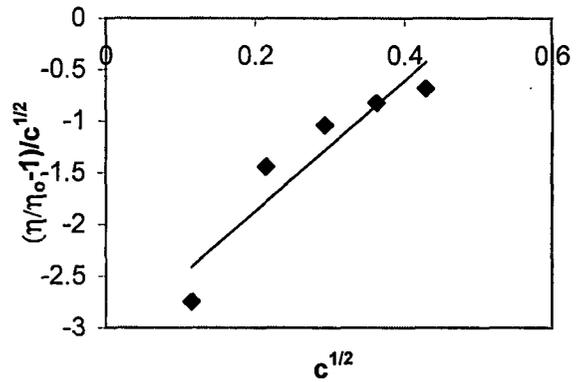


Fig.2(d) at 308K

□ = LiCl  
 ○ = NaCl  
 △ = KCl

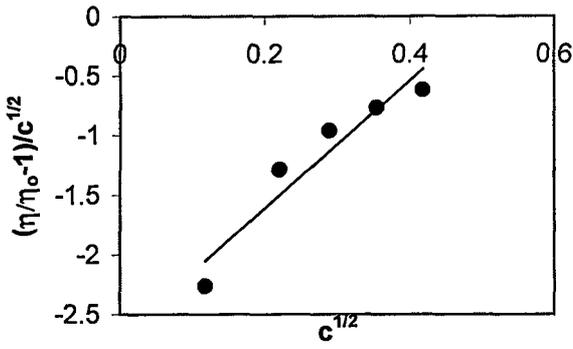


Fig.2(e) at 308K

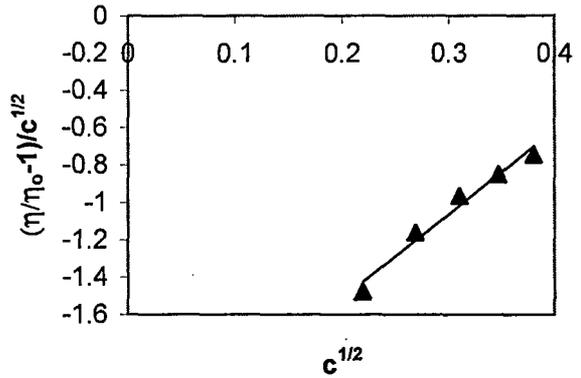


Fig.2(f) at 308K

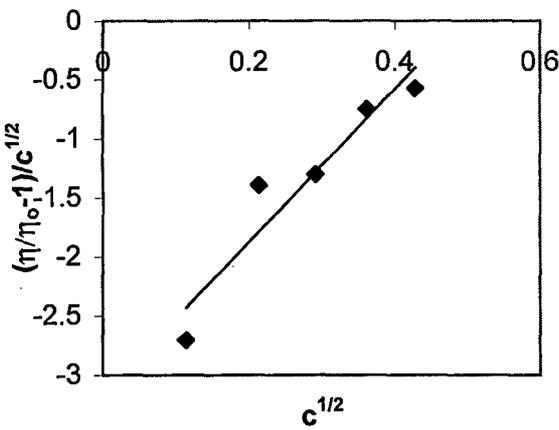


Fig.2(g) at 313K

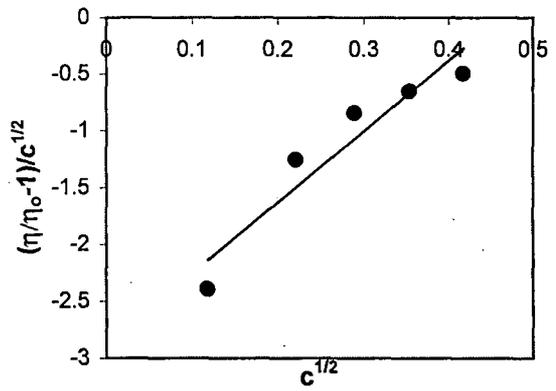


Fig.2(h) at 313K

□ = LiCl  
 ○ = NaCl  
 △ = KCl

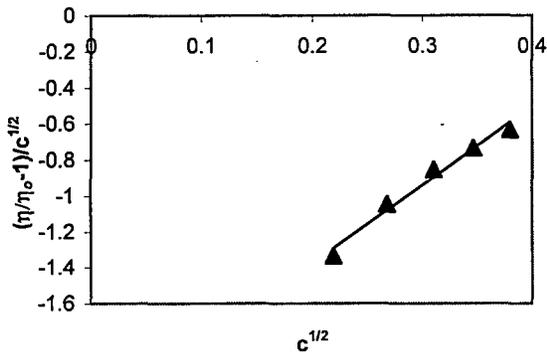


Fig.2(i) at 313K

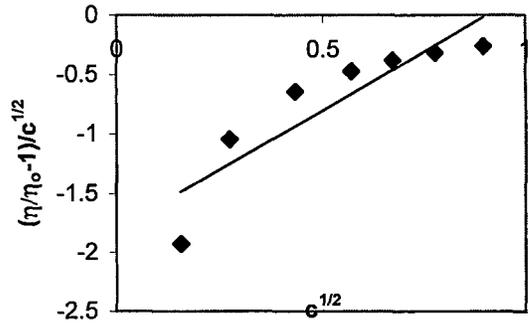


Fig.2(j) at 318K

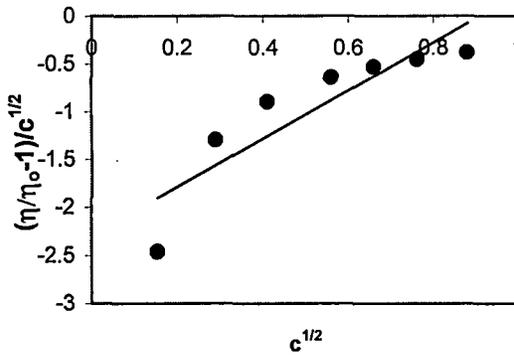


Fig.2(k) at 318K

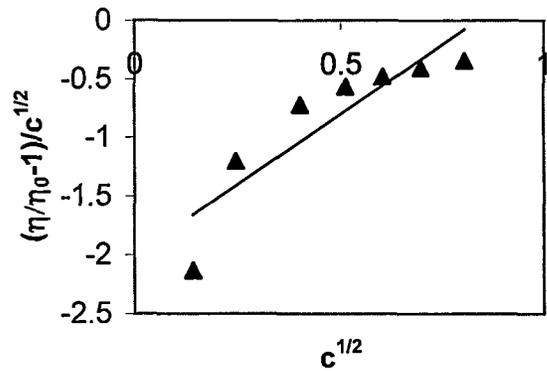


Fig.2(l) at 318K

□ = LiCl  
 ○ = NaCl  
 △ = KCl  
 60 mass% THF + Water mixture

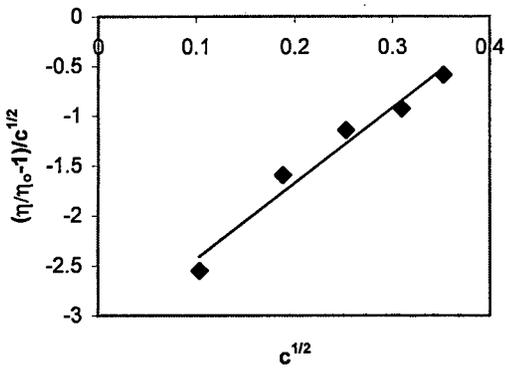


Fig.2(a) at 303K

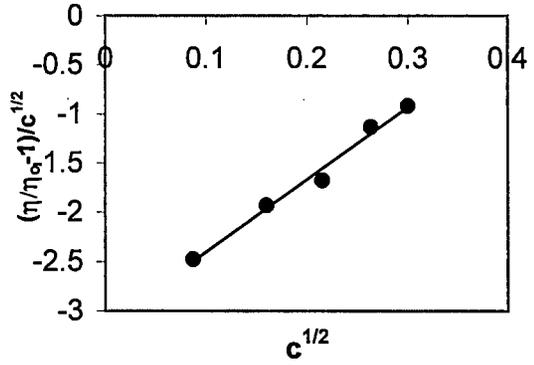


Fig.2(b) at 303K

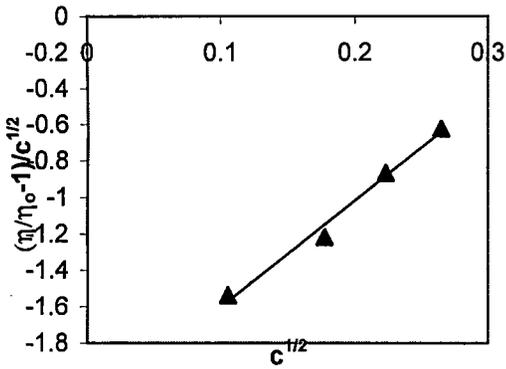


Fig.2(c) at 303K

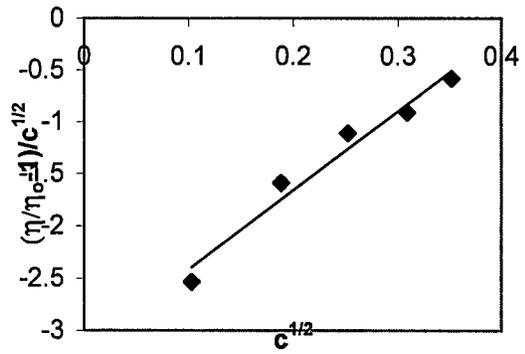


Fig.2(d) at 308K

- = LiCl
- = NaCl
- △ = KCl

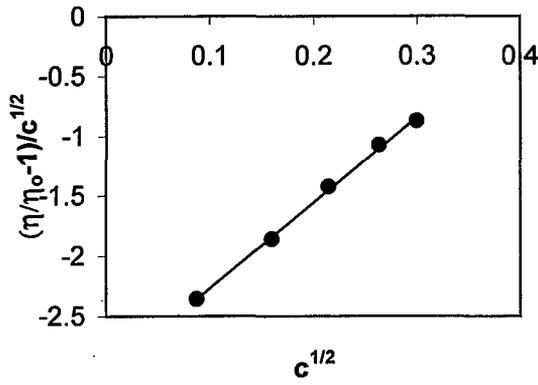


Fig.2(e) at 308K

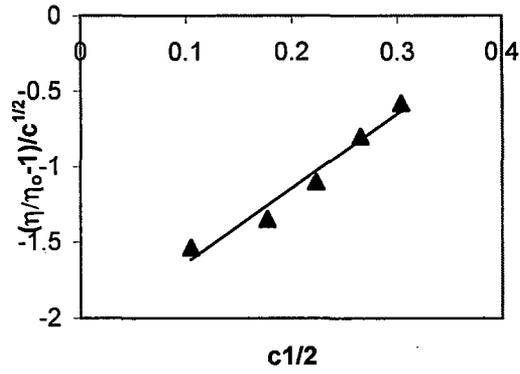


Fig.2(f) at 308K

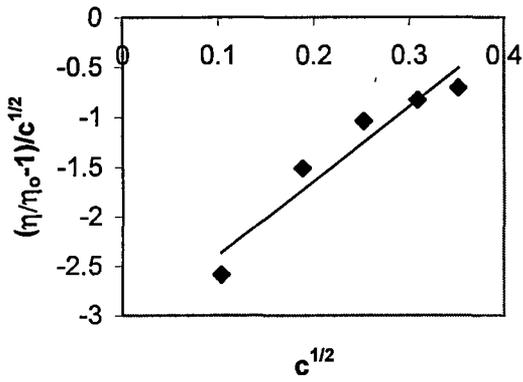


Fig.2(g) at 313K

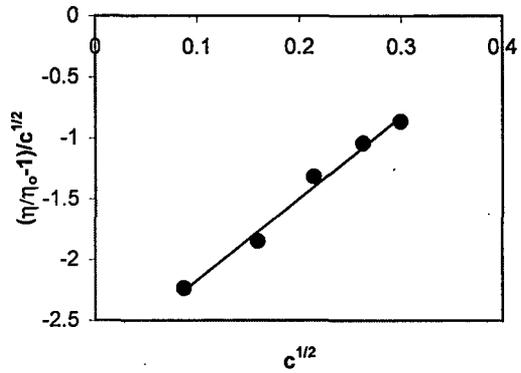


Fig.2(h) at 313K

- = LiCl
- = NaCl
- △ = KCl

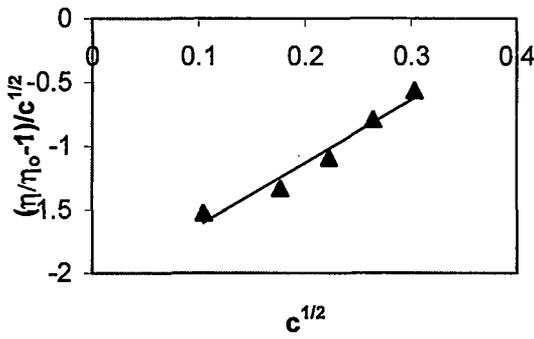


Fig.2(i) at 313K

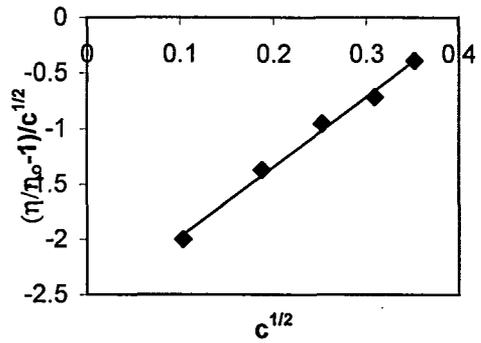


Fig.2(j) at 318K

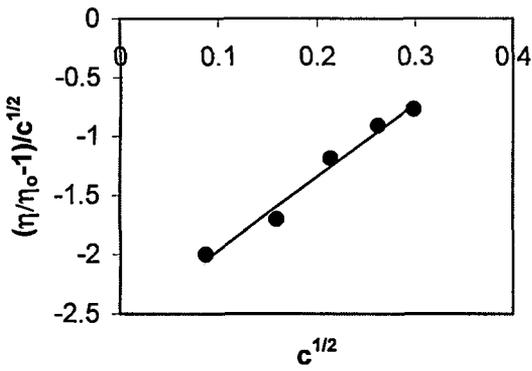


Fig 2(k) at 318K

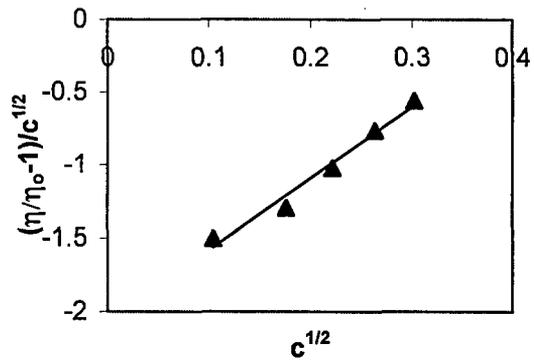


Fig 2(l) at 318K

80 mass% THF + Water mixture

- = LiCl
- = NaCl
- △ = KCl

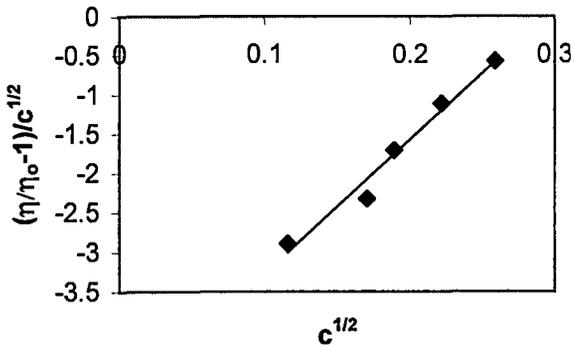


Fig 2(a) at 303K

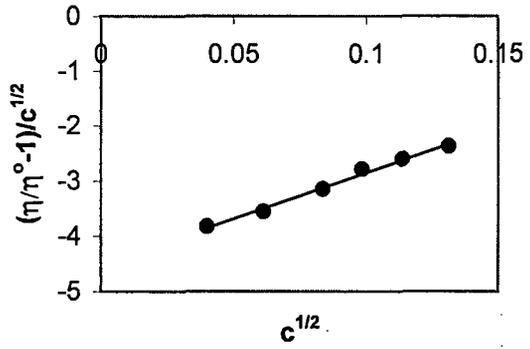


Fig 2(b) at 303K

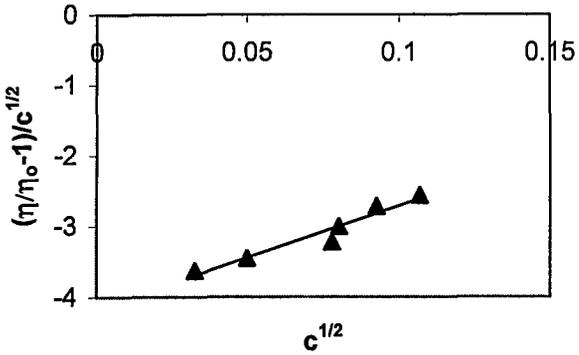


Fig 2(c) at 303K

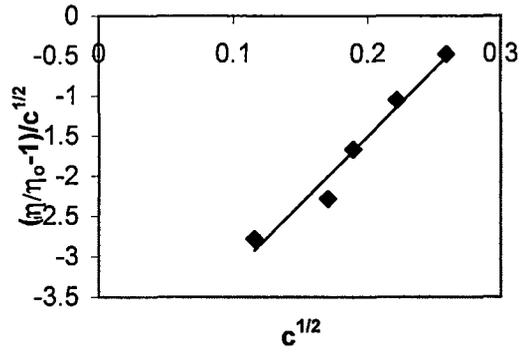


Fig 2(d) at 308K

- = LiCl
- = NaCl
- △ = KCl

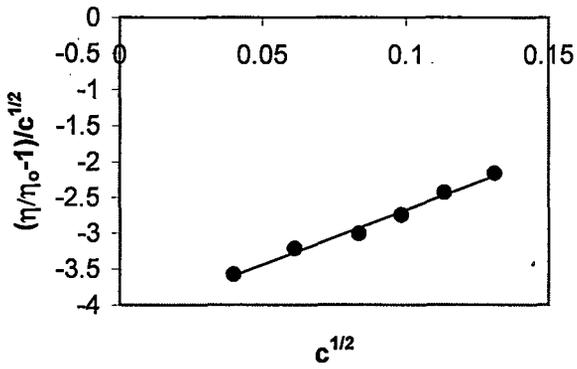


Fig 2(e) at 308K

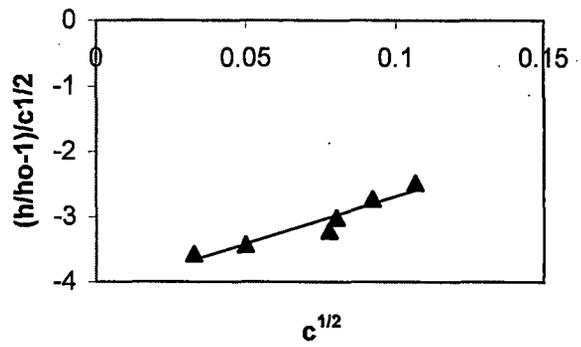


Fig 2(f) at 308K

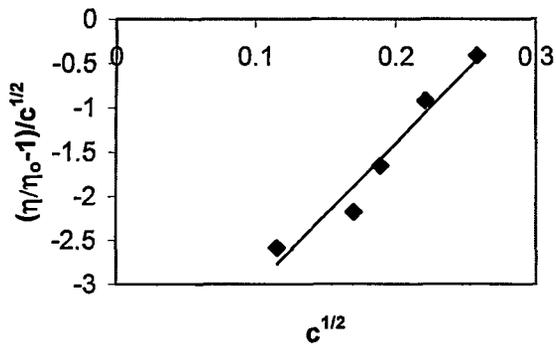


Fig 2(g) at 313K

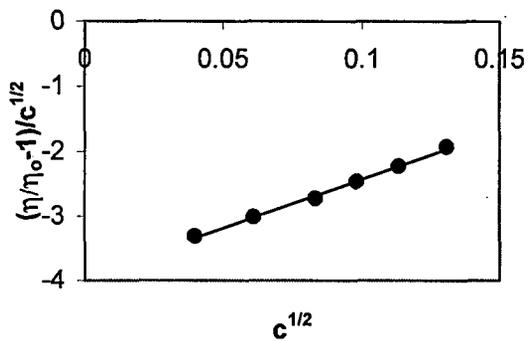


Fig 2(h) at 313K

- = LiCl
- = NaCl
- △ = KCl

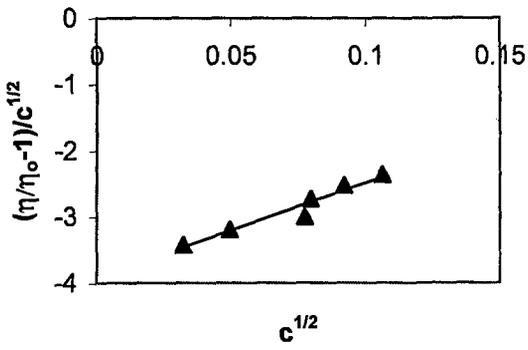


Fig 2(i) at 313K

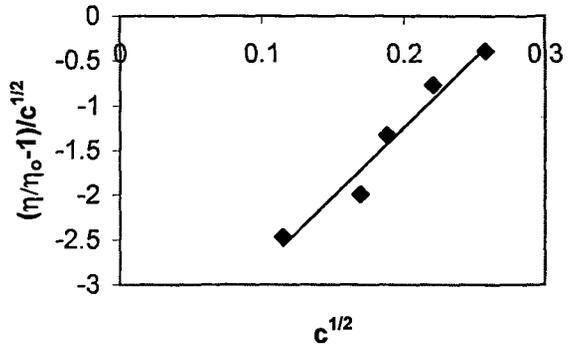


Fig 2(j) at 318K

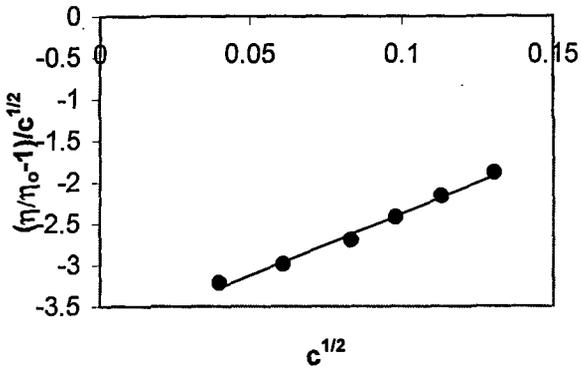


Fig 2(k) at 318K

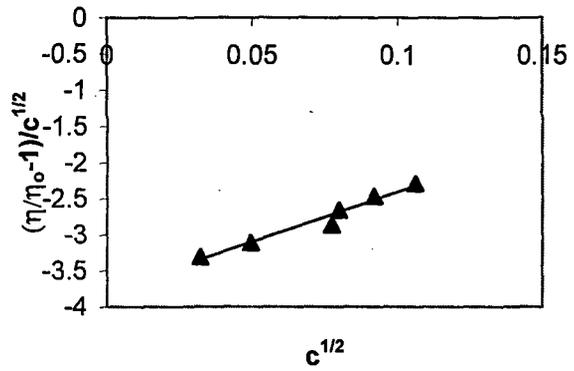


Fig 2(l) at 318K

## CHAPTER V

### **Electrical Conductances of Tetraalkylammonium and Alkali Metal Salts in Aqueous Binary Mixtures of Tetrahydrofuran at Different Temperatures**

#### **Abstract**

Electrical conductance measurements are reported for tetraethylammonium bromide ( $\text{Et}_4\text{NBr}$ ), tetrapropylammonium bromide ( $\text{Pr}_4\text{NBr}$ ) and lithium bromide ( $\text{LiBr}$ ) 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 ( $\Lambda^0$ ), 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.

#### **5.1 Introduction**

Extensive studies on electrical conductivities in various mixed organic solvents have been performed in recent years<sup>1-8</sup> 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 ( $\epsilon = 7.58$ ), has been found its probability of applications in high energy batteries<sup>2</sup>, modern technology<sup>1</sup> and organic syntheses as manifested from the physico-chemical studies in this medium.<sup>11</sup> Renard and Justice<sup>12</sup> studied the conductances of  $\text{CsCl}$  in  $\text{THF} + \text{H}_2\text{O}$  mixtures to reveal the nature of ionic

association and mobility of ions in the mixed solvent system. In the present communication, an attempt has been made to ascertain the complete nature of ion-solvent interactions of tetraalkylammonium and alkali metal bromide salts in THF + H<sub>2</sub>O mixtures through the measurements of their conductances at various temperatures.

## 5.2 Experimental Section

Tetrahydrofuran (THF), Merck was kept several days over KOH, then refluxed for 24 h and distilled over LiAlH<sub>4</sub>. Its boiling point, density and viscosity compared well with the literature values<sup>14</sup>. The specific conductance of THF was Ca.  $0.81 \times 10^{-6}$  S. cm<sup>2</sup>mol<sup>-1</sup>.

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.<sup>1, 15</sup>

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 the density values.

The densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (303, 313 and 323) K with doubly distilled water and benzene. Details have been described earlier<sup>16</sup>.

Conductance measurements were carried out on a Systronic 306 conductivity bridge (accuracy  $\pm 0.1\%$ ) 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<sup>17</sup> using aqueous potassium chloride solution. Measurements were made in a water bath maintained at (303±0.005, 313±0.005 and 323±0.005) K as described earlier.<sup>1□□</sup> Several independent solutions were prepared, and conductance measurements were performed with each of these to ensure the reproducibility of the result. Corrections were made for the specific conductances of the solvent.

The solvent properties of THF + H<sub>2</sub>O mixtures were reported earlier<sup>1</sup> by us, where  $\epsilon$  is the dielectric constant,  $\rho$  the density,  $\eta$  the viscosity and  $L$  the specific conductance,  $W$  the weight per cent of THF in the aqueous mixtures and  $X_2$  the corresponding mole-fraction. Dielectric constants of the solvent mixtures were obtained by extrapolation of  $\epsilon$  versus  $W$  % plots, the original values were taken from the work of Renard and Justice<sup>13</sup>.

### 5.3 Results and Discussions

Molar conductances ( $\Lambda$ ) 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 equation<sup>2</sup>. For a set of conductivity values ( $c_j, \Lambda_j; j=1, \dots, n$ ), three adjustable parameters, the limiting molar conductivity ( $\Lambda$ ), the association constant ( $K_A$ ) and the distance of closest approach of ions ( $R$ ) are derived from the following set of equations:

$$\Lambda = P[\Lambda (1 + R_X) + E_L] \quad (1)$$

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

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

$$-\ln f = \beta \kappa / 2 (1 + \kappa R) \quad (4)$$

$$\beta = e^2/DK_B T \quad (5)$$

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

Where  $R_x$  is the relaxation field effect,  $E_L$  is the electrophoretic countercurrent,  $\kappa^{-1}$  is the radius of the ion atmosphere,  $D$  is the relative permittivity of the solvent,  $e$  is the electron charge,  $K_B$  is the Boltzmann constant,  $\gamma$  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  $\beta$  is twice the Bjerrum distance. The computations were performed on a computer using the programmes suggested by Fuoss. The initial  $\Lambda$  values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the programme is the set  $(c_j, \Lambda_j; j = 1, \dots, n)$ ,  $n$ ,  $D$ ,  $\eta$ ,  $T$ , initial value of  $\Lambda$ , and an instruction to cover a pre selected range of  $R$  values.

In practice calculations are performed by finding the values of  $\Lambda$  and  $\alpha$  which minimise the standard deviation

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

for a sequence of  $R$  values and then plotting  $\sigma$  against  $R$ ; the best-fit  $R$  corresponds to the minimum of the  $\sigma$  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  $\Lambda$  and  $K_A$  are calculated.

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

The computations in these cases were carried out from arbitrarily presetting<sup>2</sup> of  $R$  values at  $R = a + d$ . Here  $a$  is the sum of the crystallographic

radii of the ions and  $d$  the average distance corresponding to the side of a cell occupied by a solvent molecules. The distance  $d$  is given by

$$d(\text{\AA}) = (M/N_p)^{1/3} = 1.183(M/\rho)^{1/3} \quad (8)$$

Where  $M$  is the molecular weight of solvent and  $\rho$  is the density. For mixed solvents,  $M$  is replaced by the mole-fraction average molecular weight ( $M_{av}$ ) which is given by

$$M_{av} = M_1M_2/(W_1M_2 + W_2M_1) \quad (9)$$

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 Table 2, we see that  $\Lambda^0$  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,  $\Lambda^0$  values increase with increase in temperature as well as with increase of THF in the mixtures. The viscosity of solvent mixture does not coincide with the observed trend in  $\Lambda^0$  value. Further, the  $\Lambda^0$  for the lithium bromide is greater than those for the tetramethyl and tetrapropylammonium bromide in any particular temperature. It has also been observed that the values of  $\Lambda^0$  calculated from the previous conductance equation do not differ significantly from the values of  $\Lambda^0$  calculated from the 1978 Fuoss conductance-concentration equation<sup>2</sup>. The trend of variation of  $\Lambda^0$  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:

$\text{Et}_4\text{N} < \text{Pr}_4\text{N} < \text{Li}$ . This shows that Li is the most solvated and  $\text{Pr}_4\text{N}$  is the least one in any mole-fraction of tetrahydrofuran (THF) and in any particular temperature.

Table 2 shows that  $K_A$  values for  $\text{R}_4\text{NBr}$  salts in a given solvent-mixture decrease with increasing size of the cation in the order  $\text{Et}_4\text{N} > \text{Pr}_4\text{N}$ , similar to those observed earlier<sup>6,21</sup>, 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<sup>22</sup>. 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 maximum 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 other 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 interaction 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 characteristic is also a manifestation of

strong specific interaction<sup>23</sup> between unlike molecules predominated by hydrogen bonding interaction.

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**Table 1: Concentration (c), Equivalent Conductance ( $\Lambda$ ) of some Tetraalkylammonium and Alkali Metal Bromide Salts in various (THF + H<sub>2</sub>O) mixtures at different temperatures**

$c \times 10^4 /$ mol lit <sup>-1</sup>	$\sqrt{c} \times 10^2 /$ mol <sup>1/2</sup> lit <sup>-1/2</sup>	$\Lambda / \text{Scm}^2$ mole <sup>-1</sup>	$c \times 10^4 /$ mol lit <sup>-1</sup>	$\sqrt{c} \times 10^2 /$ mol <sup>1/2</sup> lit <sup>-1/2</sup>	$\Lambda /$ Scm <sup>2</sup> mole <sup>-1</sup>	$c \times 10^4 /$ mol lit <sup>-1</sup>	$\sqrt{c} \times 10^2 /$ mol <sup>1/2</sup> lit <sup>-1/2</sup>	$\Lambda /$ Scm <sup>2</sup> mole <sup>-1</sup>
<b>20 mass % THF + H<sub>2</sub>O mixture</b>								
<b>T = 303 K</b>								
<b>Et<sub>4</sub>NBr (M.W. = 210.17)</b>			<b>Pr<sub>4</sub>NBr (M.W. = 266.27)</b>			<b>LiBr (M.W. = 86.85)</b>		
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
266.092	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
<b>T = 313 K</b>								
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

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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
<b>T = 323 K</b>								
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
<b>40 mass % THF + H<sub>2</sub>O Mixture</b>								
<b>T = 303 K</b>								
13.229	3.637	99.627	12.752	3.570	94.994	15.392	3.923	50.696

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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
<b>T = 313 K</b>								
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	125.976	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 + H<sub>2</sub>O 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
<b>T = 313 K</b>								
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
<b>T = 323 K</b>								
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
<b>80 mass % THF + H<sub>2</sub>O Mixture</b>								
<b>T = 303 K</b>								
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
<b>T = 313 K</b>								
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

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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
<b>T = 323 K</b>								
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	90.171	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

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**Table 2: Derived conductance Parameters for Tetraalkylammonium and Alkali Metal Bromides in THF + H<sub>2</sub>O at various Temperatures**

$X_1$	$\Lambda^d$	$K_A$	R	$\Lambda^d \eta_{01}$	$\sigma$
<b>T = 303 K</b>					
<b>Et<sub>4</sub>NBr</b>					
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	–
<b>Pr<sub>4</sub>NBr</b>					
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	–
<b>LiBr</b>					
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	–
<b>T = 313 K</b>					
<b>Et<sub>4</sub>NBr</b>					
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	–
<b>Pr<sub>4</sub>NBr</b>					
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	-
<b>LiBr</b>					
0.000	122.07	-	5.67	0.79	-
0.059	97.98 ±0.05	124.86	6.01	1.03	0.05
0143	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	-
<b>T = 323 K</b>					
<b>Et<sub>4</sub>NBr</b>					
0.000	135.52	-	14.86	0.74	-
0.059	153.41 ±0.02	86.10	15.21	1.37	0.02
0143	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	-
<b>Pr<sub>4</sub>NBr</b>					
0.000	129.23	-	14.77	0.70	-
0.059	138.94 ±0.06	101.64	15.21	1.24	0.06
0143	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	-
<b>LiBr</b>					
0.000	124.61	-	5.68	0.68	-
0.059	100.22 ±0.02	122.49	6.22	0.89	0.02
0143	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	-

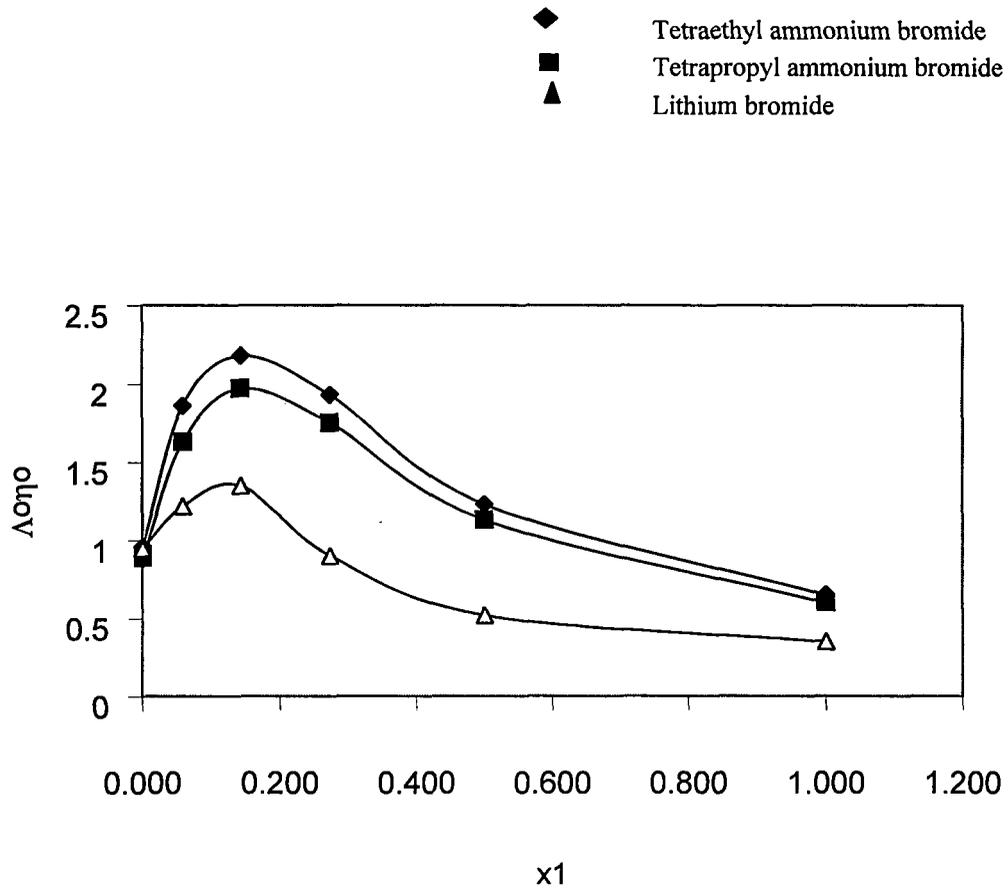


Figure 1 : Plot of mole fraction of THF ( $x_1$ ) vs Waldem product at temperature 303K

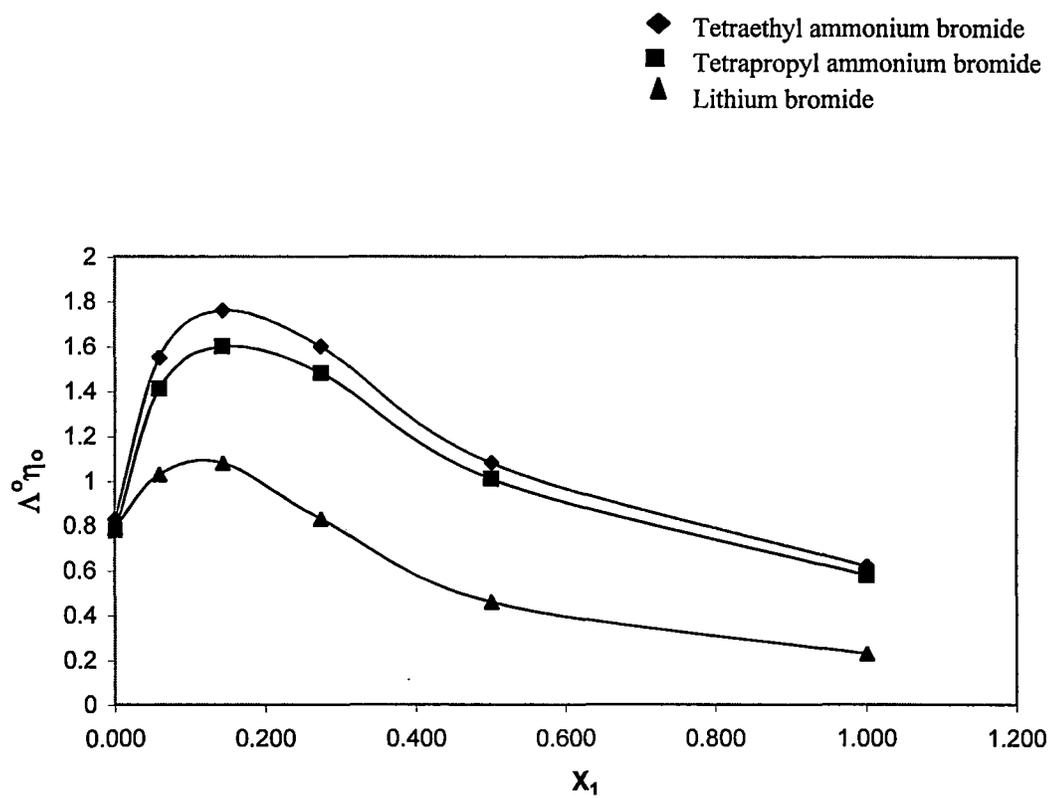


Figure 2 : Plot of mole fraction of THF ( $x_1$ ) vs Waldem product at temperature 313K

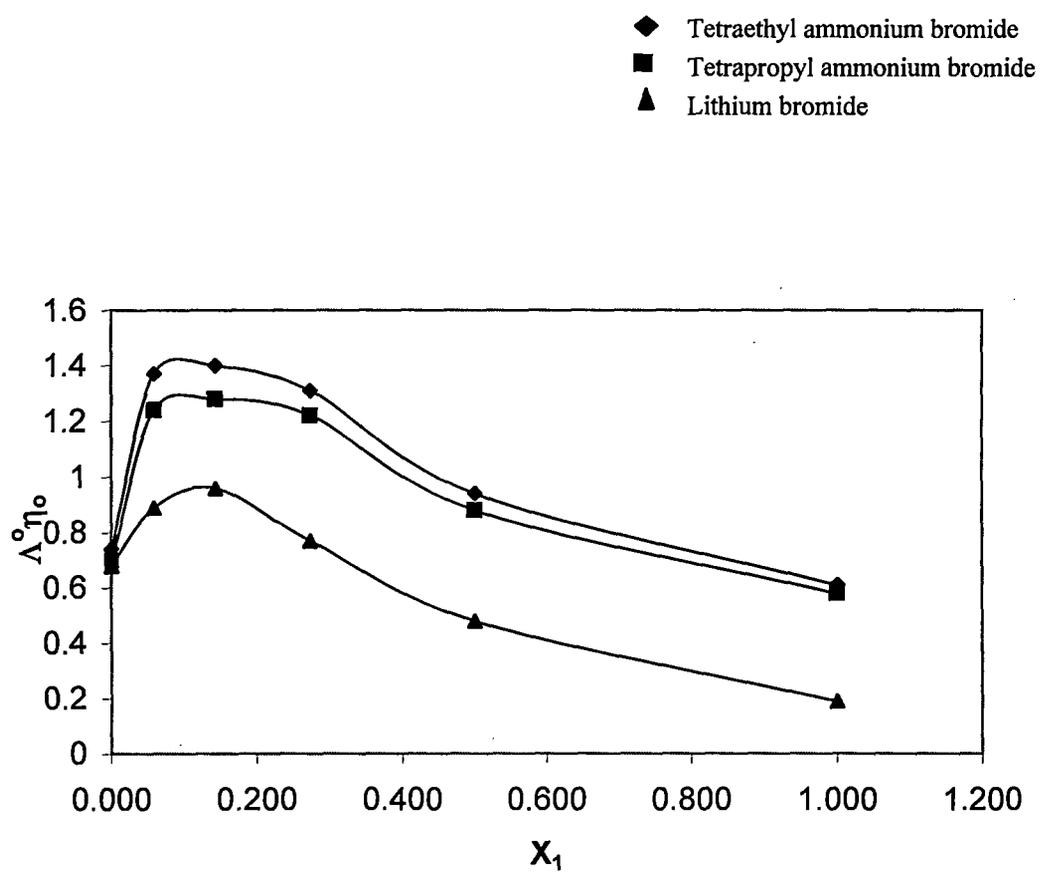


Figure 3 : Plot of mole fraction of THF ( $x_1$ ) vs Waldem product at temperature 323K

## CHAPTER VI

### **Excess Molar Volume, Excess Free Energy and Viscosity Deviation of Binary Mixtures of Tetrahydrofuran with Benzene and n-Hexane at Various Temperatures**

#### **Abstract**

The densities and viscosities have been determined for the binary systems of tetrahydrofuran with benzene and n-hexane at 303.15K, 308.15K, 313.15K, 318.15K and 323.15K. From the experimental results, the excess molar volumes ( $V^E$ ) have been derived. These are explained on the basis of molecular interactions between the components of the mixtures.

#### **6.1 Introduction**

Grouping of solvents into classes often is based on the intermolecular forces because the manner whereby solute and solvent molecules are associated with one another brings about a marked effect on the resulting properties. After the introduction of the concept of ionization power of solvent<sup>1</sup>, much work has been devoted to the solvent effects on the rate and equilibrium processes.<sup>2</sup> Because of close connection between liquid structure and macroscopic properties, determination of volumetric and viscometric properties is a valuable tool to learn the liquid state.<sup>3</sup> On the other hand, the obtaining of reliable measurements of solvent properties over a wide range of composition, pressure and temperature often is not feasible; hence, prediction and correlation methods constitute a valuable option to overcome such difficulties.<sup>4,5</sup>

The present work contributes to the study of the structure and interactions of ether (THF) containing binary mixtures. Tetrahydrofuran is a good industrial solvent. It figures prominently in the high energy battery industry and has found its applications in organic syntheses as manifested from the physiochemical studies.<sup>6,7</sup>

There has been a recent upsurge of interest<sup>8-10</sup> in the thermodynamic properties of binary liquid mixtures. These have been extensively used to obtain information on the intermolecular interactions and geometrical effects in these systems.<sup>11</sup> We have presented here the densities and viscosities for tetrahydrofuran - benzene and tetrahydrofuran-n-hexane mixtures at 303.15K, 308.15K, 313.15K, 318.15K and 323.15K.

## 6.2 Experimental :

Tetrahydrofuran (THF, Merck) kept several days over KOH, was refluxed for 24h and then distilled over  $\text{LiAlH}_4$ . The density ( $880.72 \text{ kgm}^{-3}$ ) and viscosity (0.4630 mpas) at 298K of the solvent compared well with the reported values. All solutions were prepared by weight with deionized distilled water.

Normal hexane and benzene were purified according to the standard procedures. The purities were checked by density determination dilatometrically at (303.15, 308.15, 313.15K etc.)  $\pm 0.1\text{K}$  which almost agreed within the accuracy of  $\pm 1 \times 10^{-4} \text{ g cm}^{-3}$  the available literature values. All the studies were prepared volumetrically in stoppered bottles.

The densities ( $\rho$ ) were measured with an Ostwald-Sprengel type Pycnometer having a bulb volume of  $25 \text{ cm}^3$  and an internal diameter of the capillary of about 0.1 cm. The Pycnometer was calibrated at (303.15, 308.15, 313.15, 318.15 and 323.15K) with doubly distilled water and benzene. The Pycnometer with the test solution was equilibrated in a water bath

maintained at  $\pm 0.01\text{K}$  of the desired temperature by means of a mercury in glass thermoregulator, and the temperature was determined with a calibrated thermometer and an 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. Averages of triplicate measurements were taken into account. The densities values were reproducible to  $\pm 3 \times 10^{-5} \text{ g cm}^{-3}$ . Details have been described earlier.

The viscosities were measured by means of suspended-level Ubbelohde viscometer at the desired temperature (accuracy  $\pm 0.01\text{K}$ ). The precision of the viscosity measurements was 0.05%. Details have been described earlier.

### 6.3 Results and Discussion

The physical properties of tetrahydrofuran (THF), normal hexane and benzene at various temperatures are given in Table 1. The experimental values of mole-fraction( $x_1$ ), densities ( $\rho$ ), viscosities and various derived parameters of various binary mixtures of solvents studied here at different temperatures are recorded in Table 2.

The experimental density ( $\rho$ ) values (Table 1) have been used to calculate the excess molar volume ( $V^E$ ), viscosity deviation ( $\Delta\eta$ ) and interaction parameter ( $d$ ) using the following equations (1-3) :

$$V^E = \frac{M}{\rho} - \sum_{i=1}^c x_i \frac{M_i}{\rho_i} \quad (1)$$

$$\Delta\eta = \eta - \sum_{i=1}^c x_i \eta_i \quad (2)$$

$$\ln \eta = \sum_{i=1}^c x_i \ln \eta_i + d \prod_{i=1}^c x_i \quad (3)$$

where  $c$  stands for the number of components of the mixture,  $M$  and  $M_i$  are the molar mass of the mixture and of the pure components,  $\rho$  and  $\rho_i$  represent the density of the mixture and pure components,  $\eta$  and  $\eta_i$  are the corresponding viscosities. The values of these functions and  $d$  are presented in Table 2 along the values of  $\rho$ ,  $\eta$  and mole fraction.

The excess molar volume were correlated by Redlich-Kister equation.

$$V^E = x_1 x_2 \sum a_i (x_1 - x_2)^i \quad (4)$$

The coefficient in equation (4) was estimated by the least-squares fit method, where the squares of the difference between the calculated and experimental excess molar volumes results is minimized. The optimal values of the coefficients in eqn. (4) are listed in table 3. The standard deviation was calculated by

$$\sigma(V^E) = [\sum (V_{\text{exp}}^E - V_{\text{cal}}^E)^2 / (D - N)^{0.5}] \quad (5)$$

where  $D$  and  $N$  are the number of data points and parameters, respectively. The experimental values of  $\delta\eta$  are also reported in Table 1. The viscosity deviations were correlated by the following equation :

$$Q = X_1 X_2 \sum H_i (x_1 - x_2)^i \quad (6)$$

Where  $Q = \Delta\eta / (\text{m Pa s})$ . The coefficient in equation (6) are also regressed by employing the least square fit method. Standard deviations for the viscosity calculations were determined by equation (7).

$$\sigma(\Delta\eta) = [\sum (\Delta\eta_{\text{exp}} - \Delta\eta_{\text{cal}})^2 / (D - N)^{0.5}] \quad (7)$$

The optimal parameters in correlating deviations of viscosity are listed in Table 4.

The plots of  $V^E$  Vs mole fraction of THF and  $\Delta\eta$  Vs mole fraction of THF for two binary mixtures are represented in figs. 1, 2, 3 & 4.

The graphical presentation of the excess molar volumes ( $V_m^E$ ) for the binary mixture of THF (1) + benzene (2) shown in fig. 1 shows that  $V_m^E$  is negative over the entire range of composition at all measured temperature. Maximum deviation in the excess molar volume occurs at 0.6190 mole fraction. Maximum negative<sup>11,12</sup> values of excess molar volumes in this temperature range is  $0.9501 \text{ cm}^3$ . These large negative values of  $V_m^E$  arise due to increased interactions<sup>13</sup> between unlike molecules<sup>14</sup>. The values of  $V_m^E$  becomes more negative with decreasing temperature. This indicates that the temperature coefficient of  $V_m^E$  depends on the increase in molar volume of complex formation. The magnitude of  $V_m^E$  suggests that there is a weak interaction of the unlike molecules due to non-covalent bonds.

But in case of binary mixture of THF(1) + n-hexane (2) same conclusion can be drawn from the same results of  $V_m^E$ . But in this case, maximum negative values of  $V_m^E$  is observed is about  $0.8010 \text{ cm}^3$  at the 0.5445 mole fraction. These results are shown in the table 2 at the fig. 2.

The experimental values of  $\Delta\eta$  are also reported in Table 2. Graphical presentation of the experimental  $\Delta\eta$  plotted against the mole fraction is shown in fig 3 and fig. 4 for the systems THF (1) + benzene (2) and THF(1) + n-hexane(2). The  $\Delta\eta$  is negative and the negativity decrease with increasing temperature<sup>14</sup> in both cases. Maximum deviation of viscosity occurs at 0.619 mole fraction and maximum negative value of deviation of viscosity in this temperature range is 0.0466 in case of the binary mixture, THF (1) + benzene (2) whereas these values are 0.5445 and 0.045 respectively of the binary mixture THF (1) + n-hexane. These types of characteristics of these two binary mixtures can be explained on the basis of known phenomenon, dissociation due to presence of weak interactions between the unlike solvent molecules.

Grunberg-Nissom parameter ( $d$ ) is found to be negative in both binary solvent mixtures. This indicates that inter molecular complex formation is not favourable in these mixed solvent systems.

A similar results was reported<sup>15</sup> by the workers in the case of thermodynamic studies of formamide with various glycol at 308K.

### Acknowledgement

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

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**Table-1**

**Tetrahydrofuran (THF)**

Temperature	$\rho \times 10^{-3} \text{ kg/N}^3$ this work	Lit. value	$\eta(\text{cp})$ this work	Lit. value
303.15K	0.87697	0.87697	0.39922	0.39922
308.15K	0.87402	0.87401	0.39259	0.39259
313.15K	0.87115	0.87115	0.38343	0.38342
318.15K	0.86611	0.86610	0.38215	0.38216
323.15K	0.86216	0.86215	0.35980	0.35980

**Benzene (C<sub>6</sub>H<sub>6</sub>)**

303.15K	0.86865	0.86864	0.46456	0.46456
308.15K	0.86518	0.86517	0.43455	0.43455
313.15K	0.85523	0.83524	0.40578	0.40577
318.15K	0.85250	0.85251	0.39758	0.39758
323.15K	0.84849	0.84849	0.38369	0.38368

**n-hexane (C<sub>6</sub>H<sub>14</sub>)**

303.15K	0.64968	0.64967	0.26864	0.26863
308.15K	0.64828	0.64828	0.26585	0.26584
313.15K	0.64549	0.64549	0.27197	0.27197
318.15K	0.64235	0.64236	0.26639	0.26638
323.05K	0.63852	0.63851	0.25763	0.25764

**Table -2 : Values of densities ( $\rho$ ), viscosities ( $\eta$ ), Grunberg-Nissan Parameter ( $d$ ), excess molar volumes ( $V^E$ ) and deviations of viscosities of various solvent mixures at different temperatures.**

**I) Tetrahydrofuran (1) - benzene(2)**

**303.15K**

$X_1$	$\rho \times 10^{-3} \text{ kg m}^{-3}$	$\eta(\text{cp})$	$d$	$V^E(\text{cm}^3\text{mol}^{-1})$	$\Delta\eta(\text{cp})$
0.0000	0.8686	0.4645	0.0000	0.0000	0.0000
0.1074	0.8705	0.4608	-0.0374	-0.1213	-0.0056
0.2131	0.8722	0.4741	-0.1747	-0.2105	-0.0113
0.3170	0.8728	0.5609	-0.9321	-0.3243	-0.0156
0.3684	0.8740	0.6532	-0.5395	-0.3487	-0.0201
0.4193	0.8749	0.5139	-0.4879	-0.4025	-0.0215
0.4698	0.8758	0.5082	-0.4902	-0.4663	-0.0231
0.5199	0.8760	0.5064	-0.5103	-0.5305	-0.0245
0.5697	0.8765	0.4176	-0.3361	-0.5732	-0.0263
0.6190	0.8767	0.4207	-0.3091	-0.5962	-0.0275
0.6679	0.8771	0.4175	-0.3382	-0.5325	-0.0256
0.7165	0.8775	0.4163	-0.332	-0.4705	-0.0236
0.7646	0.8781	0.4290	-0.2629	-0.4235	-0.0205
0.8124	0.8770	0.4104	-0.3436	-0.3425	-0.0152
0.9069	0.8772	0.4003	-0.312	-0.1945	-0.0081
1.0000	0.8769	0.3930	0.0000	0.0000	0.0000

**308.15K**

0.0000	0.8652	0.4345	0.0000	0.0000	0.0000
0.1074	0.8692	0.4391	-0.1059	-0.1725	-0.0088
0.2131	0.8702	0.4412	-0.1108	-0.3095	-0.0153
0.3170	0.8712	0.4641	-0.2069	-0.4402	-0.0212
0.3684	0.8738	0.4461	-0.2105	-0.4992	-0.0252
0.4193	0.8742	0.4059	-0.2521	-0.5472	-0.0262
0.4698	0.8746	0.3976	-0.3270	-0.5721	-0.0289
0.5199	0.8745	0.4048	-0.2506	-0.6378	-0.0305
0.5697	0.8746	0.4017	-0.2836	-0.6878	-0.0325
0.6190	0.87501	0.3987	-0.323	-0.7285	-0.0340
0.6679	0.8761	0.3992	-0.3345	-0.6934	-0.3120

0.7165	0.8762	0.3922	-0.4207	-0.6610	-0.0289
0.7646	0.8763	0.3909	-0.5201	-0.6010	-0.0240
0.8124	0.8758	0.3854	-0.7032	-0.5588	-0.2050
0.9069	0.8766	0.3919	-0.1432	-0.3532	-0.0102
1.0000	0.8770	0.4049	0.0000	0.0000	0.0000

**313.15K**

0.0000	0.8552	0.4043	0.0000	0.0000	0.0000
0.1074	0.8601	0.4053	-0.0032	-0.2035	-0.0132
0.2131	0.8653	0.3988	-0.0166	-0.3802	-0.0202
0.3170	0.8664	0.4012	-0.0912	-0.5519	-0.0263
0.3684	0.8677	0.3943	-0.0613	-0.6225	-0.0305
0.4193	0.8681	0.3961	-0.1315	-0.6632	0.0326
0.4698	0.8653	0.3918	-0.1104	-0.7130	-0.0356
0.5199	0.8682	0.3884	-0.1575	-0.7513	-0.0372
0.5699	0.8687	0.3832	-0.1962	-0.7818	0.0389
0.6190	0.8688	0.3787	-0.2625	-0.8201	-0.0395
0.6679	0.8697	0.3852	-0.3339	-0.7733	-0.0356
0.7165	0.8694	0.3823	-0.2829	-0.7443	-0.0336
0.7646	0.8694	0.3795	-0.3643	-0.703	-0.0290
0.8124	0.8702	0.3798	-0.4401	-0.6549	-0.0245
0.9069	0.8704	0.3769	-0.9566	-0.5092	-0.0156
1.0000	0.8711	0.3719	0.0000	0.0000	0.0000

**318.15K**

0.0000	0.8525	0.3975	0.0000	0.0000	0.0000
0.1074	0.8597	0.3902	-0.1768	-0.3035	-0.0151
0.2131	0.8603	0.3890	-0.1105	-0.4503	-0.0242
0.3170	0.8611	0.3838	-0.1403	-0.6221	-0.0309
0.3684	0.8621	0.3822	-0.1654	-0.6719	-0.0353
0.4193	0.8625	0.3778	-0.1833	-0.7182	-0.0386
0.4698	0.8629	0.3759	-0.1965	-0.7525	-0.0399
0.5199	0.8636	0.3800	-0.1497	-0.8030	-0.0412
0.5697	0.8637	0.3766	-0.2156	-0.8352	-0.0421
0.6190	0.8643	0.3781	-0.2445	-0.8612	-0.0431
0.6679	0.865	0.3728	-0.2801	-0.8558	-0.0402
0.7165	0.8656	0.3774	-0.2030	-0.8443	-0.0381
0.7646	0.8657	0.3665	-0.3876	-0.8132	-0.0332
0.8124	0.8658	0.3667	-0.4508	-0.7832	-0.0288

0.9069	0.8659	0.3688	-0.7271	-0.6530	-0.0192
1.0000	0.8661	0.3654	0.0000	0.0000	0.0000

**323.15K**

0.0000	0.8484	0.3836	0.0000	0.0000	0.0000
0.1074	0.8537	0.3823	-0.0038	-0.4050	-0.0182
0.2131	0.8569	0.3801	-0.0159	-0.5671	-0.0252
0.3170	0.8575	0.3773	-0.0296	-0.7103	-0.0322
0.3684	0.8589	0.3736	-0.0631	-0.7601	-0.0381
0.4193	0.8585	0.3709	-0.0837	-0.8080	-0.0412
0.4698	0.8592	0.3721	-0.0626	-0.8588	-0.0425
0.5199	0.8597	0.3705	-0.0726	-0.9025	-0.0442
0.5697	0.8603	0.3691	-0.0835	-0.9283	-0.4530
0.6190	0.8604	0.3674	-0.0996	-0.9501	-0.0466
0.6679	0.8608	0.3641	-0.1397	-0.9302	-0.0402
0.7165	0.8609	0.3633	-0.1557	-0.9088	-0.0388
0.7646	0.8612	0.3607	-0.2057	-0.8802	-0.0362
0.8124	0.8614	0.3579	-0.2851	-0.8537	-0.0342
0.9069	0.8617	0.3618	-0.3492	-0.7501	-0.0272
1.0000	0.8621	0.3598	0.0000	0.0000	0.0000

**2) Tetrahydrofuran(1) + n-hexane(2)**

**303.15K**

0.0000	0.6497	0.2686	0.0000	0.0000	0.0000
0.1172	0.6622	0.2756	-0.1815	-0.1139	-0.0008
0.2301	0.6843	0.2851	-0.1592	-0.2356	-0.0136
0.3387	0.7047	0.3003	-0.1235	-0.3245	-0.0213
0.4435	0.7104	0.3102	-0.1002	-0.4751	-0.0261
0.4619	0.7293	0.3143	-0.0935	-0.5435	-0.0304
0.4944	0.7356	0.3189	-0.0654	-0.5963	-0.0361
0.5445	0.7481	0.3228	-0.0505	-0.6392	-0.0312
0.5936	0.7608	0.3328	-0.0481	-0.6214	-0.0256
0.6419	0.7756	0.3327	-0.0339	-0.5502	-0.0202
0.6894	0.7845	0.3367	-0.0246	-0.4216	-0.0151
0.7361	0.7978	0.3453	-0.1489	-0.3125	-0.0121
0.7819	0.8088	0.3625	-0.0631	-0.3006	-0.0111
0.8270	0.8176	0.3636	-0.0831	-0.2135	-0.0101
0.9149	0.8481	0.3827	-0.0726	-0.1503	-0.0072
1.0000	0.8769	0.3992	0.0000	0.0000	0.0000

**308.15K**

0.0000	0.6482	0.2658	0.0000	0.0000	0.0000
0.1172	0.6546	0.2675	-0.3805	-0.1205	-0.0035
0.2301	0.6805	0.2743	-0.3015	-0.2535	-0.0152
0.3387	0.7001	0.2895	-0.2086	-0.3503	-0.0243
0.4434	0.6923	0.2825	-0.1354	-0.5025	-0.0291
0.4619	0.7244	0.2935	-0.0988	-0.5636	-0.0332
0.4944	0.7328	0.2985	-0.3747	-0.6058	-0.0399
0.5445	0.7426	0.3050	-0.3277	-0.6120	-0.0341
0.5936	0.7552	0.3179	-0.3156	-0.6302	-0.0301
0.6419	0.7719	0.3209	-0.3366	-0.6025	-0.0276
0.6894	0.7803	0.3229	-0.3467	-0.5508	-0.0212
0.7361	0.7819	0.3436	-0.1263	-0.4508	-0.0185
0.7819	0.8054	0.3602	-0.0763	-0.4060	-0.0156
0.8270	0.8189	0.3629	-0.0893	-0.3025	-0.0120
0.9149	0.8507	0.3782	-0.0868	-0.2125	-0.0095
1.0000	0.8740	0.3925	0.0000	0.0000	0.0000

**313.15K**

0.0000	0.6454	0.2190	0.0000	0.0000	0.0000
0.1172	0.6648	0.2786	-0.1547	-0.1401	-0.0082
0.2301	0.6881	0.2801	-0.2540	-0.3022	-0.0226
0.3387	0.6988	0.2856	-0.4934	-0.3843	-0.0262
0.4434	0.7038	0.2906	-0.5601	-0.5206	-0.0325
0.4619	0.7230	0.2931	-0.3550	-0.6030	-0.0370
0.4944	0.7310	0.3045	-0.2273	-0.6356	-0.0426
0.5445	0.7409	0.3158	-0.2563	-0.7505	-0.0388
0.5936	0.7531	0.3246	-0.2103	-0.7456	-0.0336
0.6419	0.7682	0.3208	-0.1505	-0.7231	-0.0303
0.6894	0.7766	0.3315	-0.1806	-0.5613	-0.0275
0.7361	0.7905	0.338	-0.1803	-0.5012	-0.0235
0.7819	0.8031	0.3562	-0.1635	-0.4402	-0.0201
0.8270	0.8121	0.3525	-0.1723	-0.3502	-0.0152
0.9149	0.8412	0.3657	-0.0883	-0.2535	-0.0112
0.0000	0.8704	0.3834	0.0000	0.0000	0.0000

**318.15K**

0.0000	0.6423	0.2663	0.0000	0.0000	0.0000
0.1172	0.6633	0.2701	-0.2022	-0.2312	-0.0115
0.2301	0.6850	0.2703	-0.3856	-0.3702	-0.0256
0.3387	0.6953	0.2894	-0.4035	-0.5035	-0.0320
0.4434	0.7003	0.2899	-0.5056	-0.6135	-0.0361
0.4619	0.7191	0.2912	-0.5104	-0.6592	-0.0412
0.4944	0.7277	0.2932	-0.3563	-0.7011	-0.0452
0.5445	0.7390	0.3052	-0.2437	-0.7523	-0.0415
0.5936	0.7409	0.3152	-0.2025	-0.7413	-0.0370
0.6419	0.7654	0.3196	-0.1004	-0.7321	-0.0342
0.6894	0.7740	0.3274	-0.0803	-0.6235	-0.0308
0.7361	0.7875	0.3334	-0.1058	-0.5501	-0.0275
0.7819	0.7985	0.3406	-0.2131	-0.5003	-0.0226
0.8270	0.8105	0.3513	-0.2563	-0.4054	-0.0195
0.9149	0.8385	0.3631	-0.0838	-0.2835	-0.0166
0.0000	0.8681	0.3821	0.0000	0.0000	0.0000

**323.15K**

0.0000	0.6385	0.2576	0.0000	0.0000	0.0000
0.1172	0.6559	0.2603	-0.2715	-0.3920	-0.0156
0.2301	0.6532	0.2685	-0.2998	-0.4205	-0.0315
0.3387	0.6647	0.2753	-0.3047	-0.5201	-0.0356
0.4434	0.6902	0.2733	-0.3343	-0.6503	-0.0415
0.4619	0.7162	0.2890	-0.3441	-0.7012	-0.0443
0.4944	0.7281	0.2901	-0.2135	-0.7510	-0.0491
0.5445	0.7343	0.2981	-0.1588	-0.8010	-0.0450
0.5936	0.7401	0.3065	-0.1049	-0.7520	-0.0412
0.6419	0.7580	0.3169	-0.0844	-0.7401	-0.0370
0.3894	0.7666	0.3204	-0.0385	-0.7012	-0.0339
0.7361	0.7743	0.3225	-0.0257	-0.5924	-0.0312
0.7819	0.7966	0.3262	-0.0214	-0.5502	-0.0275
0.8270	0.8098	0.3356	-0.2003	-0.4902	-0.0225
0.9149	0.8262	0.3468	-0.0635	-0.3501	-0.0185
1.0000	0.8684	0.3577	0.0000	0.0000	0.0000

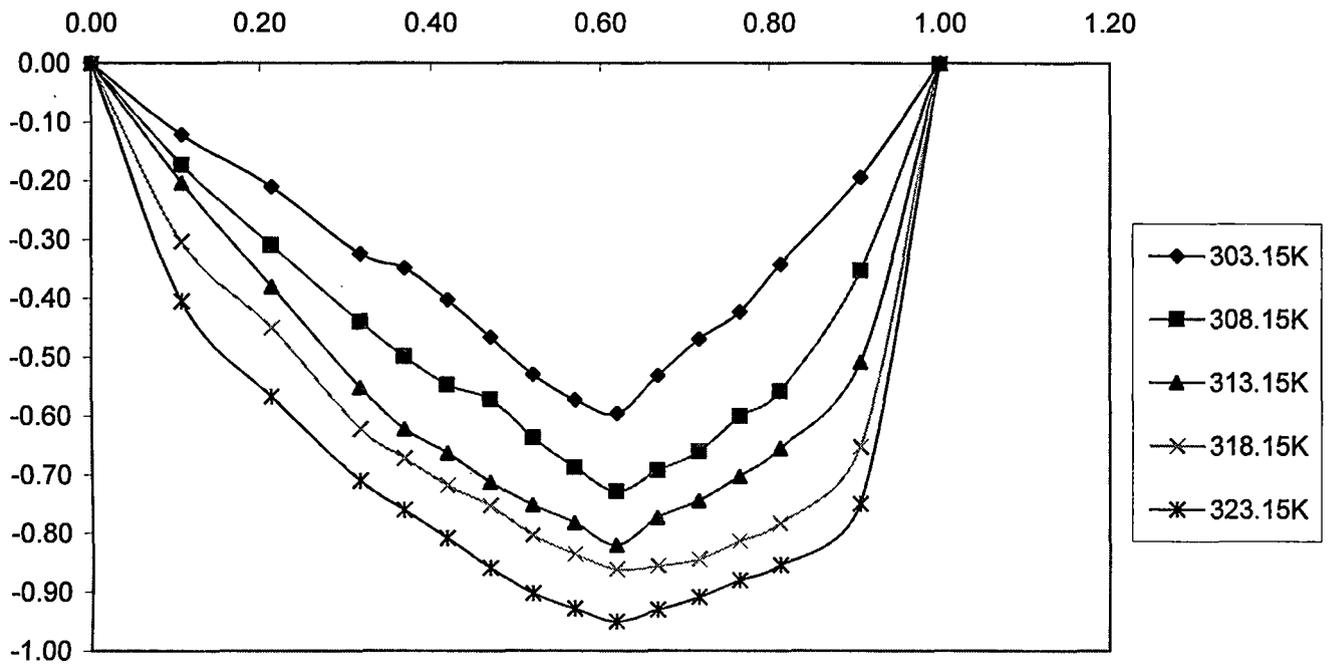
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**Table 3 : Regression results for the excess volumes( $V^E$ ) of THF + Hydrocarbons mixture at various temperatures**

<b>System</b>	<b>Temp.K</b>	<b><math>a_0</math></b>	<b><math>a_1</math></b>	<b><math>a_2</math></b>	<b><math>a_3</math></b>	<b><math>a_4</math></b>	<b><math>a_5</math></b>	<b><math>\sigma</math></b>
<b>THF + benzene</b>	303.15	-2.04616	-2.15376	1.06516	6.01918	-0.92422	-5.82801	0.01506
	308.15	-2.51083	-1.67459	-0.59311	0.51968	-	-	0.017046
	318.15	-2.61132	-1.40351	-	-	-	-	0.017933
<b>THF + n-hexane</b>	303.15	-2.46316	-2.11342	1.93241	5.6635	-3.70483	-7.8113	0.01398
	308.15	-2.36352	-2.10188	2.66791	6.32882	-2.86703	-6.91708	0.01566
	318.15	-2.81954	-2.00867	2.16482	6.84537	-3.36652	-7.65758	0.01621
	323.15	-2.97891	-1.90855	2.90931	4.88967	-7.55756	-3.06926	0.01703

**Table 4 :Regression results for the deviation of viscosity( $\Delta\eta$ ) of THF + Hydrocarbons mixture at various Temperatures**

System	Temp.K	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$\sigma$
THF + benzene	303.15	-0.09951	-0.06466	0.03548	0.07377	-	-	0.000754
	308.15	-0.24854	-0.56271	-	-	-	-	0.07623
	313.15	-0.05543	-0.05065	-0.27146	-	-	-	0.02368
	318.15	-0.16569	-0.04498	-	-	-	-	0.00116
	323.15	-0.33999	-0.19474	-	-	-	-	0.10285
THF + n-hexane	303.15	-0.12335	0.03936	0.30288	-0.13454	-0.3027	-	0.00256
	308.15	-0.13808	0.00707	0.27469	-0.07436	-0.27637	-	0.002308
	313.15	-0.14598	-0.00659	0.09303	-	-	-	0.00283
	318.15	-0.16421	-0.02229	0.16855	0.21976	-0.23001	-0.42124	0.00201
	323.15	-0.17178	0.00508	-	-	-	-	0.00284



**Fig.1 : Excess molar volumes ( $V_mE$ ) for the system tetrahydrofuran (1) + benzene(2) from 303.15 to 323.15K**

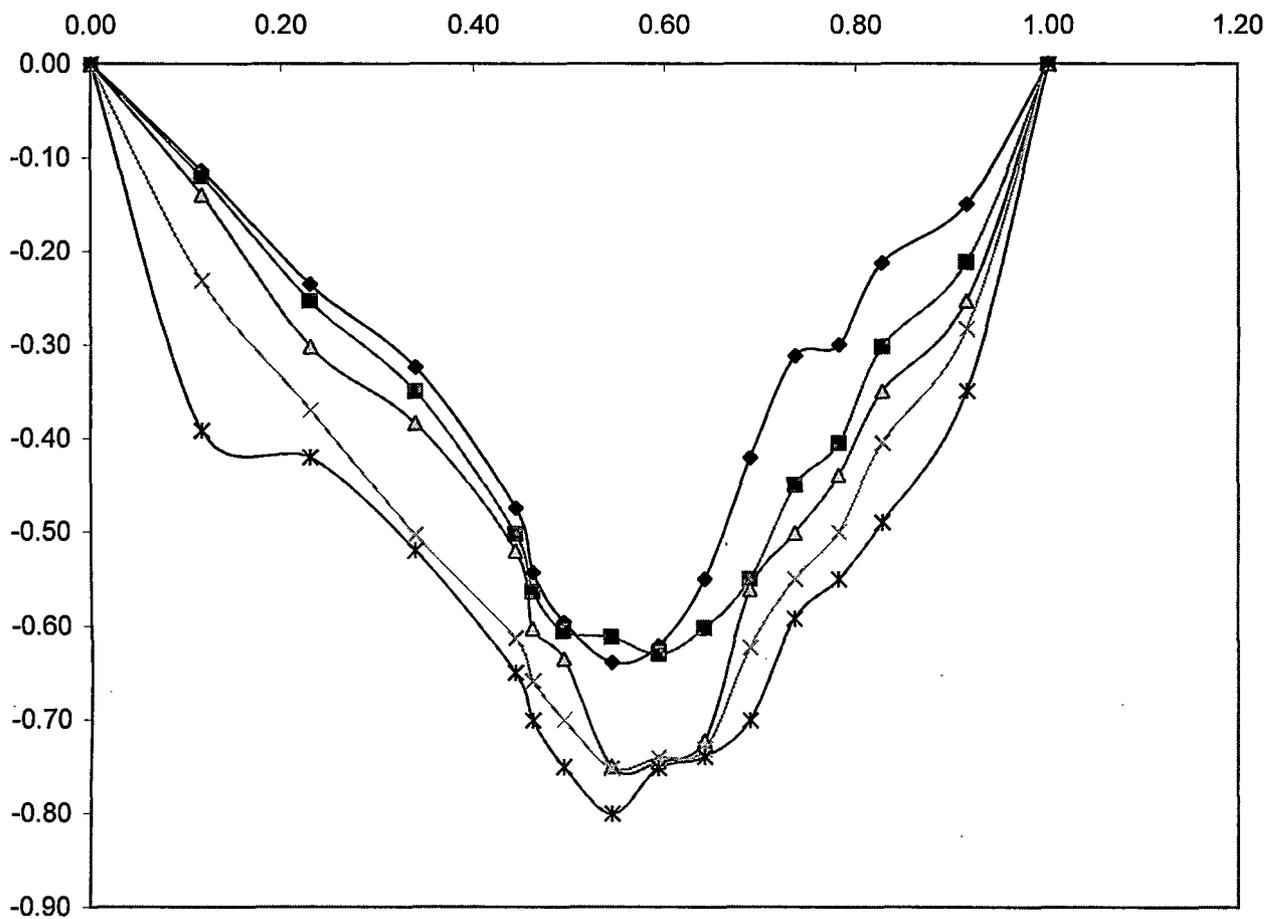
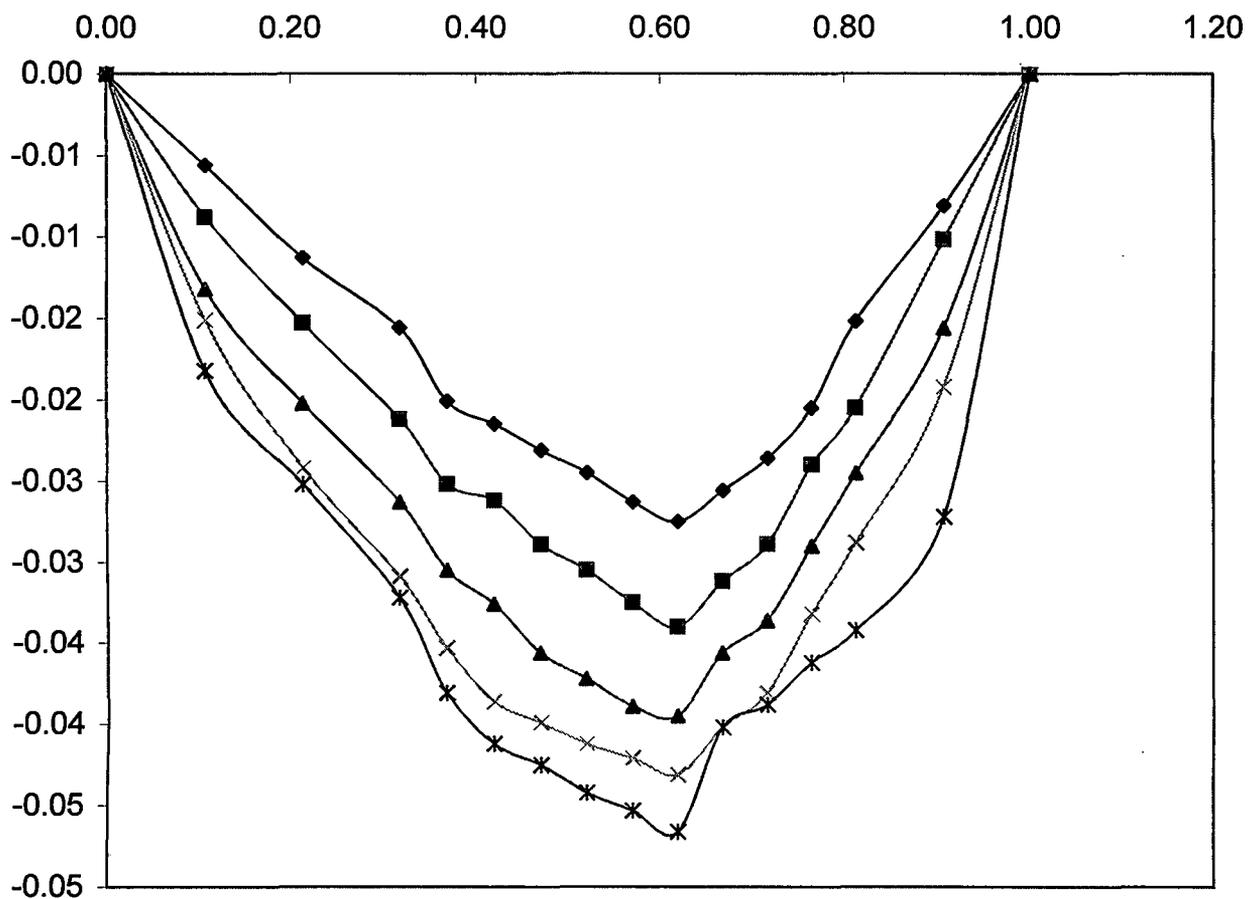
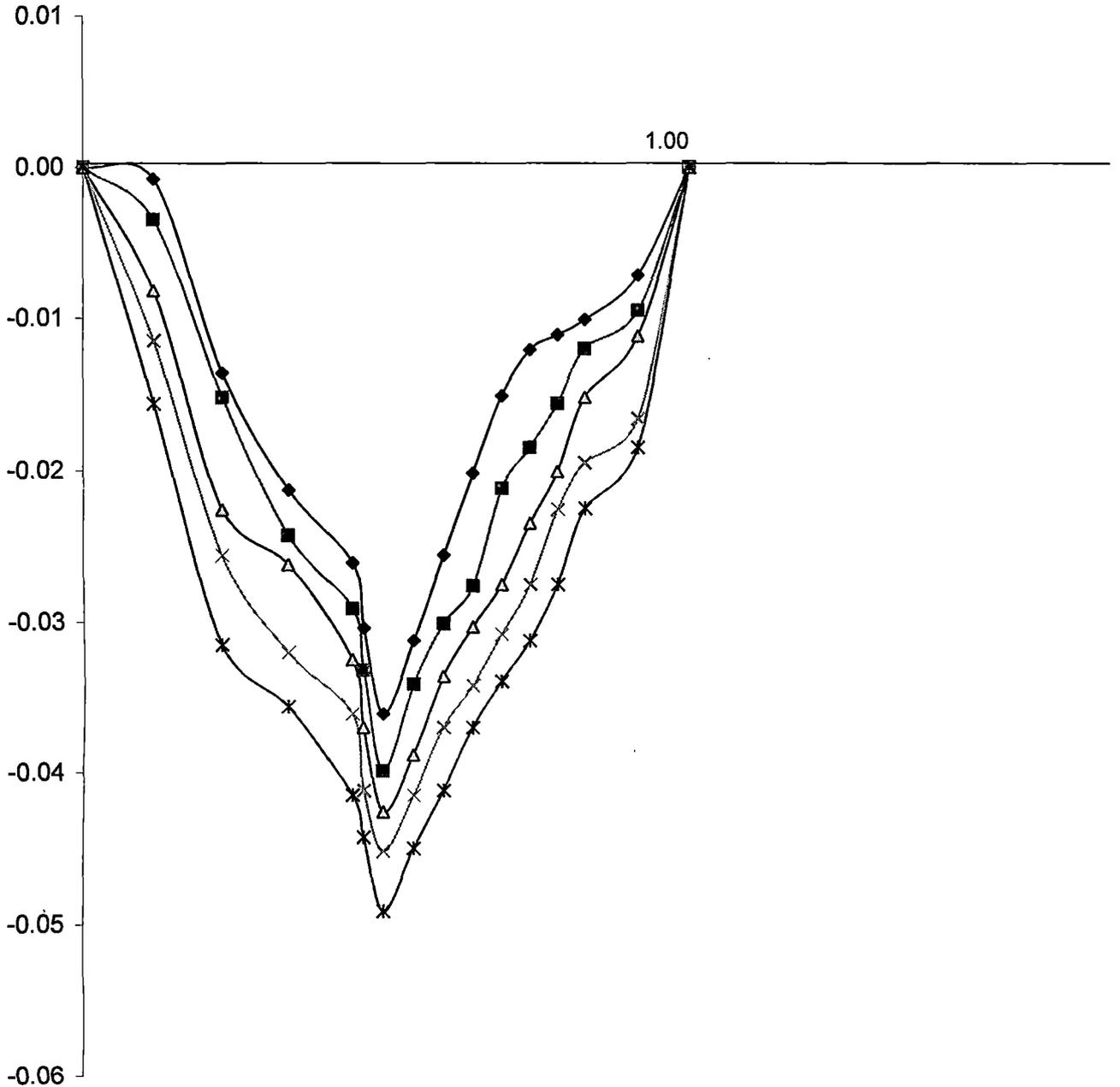


Fig.2 : Excess molar volume ( $V_m^E$ ) for the system tetrahydrofuran(1) + n-hexane(2) from 303.15 to 323.15K.



**Fig.3 : Viscosity deviation ( $\Delta\eta$ ) for the system tetrahydrofuran(1) + benzene (2) from 303.15 to 323.15K.**



**Fig.4 : Viscosity deviation ( $\Delta\eta$ ) for the system tetrahydrofuran(1) + n-hexane(2) from 303.15 to 323.15K**

## **CHAPTER VII**

### **A Study on Ion-Solvent Interactions of Some Sulfate Compounds in Aqueous Tetrahydrofuran at Different Temperatures**

#### **Abstract**

The densities and viscosities of ammonium sulfate, sodium sulfate, magnesium sulfate and aluminium sulfate in 20, 30 and 40 mass% tetrahydrofuran + water mixture have been measured at temperatures 303, 308, 313 and 318K. Apparent molar volumes ( $V_\phi$ ) and viscosity B-coefficients of these electrolytes are derived from these data supplemented with their densities and viscosities, respectively. The limiting apparent molar volumes ( $V_\phi^\circ$ ) 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  $V_\phi^\circ$  values vary with temperatures 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.

#### **7.1 Introduction**

The volumetric behavior of solutes has been proved to be very useful in elucidate of various interactions occurring in aqueous and non-aqueous solutions.<sup>1</sup> It has been found by a number of workers<sup>2</sup> 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.<sup>3</sup> THF + H<sub>2</sub>O mixtures are also important owing to the H-bonding between water and tetrahydrofuran.

As a part of a series of our earlier investigations<sup>4-9</sup> on the classical nature of solutes and their mutual and specific interactions with the solvent molecules, 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.

## 7.2 Results and Discussion

The experimental values of densities ( $\rho_o$ ) and viscosities ( $\eta_o$ ) of pure THF and different mass% of THF + H<sub>2</sub>O mixture at 298, 303, 308, 313 and 318K are recorded in Table 1. The results reveal that  $\eta_o$  of the solvent mixtures (THF + H<sub>2</sub>O) 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<sup>8</sup> between unlike molecules predominated by H-bonding interaction.

The apparent molar volumes ( $V_\phi$ ) were determined from the solvent-mixture and solution densities using the equation,

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

where M is the molecular weight of the solute, c the molarity of the solution and the other symbols have their usual significance. The correction to  $V_\phi$  due to hydrolysis of the electrolytes may be negligible, since the strong H-bonding<sup>8</sup> between THF and H<sub>2</sub>O will reduce the hydrolysis of these electrolytes by free water molecules considerably.

Application of Redlich-Meyer equation<sup>9</sup> 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 ( $V_\phi^o$ ) and experimental slopes ( $S_v^*$ ) were obtained by computerized least-square methods using Masson equation.<sup>10</sup> Within the experimental error, our values for  $V_\phi$  varied linearly with  $c^{1/2}$  to follow the following equation.

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

Where  $S_v^*$  is a constant dependent on charge and salt type and can be related to ion-ion interactions and  $V_\phi^o$  is related to ion-solvent interactions. The values of  $V_\phi^o$  and  $S_v^*$  together with standard errors are listed in Table 2. The  $S_v^*$  values shown in Table 2 are positive for all salts studied here in 20 mass% THF + H<sub>2</sub>O mixture indicating strong solute-solute interactions. This type of behaviour of alkali metal chlorides, tetraalkylammonium halides and some common salts has also been observed in different solvents and solvent mixtures systems.<sup>13,14</sup> The possible explanation for the positive slopes for 20 mass% solvent mixture here may be that ionic association would become quite appreciable in 20 mass% medium as the concentration of electrolyte is increased thereby weakening the solutes-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.<sup>15</sup>

In case of 30 mass% THF + H<sub>2</sub>O mixture, the experimental  $S_v^*$  values (Table 2) at various temperatures are all large and positive for all studied

electrolytes which indicate the presence of strong solute-solute interactions. This type of behaviour has also been observed of some alkali metal chlorides and some common salts in propylene-glycol and THF + water mixtures.<sup>5-13</sup> The increase of  $S_v^*$  with increasing temperature for studied 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. In 40 mass% THF + water mixture, the negative values of  $S_v^*$  for all temperatures indicate the presence of weak ion-ion interactions in case of ammonium sulfate, 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).<sup>13</sup> 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 40 mass% THF + water 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.

The  $V_\phi^o$  values can be used with a view to interpreting the solute-solvent interactions. Table 2 shows that in 20 mass% THF + water mixture  $V_\phi^o$  values are positive (negative in case of ammonium sulphate at 303 K) and increase with increasing temperature. This indicates the presence of ion-solvent interaction and the solvent molecules are loosely attached to solute which expands with increase of temperature, thus resulting in higher values of  $V_\phi^o$  at higher temperature in 20 mass% THF + water mixture system.

Table 2 also shows that for 30 mass% THF + water mixture the  $V_\phi^o$  values are negative and decrease with rise in temperature for all the sulphate

salts studied 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<sub>2</sub>O mixture.<sup>16</sup> The negative values of  $V_{\phi}^o$  also indicate the presence of weak ion-solvent interactions of the investigated electrolytes in 30 mass% solvent-mixture system.

Table 2 reveals that in 40 mass% THF + water mixture  $V_{\phi}^o$  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  $V_{\phi}^o$  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 electrolyte in DMF + H<sub>2</sub>O mixture.<sup>16</sup>

The variation of  $V_{\phi}^o$  with temperature of the electrolyte in various solvent-mixture follows the polynomial equation,

$$V_{\phi}^o = a_1 + a_2T + a_3T^2 \quad (3)$$

over the temperature range under the investigation. The coefficients  $a_i$ 's are evaluated for 20, 30 and 40 mass% THF + H<sub>2</sub>O and the following equations are obtained :

**20 mass% THF + H<sub>2</sub>O mixture**

$$V_{\phi}^o/cm^3 mol^{-1} = - 1091.66/cm^3 mol^{-1} + 6.381T/cm^3 mol^{-1}K^{-1} + 0.0092T^2/cm^3 mol^{-1}K^{-2}$$

for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (4)

$$V_{\phi}^{\circ}/\text{cm}^3 \text{mol}^{-1} = -567.594/\text{cm}^3 \text{mol}^{-1} + 3.393T/\text{cm}^3 \text{mol}^{-1} \text{K}^{-1} + 0.0050 T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for  $\text{Na}_2\text{SO}_4$  (5)

$$V_{\phi}^{\circ}/\text{cm}^3 \text{mol}^{-1} = -1019.777/\text{cm}^3 \text{mol}^{-1} + 6.368T/\text{cm}^3 \text{mol}^{-1} \text{K}^{-1} + 0.0096 T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for  $\text{MgSO}_4$  (6)

$$V_{\phi}^{\circ}/\text{cm}^3 \text{mol}^{-1} = -507.192/\text{cm}^3 \text{mol}^{-1} + 3.615T/\text{cm}^3 \text{mol}^{-1} \text{K}^{-1} + 0.0046T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for  $\text{Al}_2(\text{SO}_4)_3$  (7)

### 30 mass% THF + H<sub>2</sub>O mixture

$$V_{\phi}^{\circ}/\text{cm}^3 \text{mol}^{-1} = 68128.194/\text{cm}^3 \text{mol}^{-1} - 432.292T/\text{cm}^3 \text{mol}^{-1} \text{K}^{-1} + 0.68118T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for  $(\text{NH}_4)_2\text{SO}_4$  (8)

$$V_{\phi}^{\circ}/\text{cm}^3 \text{mol}^{-1} = 160149.196/\text{cm}^3 \text{mol}^{-1} - 1034.524T/\text{cm}^3 \text{mol}^{-1} \text{K}^{-1} + 1.66590T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for  $\text{Na}_2\text{SO}_4$  (9)

$$V_{\phi}^{\circ}/\text{cm}^3 \text{mol}^{-1} = 39961.653/\text{cm}^3 \text{mol}^{-1} - 254.053T/\text{cm}^3 \text{mol}^{-1} \text{K}^{-1} + 0.40134T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for  $\text{MgSO}_4$  (10)

$$V_{\phi}^{\circ}/\text{cm}^3 \text{mol}^{-1} = 108280.710/\text{cm}^3 \text{mol}^{-1} - 695.846T/\text{cm}^3 \text{mol}^{-1} \text{K}^{-1} + 1.11344T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for  $\text{Al}_2(\text{SO}_4)_3$  (11)

### 40 mass% THF + H<sub>2</sub>O mixture

$$V_{\phi}^{\circ}/\text{cm}^3 \text{mol}^{-1} = -516083.699/\text{cm}^3 \text{mol}^{-1} + 3250.867T/\text{cm}^3 \text{mol}^{-1} \text{K}^{-1} - 5.1055T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for  $(\text{NH}_4)_2\text{SO}_4$  (12)

$$V_{\phi}^{\circ}/\text{cm}^3 \text{mol}^{-1} = 494125.408/\text{cm}^3 \text{mol}^{-1} - 3171.497T/\text{cm}^3 \text{mol}^{-1} \text{K}^{-1} + 5.0933 T^2/\text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$$

for  $\text{Na}_2\text{SO}_4$  (13)

$$V_{\phi}^{\circ}/\text{cm}^3\text{mol}^{-1} = 222426.752/\text{cm}^3\text{mol}^{-1} - 1399.032T/\text{cm}^3\text{mol}^{-1}\text{K}^{-1} + 2.1865T^2/\text{cm}^3\text{mol}^{-1}\text{K}^{-2}$$

for  $\text{MgSO}_4$  (14)

$$V_{\phi}^{\circ}/\text{cm}^3\text{mol}^{-1} = -9814543.783/\text{cm}^3\text{mol}^{-1} + 63218.323T/\text{cm}^3\text{mol}^{-1}\text{K}^{-1} - 101.729T^2/\text{cm}^3\text{mol}^{-1}\text{K}^{-2}$$

for  $\text{Al}_2(\text{SO}_4)_3$  (15)

The limiting molar expansibilities  $\phi_E^{\circ} = (\delta|v_{\phi}^{\circ}|/\delta T)_p$  calculated from the equations (4-15) for various electrolytes for three different mass% THF + H<sub>2</sub>O mixtures at different temperatures are reported in Table 3. For 20 mass% THF + water mixture it reveals that the values of  $\phi_E^{\circ}$  decrease with rise of temperature, suggesting that these salts behave like common salts in this mixed solvent system. This can be ascribed to the caging or packing effect.<sup>15</sup>

For 30 mass% THF + H<sub>2</sub>O mixture the values of  $\phi_E^{\circ}$  increase with rise of temperature, suggesting that these salts behave like common salts in 30 mass% THF + H<sub>2</sub>O mixture. This can also be ascribed to the caging or packing effect.<sup>15</sup> Table 3 also shows that in 40 mass% THF + water mixture the values of  $\phi_E^{\circ}$  decrease with increase in temperature for ammonium and aluminium sulfates and is in accordance with the findings of Millero<sup>17</sup>. Table 3 also shows that  $\phi_E^{\circ}$  with rise in temperature for sodium and magnesium sulfates. The increase and decrease in  $\phi_E^{\circ}$  with the increase in temperature can be ascribed to the presence and absence of caging effect<sup>2d</sup>, respectively.

For determining long-range structure-making and structure-breaking capacities of electrolytes in various solvent system following equation of Hepler<sup>18</sup> was used.

$$(\delta c_p/\delta p)_T = -(\delta^2 V_{\phi}^{\circ}/\delta T^2)_p \quad (16)$$

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

It is also observed that  $(\delta^2 V_{\phi} / \delta T^2)_p$  for solutions of all electrolytes under investigation is negative for 20 mass% THF + H<sub>2</sub>O mixture showing thereby that these electrolytes behave as structure breaker. But in case of 30 mass% THF + H<sub>2</sub>O system  $(\delta^2 V_{\phi} / \delta T^2)_p$  for solutions of all electrolytes is positive which indicates that this electrolytes behave as structure maker/promoters in this solvent system. In case of 40 mass% THF + water system it is also observed that  $(\delta^2 V_{\phi} / \delta T^2)_p$  for solutions of ammonium and aluminium sulphates is negative whereas it is positive for sodium and magnesium sulphates showing thereby that ammonium and aluminium sulphates behave as structure-breaker while sodium and magnesium sulphates behave as structure-maker. Same results are found in some alkali metal halides in THF + H<sub>2</sub>O mixture.<sup>5</sup>

The relative viscosities of solutions for various electrolytes (ammonium, sodium, magnesium and aluminium sulfates) in 20, 30 and 40 mass% THF + H<sub>2</sub>O mixtures at different temperatures were determined and analyzed by Jones-Dole<sup>19</sup> equation

$$(\eta/\eta_0 - 1)/c^{1/2} = A + B c^{1/2} \quad (17)$$

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

$\eta_0$  and  $\eta$  are the viscosities of solvent-mixture and solution, respectively, A and B are constant,  $\rho$  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 a 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<sub>2</sub>O mixtures<sup>20</sup> at different temperatures.

It has been reported by a number of workers that  $dB/dT$  is a good and reasonable criterion<sup>21</sup> 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 the 40 mass% THF + H<sub>2</sub>O mixed solvent system. Whereas the values of  $dB/dT$  are positive for all the sulfate salts in 20 mass% and 30 mass% THF + water mixture suggesting the structure-making tendency for those salts. These conclusions are in excellent agreement with that drawn from  $(\delta^2 V_\phi^o / \delta T^2)_p$ .

### 7.3 Experimental

Tetrahydrofuran (Merck) was kept several days over KOH, refluxed for 24h and distilled over LiAlH<sub>4</sub>. The boiling point (66°), density (0.8807 g cm<sup>-3</sup>) and viscosity (0.0046p) compared well with the literature values.<sup>22</sup> The specific conductance of tetrahydrofuran was ca.  $0.81 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$  at 25°.

Ammonium sulfate, sodium sulfate, magnesium sulfate and aluminium sulfate (SD fine chemicals, A.R.) were used as such, after drying over P<sub>2</sub>O<sub>5</sub>. 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<sup>3</sup> and an internal diameter of the capillary of – 0.1 cm. It was calibrated at 298, 308 and 318K with double –distilled water and benzene. The pycnometer with the test solution was equilibrated in a water-bath maintained at the desired temperature ( $\pm 0.01\text{K}$ ) 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  $\pm 3 \times 10^{-5} \text{g cm}^{-3}$ . Details have been described earlier.<sup>9</sup> The viscosity was measured by means of a suspended-level Ubbelohde<sup>23</sup> viscometer at the desired temperature (accuracy  $\pm 0.01^\circ$ ). The precision of the viscosity measurement was 0.05%. Details have been described earlier.<sup>4</sup>

### **Acknowledgement**

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

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**Table 1 : Physical properties of pure tetrahydrofuran (THF) and different mass% of THF + H<sub>2</sub>O mixtures at different temperatures.**

T/K	Mass % THF	$\eta_o/g.cm^3$		$\eta_o/cp$	
		This work	lit.	This work	lit.
298	20	0.98668	0.98668 <sup>3-9</sup>	1.49002	1.49002 <sup>4,7</sup>
303	"	0.98488	-	1.31155	-
308	"	0.98309	0.98309 <sup>3-9</sup>	1.13310	1.13310 <sup>4,7</sup>
313	"	0.98019	-	1.05991	-
318	"	0.97730	0.97730 <sup>3-9</sup>	0.89670	0.89670 <sup>4,7</sup>
298	30	0.97833	0.97833 <sup>3-9</sup>	1.67977	1.67977 <sup>4,7</sup>
303	"	0.97634	-	1.47326	-
308	"	0.97434	0.97434 <sup>3-9</sup>	1.26674	1.26674 <sup>4,7</sup>
313	"	0.97058	-	1.13165	-
318	"	0.96681	0.96681 <sup>3-9</sup>	0.99656	0.99656 <sup>4,7</sup>
298	40	0.96640	0.96640 <sup>3-9</sup>	1.73210	1.73210 <sup>4,7</sup>
303	"	0.96381	-	1.52760	-
308	"	0.96120	0.96120 <sup>3-9</sup>	1.32310	1.32310 <sup>4,7</sup>
313	"	0.95359	-	1.18412	-
318	"	0.94598	0.94598 <sup>3-9</sup>	1.04516	1.04516 <sup>4,7</sup>
298	60	0.94600	0.94601 <sup>3-9</sup>	1.49040	1.49042 <sup>4,7</sup>
303	"	0.94204	-	1.33984	-

308	"	0.93810	0.93810 <sup>3-9</sup>	1.18930	1.18931 <sup>4,7</sup>
313	"	0.93338	-	1.07421	-
318	"	0.92864	0.92863 <sup>3-9</sup>	0.95910	0.95909 <sup>4,7</sup>
298	80	0.91592	0.91592 <sup>3-9</sup>	0.92237 <sup>7-11</sup>	0.92371 <sup>4,7</sup>
303	"	0.91181	-	0.85386	-
308	"	0.90768	0.90768 <sup>3-9</sup>	0.78401	0.78400 <sup>4,7</sup>
313	"	0.90251	-	0.72270	-
318	"	0.89732	0.89732 <sup>3-9</sup>	0.66141	0.66140 <sup>4,7</sup>
100(pure THF)		0.88072	0.88072 <sup>3-9</sup>	0.46300	0.46300 <sup>4,7</sup>
298		0.8870 <sup>10</sup>		0.46000 <sup>10</sup>	
303	"	0.87595	-	0.44536	-
308	"	0.87116	0.87116 <sup>3-9</sup>	0.42770	0.42770 <sup>10</sup>
313	"	0.86627	-	0.40893	-
318	"	0.86140	0.86140 <sup>3-9</sup>	0.3917	0.39017 <sup>4,7</sup>

**Table 2 : Limiting apparent molar volumes ( $V_{\phi}^0$ ) and Experimental slopes ( $S_V^*$ ) together with standard errors of different salts in 20, 30 and 40 mass% Tetrahydrofuron + Water at different temperatures.**

Mass %	$(V_{\phi}^0)/\text{cm}^3 \text{ mol}^{-1}$				$S_V^*/\text{cm}^3 \cdot \text{L}^{1/2} \text{ mol}^{-3/2}$			
	303K	308K	313K	318K	303/K	308K	313K	318K
<b>THF</b>								
<b>Ammonium Sulphate</b>								
20	-8.601 (±0.22)	1.001 (±0.10)	4.342 (±0.11)	7.222 (±0.23)	144.152 (±0.31)	142.973 (±0.41)	141.672 (±0.23)	140.801 (±0.33)
30	-317.727 (±0.41)	-398.282 (±1.75)	-444.678 (±0.92)	-457.016 (±0.05)	809.398 (±0.71)	1045.079 (±0.91)	1067.496 (±0.18)	1336.469 (±0.63)
40	198.243 (±1.50)	855.277 (±1.90)	1257.036 (±1.22)	2199.71 (±1.60)	-461.341 (±0.96)	-1958.48 (±3.11)	-2954.390 (±4.61)	-5189.390 (±2.66)
<b>Sodium Sulphate</b>								
20	1.102	3.133	4.571	5.762	200.781	197.73	196.553	194.132

	(±0.14)	(±0.13)	(±0.32)	(±0.41)	(±0.33)	(±0.21)	(±0.32)	(±0.21)
30	-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)
40	772.446	474.980	432.109	395.997	-1969.370	-1111.680	-807.784	-932.239
	(±01.67)	(±2.50)	(±3.41)	(±4.10)	(±2.23)	(±3.39)	(±2.59)	(±1.63)

**Magnesium Sulphate**

20	29.522	30.752	32.785	34.333	186.722	185.722	184.473	183.332
	(±0.23)	(±0.14)	(±0.15)	(±0.24)	(±0.11)	(±0.22)	(±0.13)	(±0.32)
30	-169.762	-213.953	--	-242.095	698.95	799.572	858.725	868.047
	(±0.96)	(±1.33)	238.058	(±0.54)	(±0.54)	(±0.17)	(±0.36)	(±0.47)
			(±0.71)					
40	-741.426	-	-	-1506.240	1838.357	2656.686	3262.604	3883.211
	(±5.01)	1056.890	1263.030	(±6.11)	(±4.48)	(±3.39)	(±2.01)	(±1.11)
		(±0.9)	(±2.56)					

**Aluminium Sulphate**

20	165.822	169.732	173.523	177.082	258.460	255.532	252.662	251.390
	(±0.15)	(±0.14)	(±0.25)	(±0.17)	(±0.15)	(±0.17)	(±0.36)	(±0.11)
30	-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)
40	931.711	6239.947	6461.712	8893.751	-2978.210	-22276.500	-23213.500	-32754.800
	(±1.91)	(±2.39)	(±1.42)	(±3.61)	(±2.09)	(±1.18)	(±2.08)	(±2.05)

**Table 3 : Limiting apparent molar expansibilities ( $\phi_E^0$ ) for various electrolytes in 20, 30 and 40 mass% THF + water at different temperatures and sign of  $(\delta_1^2 v_\phi^0 / \delta T^2)_p$**

Mass% THF	303K	308K	313K	318K	Sign of $(\delta_1^2 v_\phi^0 / \delta T^2)_p$
<b>Ammonium Sulphate</b>					
20	0.743	0.714	0.622	0.530	(+ve)
30	-19.263	-12.451	-5.639	1.172	(+ve)
40	156.934	105.879	54.824	3.769	(-ve)
<b>Sodium Sulphate</b>					
20	0.342	0.313	0.263	0.213	(+ve)
30	-24.988	-8.329	8.329	24.988	(+ve)
40	-84.957	-34.025	16.908	67.841	(+ve)
<b>Magnesium Sulphate</b>					
20	0.466	0.454	0.358	0.262	(+ve)
30	-10.841	-6.827	-2.814	1.199	(+ve)
40	-74.025	-52.160	-30.205	-8.431	(+ve)
<b>Aluminium Sulphate</b>					
20	0.792	0.781	0.735	0.689	(+ve)
30	-21.102	-9.966	1.167	12.302	(+ve)
40	1570.549	553.259	-464.031	-1481.321	(-ve)

**Table 4 : Values of  $B(\text{cm}^3 \text{mol}^{-1})$  and  $A (\text{cm}^{3/2} \text{mol}^{-1/2})$  parameters together with standard errors for different electrolytes in 20, 30 and 40 mass% THF + water mixture at different temperatures.**

THF	Mass%		$B(\text{cm}^3 \text{mol}^{-1})$		$A (\text{cm}^{3/2} \text{mol}^{-1/2})$			
	303 K	308K	313K	318K	303K	308K	313K	318K
<b>Ammonium sulphate</b>								
20	5.099 (±0.26)	5.741 (±0.10)	6.012 (±0.31)	6.91 (±0.29)	-3.00 (±0.37)	-2.809 (±0.21)	-2.813 (±0.28)	-2.866 (±0.43)
30	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)
40	5.294 (±1.28)	5.676 (±1.01)	6.114 (±1.17)	7.497 (±2.01)	-2.621 (±1.77)	-2.690 (±2.78)	-2.808 (±1.36)	-3.8343 (±1.56)
<b>Sodium Sulphate</b>								
20	5.648 (±0.15)	5.703 (±0.13)	5.797 (±0.22)	5.813 (±0.31)	-2.888 (±0.13)	-2.622 (±0.27)	-2.651 (±0.31)	-2.4702 (±0.21)
30	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)
40	6.350 (±2.1)	5.378 (±2.81)	5.291 (±1.19)	5.211 (±2.18)	-2.836 (±3.02)	-2.519 (±2.81)	-2.486 (±1.35)	-2.412 (±1.55)
<b>Magnesium sulphate</b>								
20	4.121 (±0.24)	4.213 (±0.34)	4.238 (±0.19)	4.274 (±0.24)	-2.307 (±0.21)	-2.297 (±0.22)	-2.234 (±0.33)	-2.076 (±0.39)
30	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)
40	7.175 (±3.01)	6.333 (±2.19)	6.123 (±1.79)	6.003 (±1.88)	-3.376 (±1.14)	-3.037 (±0.99)	-2.968 (±2.22)	-2.955 (±1.91)
<b>Aluminium Sulphate</b>								
20	6.381 (±0.15)	6.409 (±0.24)	6.411 (±0.23)	6.569 (±0.12)	-2.436 (±0.15)	-2.353 (±0.17)	-2.319 (±0.26)	-2.372 (±0.21)

30	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)
40	15.326 (±1.83)	16.510 (±0.91)	17.408 (±1.11)	17.945 (±1.99)	-4.984 (±2.08)	-5.391 (±3.21)	-5.615 (±0.70)	-5.765 (±1.89)

**Table 5 : Molar concentration ( c), Densities ρ), Viscosities (η), Apparent molar volume (V<sub>φ</sub>) of values (η/η<sub>0</sub>-1) / c<sup>1/2</sup> of Ammonium sulphate, Sodium sulphate, Magnesium sulphate and Aluminium sulphate in different mass% of THF + H<sub>2</sub>O mixtures of different temperatures.**

**20 mass% THF + water mixture**

c/molcm <sup>-3</sup>	√C/(molcm <sup>-3</sup> ) <sup>1/2</sup>	ρ/gcm <sup>-3</sup>	η/cp	V <sub>φ</sub> /cm <sup>3</sup> mol <sup>-1</sup>	(η/η <sub>0</sub> -1) / √C
<b>Ammonium Sulfate</b>					
<b>303K</b>					
0.00504	0.07106	0.98553	1.0725	3.198	-2.564
0.02018	0.14209	0.98734	0.89317	9.992	-2.245
0.04038	0.20097	0.98948	0.79598	18.279	-1.956
0.05553	0.23566	0.99077	0.82222	26.445	-1.5832
0.08583	0.29298	0.99335	0.80894	33.856	-1.308
0.11108	0.3333	0.99497	0.88184	41.888	-0.983
0.17672	0.42039	0.99942	0.93001	50.675	-0.692
<b>308K</b>					
0.00503	0.0709	0.98369	0.94005	11.872	-2.403
0.02013	0.14187	0.98536	0.79761	19.665	-2.087
0.04029	0.20074	0.98731	0.74437	28.022	-1.709
0.05533	0.23524	0.98844	0.77165	36.001	-1.356
0.08542	0.29226	0.99073	0.78737	43.333	-1.044
0.11057	0.33253	0.99212	0.82488	51.342	-0.818
0.17647	0.42009	0.99618	0.88319	58.945	-0.525
<b>313K</b>					
0.00499	0.07068	0.98077	0.88093	15.055	-2.389
0.02004	0.14155	0.98239	0.75971	22.954	-2.001
0.04018	0.20047	0.98427	0.69636	31.022	-1.711
0.05513	0.2348	0.98652	0.72593	38.444	-1.342

0.085182	0.29186	0.987538	0.74902	46.855	-1.005
0.11002	0.33195	0.98891	0.81045	54.011	-0.709
0.17562	0.41908	0.99281	0.87868	61.542	-0.408
<b>318K</b>					
0.00498	0.07061	0.97787	0.74556	17.011	-2.387
0.019976	0.14134	0.97946	0.64334	24.777	-1.999
0.04002	0.20007	0.98122	0.59628	34.888	-1.786
0.05403	0.23446	0.98216	0.62131	43.021	-1.405
0.08482	0.29125	0.98444	0.64532	49.111	-1.001
0.10992	0.33155	0.98579	0.69692	56.088	-0.672
0.17475	0.41866	0.98958	0.76005	63.333	-0.364

]

**Sodium Sulfate**

**303K**

0.00408	0.06395	0.98539	1.09834	15.324	-2.542
0.01638	0.12802	0.98683	0.94803	23.564	-2.165
0.02869	0.16938	0.98799	0.86681	33.889	-2.002
0.04507	0.21232	0.98932	0.84651	44.231	-1.67
0.06557	0.25608	0.99053	0.85885	56.802	-1.348
0.09836	0.31363	0.99259	0.87923	64.556	-1.051
0.14344	0.37874	0.99467	0.89181	75.001	-0.845

**308K**

0.00406	0.06378	0.98359	0.970205	18.121	-2.254
0.01632	0.12777	0.98501	0.843402	24.876	-2.001
0.02863	0.16921	0.98617	0.810415	34.887	-1.683
0.04497	0.21208	0.98748	0.80484	45.089	-1.366
0.06527	0.25548	0.98946	0.84043	57.443	-1.011
0.09796	0.313	0.99147	0.86931	65.342	-0.772
0.14317	0.37839	0.99264	0.87542	76.666	-0.601

**313K**

0.004056	0.06369	0.98068	0.90835	19.931	-2.245
0.01625	0.12749	0.98343	0.78952	25.556	-2.001

0.02853	0.16888	0.98326	0.76331	35.008	-1.657
0.04482	0.21171	0.98483	0.73275	46.897	-1.458
0.06512	0.25519	0.98632	0.77023	58.098	-1.071
0.09778	0.3127	0.98774	0.78416	66.089	-0.832
0.14203	0.37688	0.98901	0.85818	77.011	-0.505

**318K**

0.004042	0.06358	0.97779	0.77703	20.006	-2.099
0.01619	0.12724	0.97932	0.70525	27.777	-1.678
0.02838	0.16847	0.98033	0.68656	36.011	-1.391
0.04458	0.21115	0.98185	0.69091	47.098	-1.108
0.06477	0.2545	0.989392	0.69427	59.122	-0.887
0.09733	0.31198	0.98475	0.74144	67.078	-0.555
0.14192	0.37671	0.98611	0.79502	77.101	-0.301

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**Magnesium Sulfate**

**303K**

0.00598	0.07739	0.98608	1.11322	45.888	-1.954
0.02396	0.15482	0.98948	0.96494	55.011	-1.707
0.04793	0.21895	0.99344	0.89516	68.754	-1.45
0.07191	0.26816	0.99684	0.88809	81.444	-1.204
0.10186	0.31915	0.99981	0.92687	92.022	-0.919
0.14381	0.37922	1.00615	0.94692	100.101	-0.743
0.19175	0.43789	1.01137	1.01003	109.955	-0.525

**308K**

0.00595	0.07716	0.98428	0.95842	47.066	-1.998
0.02383	0.15436	0.98765	0.84241	56.233	-1.662
0.04776	0.21854	0.99126	0.79806	69.233	-1.353
0.07173	0.26783	0.99497	0.77226	82.231	-1.189
0.101665	0.31885	0.99812	0.81769	93.002	-0.873
0.14364	0.37901	1.00423	0.84235	101.005	-0.677
0.19138	0.43748	1.00944	0.87235	110.666	-0.526

**313 K**

0.00594	0.07713	0.98137	0.90768	48.558	-1.862
0.02373	0.15406	0.98467	0.79506	58.555	-1.622
0.04769	0.2184	0.98861	0.74069	71.336	-1.379
0.071583	0.26755	0.00197	0.75762	83.444	-1.066
0.101264	0.31822	0.00413	0.76951	94.665	-0.861
0.14312	0.37831	1.00114	0.81652	102.211	-0.607
0.19043	0.43639	1.00621	0.87304	112.023	-0.404

**318K**

0.00592	0.07694	0.97846	0.77424	50.055	-1.775
0.02364	0.15375	0.98173	0.69472	60.323	-1.465
0.04746	0.21786	0.98554	0.67966	72.333	-1.111
0.07125	0.26692	0.98901	0.68584	84.008	-0.881
0.10091	0.31766	0.99211	0.71126	95.342	-0.651
0.14227	0.37719	0.99796	0.73131	103.559	-0.489
0.18957	0.4354	1.00308	0.79089	113.055	-0.271

**Aluminium Sulfate**

**303 K**

0.00398	0.06316	0.98666	1.14579	184.033	-2.001
0.015959	0.12633	0.99184	1.03799	197.054	-1.651
0.03192	0.17866	0.99841	0.99709	209.565	-1.342
0.04788	0.21883	1.00454	1.01736	223.029	-1.025
0.06784	0.26046	1.01196	1.05022	234.675	-0.765
0.09577	0.30948	1.02213	1.12762	245.088	-0.453
0.12731	0.3568	1.03272	1.23714	258.523	-0.159

**308K**

0.00396	0.06291	0.98485	1.00136	187.778	-1.848
0.01591	0.12614	0.98999	0.90313	200.066	-1.609
0.03169	0.17802	0.99643	0.92043	212.808	-1.302
0.04779	0.21849	1.00257	0.93962	226.555	-0.982
0.06765	0.26011	1.00993	0.94652	237.551	-0.667
0.09503	0.30828	1.01832	1.01183	248.888	-0.347
0.12686	0.35618	1.03059	1.11292	260.333	-0.05

**313 K**

0.00395	0.06287	0.98193	0.93436	191.432	-1.884
0.01578	0.12565	0.98665	0.85295	203.654	-1.554
0.03158	0.17771	0.99408	0.83351	215.512	-1.202
0.04736	0.21764	0.99938	0.85114	229.541	-0.905
0.06722	0.25927	1.00632	0.88101	240.611	-0.651
0.09442	0.30728	1.01646	0.94983	251.222	-0.338
0.12607	0.35506	1.02715	0.95962	263.065	-0.049

**318K**

0.00394	0.06283	0.97903	0.79033	194.761	-1.888
0.01575	0.12553	0.98393	0.71299	207.055	-1.632
0.03133	0.177	0.99198	0.69752	218.999	-1.255
0.04728	0.21745	0.99634	0.72179	232.962	-0.897
0.06711	0.25906	1.00365	0.74756	243.089	-0.642
0.09462	0.3076	1.01446	0.80816	254.789	-0.321
0.12588	0.35479	1.02392	0.88143	266.0598	-0.048

**30 mass% THF + water mixture**

**AMMONIUM SULPHATE**

**303 K**

0.00397	0.06301	0.97756	1.22694	-179.9901	-2.65342
0.01984	0.14089	0.98175	0.97627	-143.8231	-2.39432
0.03175	0.17821	0.98369	0.93423	-101.7654	-2.05308
0.04763	0.21824	0.98554	0.93509	-62.3876	-1.6738
0.07144	0.2673	0.98784	0.93601	-29.5621	-1.36427
0.09923	0.31502	0.98933	0.99421	1.172045	-1.03219
0.10793	0.32858	0.98648	1.14844	39.0964	-0.67098

**308K**

0.00234	0.04839	0.97523	1.08381	-253.9342	-2.98432
0.01684	0.12975	0.98005	0.85418	-212.0987	-2.51009
0.03094	0.17595	0.98316	0.79643	-156.9342	-2.11009
0.04533	0.21291	0.98475	0.80312	-99.7652	-1.719

0.07104	0.26655	0.98718	0.78732	-45.8453	-1.41987
0.09725	0.31185	0.98841	0.79319	-12.8734	-1.19876
0.10596	0.32552	0.9847	0.86864	35.2198	-0.96543

**313 K**

0.00184	0.04301	0.97138	0.99582	-312.9867	-2.79065
0.01425	0.11937	0.97583	0.80055	-243.8976	-2.45098
0.03024	0.17391	0.98061	0.71626	-205.4532	-2.11067
0.04423	0.21031	0.98181	0.71756	-145.9867	-1.73987
0.07085	0.26619	0.98571	0.69791	-98.4532	-1.43987
0.09632	0.31035	0.98665	0.74497	-45.2432	-1.10098
0.10455	0.32335	0.98479	0.87384	-3.9087	-0.704532

**318K**

0.00156	0.03949	0.9676	0.89213	-387.3987	-2.65341
0.01298	0.11394	0.97243	0.73213	-311.7645	-2.32876
0.02915	0.17073	0.97741	0.67085	-239.4446	-1.91432
0.04235	0.20579	0.98008	0.67499	-187.4821	-1.56798
0.07002	0.26461	0.9837	0.66075	-112.843	-1.27342
0.09531	0.30872	0.98341	0.71281	-43.4876	-0.92229
0.10356	0.32182	0.98126	0.78493	-7.6548	-0.65987

**SODIUM SULPHATE**

**303K**

0.00359	0.05992	0.97794	1.17774	-311.0987	-3.34765
0.01415	0.11899	0.98199	0.99002	-263.876	-2.75654
0.02476	0.15738	0.98464	0.91218	-197.9807	-2.41987
0.03538	0.18812	0.98654	0.92573	-149.9856	-1.97554
0.05309	0.23042	0.98904	0.98471	-99.453	-1.43916
0.07787	0.27906	0.99127	1.01598	-51.00056	-1.11224
0.13734	0.37059	0.99724	1.04961	-10.4322	-0.77595

**308K**

0.00323	0.05686	0.97603	1.02826	-392.9856	-3.31098
0.01326	0.11519	0.98039	0.85038	-322.9087	-2.85342
0.02423	0.15565	0.98318	0.79334	-254.9321	-2.40098

0.03438	0.18544	0.98542	0.81343	-185.0967	-1.92976
0.05213	0.22832	0.98798	0.82973	-122.9087	-1.51098
0.07685	0.27722	0.98963	0.86854	-58.376	-1.13394
0.13619	0.36904	0.99536	0.87633	-12.6798	-0.83514

**313K**

0.00313	0.05603	0.97272	0.91727	-556.8342	-3.38097
0.01315	0.11467	0.97824	0.75201	-453.9087	-2.92554
0.02314	0.15212	0.98161	0.69271	-345.0342	-2.54982
0.03285	0.18125	0.98302	0.70204	-243.6754	-2.09453
0.05138	0.22669	0.98513	0.70071	-156.0342	-1.67987
0.07472	0.27334	0.98762	0.73914	-66.5568	-1.26892
0.13556	0.36818	0.99009	0.75061	-1.9675	-0.91475

**318K**

0.00308	0.05558	0.96919	0.81772	-654.0987	-3.22876
0.13069	0.11432	0.97613	0.68504	-532.998	-2.73437
0.02255	0.15019	0.97901	0.66195	-399.0987	-2.23561
0.03195	0.17877	0.98058	0.69216	-299.0089	-1.70859
0.05084	0.22549	0.98384	0.68364	-198.8897	-1.39255
0.07255	0.26936	0.98541	0.67359	-121.3593	-1.20315
0.13504	0.36749	0.98884	0.72974	-21.876	-0.72858

**MAGNESIUM SULPHATE**

**303K**

0.00585	0.07648	0.97848	1.16185	-122.7687	-2.76376
0.02339	0.152937	0.98398	0.92428	-82.09792	-2.43646
0.04093	0.20233	0.98733	0.93037	-22.74344	-1.82123
0.05884	0.241847	0.9897	0.91481	18.4326	-1.56734
0.09357	0.3059	0.99409	0.98629	58.0543	-1.08054
0.14037	0.37467	0.99754	1.00652	97.70161	-0.84555
0.20704	0.45502	1.00148	1.13146	128.0564	-0.50987

**308K**

0.00532	0.072938	0.97647	1.02976	-159.3421	-2.56438
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0.02149	0.14662	0.98175	0.87694	-111.0987	-2.09876
0.04002	0.200074	0.98436	0.84986	-54.0978	-1.64482
0.05732	0.23942	0.98752	0.86363	-1.0945	-1.32916
0.09331	0.30546	0.99105	0.89236	34.0976	-0.96752
0.14014	0.37436	0.99597	0.9248	94.49882	-0.72106
0.20595	0.45382	0.99843	1.01898	132.8765	-0.43098

**313K**

0.00485	0.06964	0.97261	0.93385	-176.9453	-2.50987
0.02237	0.14959	0.97875	0.77109	-120.3727	-2.12987
0.03955	0.19889	0.98113	0.72597	-79.0453	-1.80242
0.05643	0.23205	0.98446	0.73897	-22.7564	-1.49532
0.09263	0.30389	0.99044	0.77022	32.9453	-1.05097
0.13991	0.37405	0.99263	0.78695	92.9096	-0.81434
0.20481	0.45116	0.99491	0.89993	134.8934	-0.45387

**318K**

0.00456	0.06753	0.96892	0.83303	-223.5412	-2.42987
0.02214	0.14882	0.97572	0.69911	-161.1251	-2.00564
0.03334	0.19581	0.97993	0.66021	-98.9987	-1.72398
0.05254	0.22922	0.98159	0.71336	-63.98012	-1.23975
0.09194	0.30323	0.98781	0.70082	-12.9871	-0.97865
0.13922	0.37313	0.98913	0.74216	60.5643	-0.68416
0.20252	0.45002	0.99769	0.78638	97.22806	-0.46864

**ALUMINIUM SULPHATE**

**303K**

0.00242	0.04919	0.97844	1.18538	-243.9856	-3.97342
0.00967	0.09838	0.98408	1.00646	-174.3524	-3.2206
0.01693	0.13012	0.98862	0.91819	-97.4564	-2.89553
0.02418	0.15553	0.99161	0.97972	-1.30725	-2.15392
0.03627	0.19047	0.99741	1.03052	88.9867	-1.57776
0.05322	0.23069	1.00142	1.07825	162.9946	-1.16225
0.09336	0.30556	1.01487	1.17375	222.8979	-0.66532

**308K**

0.00224	0.04743	0.97641	1.02961	-301.8976	-3.94675
0.00931	0.09648	0.98169	0.84847	-201.8967	-3.42233
0.01635	0.12786	0.98496	0.80872	-97.0987	-2.82786
0.02395	0.15475	0.98815	0.82809	21.9654	-2.23765
0.03585	0.18934	0.99318	0.86996	145.0342	-1.65432
0.05356	0.22925	0.99688	0.94002	232.0454	-1.12505
0.09289	0.30479	1.00367	0.94384	322.8745	-0.83634

**313K**

0.00197	0.04593	0.97413	0.92705	-345.0987	-3.98675
0.00901	0.09534	0.97856	0.77075	-234.6754	-3.34502
0.01582	0.12708	0.98245	0.73957	-123.9342	-2.72635
0.02349	0.15218	0.98575	0.75014	-21.8054	-2.2153
0.03432	0.18686	0.98918	0.76314	89.0987	-1.74269
0.05186	0.22771	0.99235	0.81635	167.0299	-1.22356
0.09266	0.30353	0.99902	0.84188	261.3275	-0.84356

**318K**

0.00194	0.04415	0.96878	0.82185	-398.3453	-3.97089
0.00888	0.09428	0.97468	0.68098	-264.7912	-3.35876
0.01532	0.12617	0.97891	0.62381	-145.8343	-2.96453
0.02283	0.15083	0.98313	0.64791	-67.9453	-2.31987
0.03401	0.18442	0.98642	0.65852	56.55383	-1.89343
0.05142	0.22594	0.9918	0.69262	149.1497	-1.34987
0.09162	0.30268	0.99182	0.72703	225.4925	-0.89354

**40 mass % THF + water mixture**

**AMMONIUM SULFATE**

**303K**

0.00728	0.08532	0.95966	1.23697	161.151	-2.22987
0.02184	0.14778	0.96354	1.10297	139.455	-1.88098
0.03641	0.19082	0.96394	1.06183	105.943	-1.59787
0.0546	0.23366	0.96781	1.07249	81.091	-1.27503
0.09101	0.30167	0.97181	1.08296	55.785	-0.96486

0.12741	0.35694	0.98321	1.10584	31.124	-0.70981
0.18202	0.42663	0.98562	1.22831	9.119	-0.45923
<b>308K</b>					
0.007095	0.08423	0.93775	1.07305	711.09823	-2.24365
0.021636	0.14709	0.93789	0.95076	601.34098	-1.91321
0.03585	0.18934	0.94155	0.91729	454.98076	-1.61987
0.05417	0.23274	0.94941	0.93001	363.907	-1.27654
0.09056	0.30093	0.95352	0.95837	245.23098	-0.91604
0.12693	0.35627	0.96141	0.97128	155.08967	-0.64236
0.182001	0.42662	0.96913	1.12061	52.98123	-0.35874
<b>313K</b>					
0.00704	0.08388	0.92921	0.95476	1051.8845	-2.35098
0.02158	0.1469	0.93693	0.91243	857.92311	-2.05002
0.03539	0.18812	0.94046	0.84033	665.91002	-1.54333
0.05342	0.23113	0.94801	0.87052	501.43212	-1.30812
0.090136	0.30023	0.95266	0.89445	380.99125	-0.88148
0.12585	0.35475	0.96791	0.92871	165.99213	-0.60802
0.18185	0.42644	0.96418	0.94505	60.00987	-0.329811
<b>318K</b>					
0.007012	0.08373	0.90796	0.89489	1809.01243	-2.85981
0.02134	0.14606	0.91006	0.83919	1512.02134	-2.32982
0.03465	0.18614	0.91211	0.85315	1190.081	-1.81266
0.05324	0.23073	0.91266	0.86025	932.01291	-1.42786
0.09004	0.30086	0.91664	0.88133	585.09123	-1.07131
0.12359	0.35155	0.92438	0.89921	324.438	-0.673289
0.18136	0.42586	0.93211	0.92025	94	-0.290123

**SODIUM SULPHATE**

**303K**

0.01443	0.12012	0.95846	1.13739	532.012	-2.12651
0.02886	0.16988	0.96023	1.06083	461.986	-1.79866
0.04329	0.20806	0.96539	1.06689	353.098	-1.4511

0.05772	0.24024	0.96913	1.07214	283.092	-1.24117
0.08658	0.29424	0.97113	1.10035	190.987	-0.95054
0.11545	0.33977	0.97412	1.18549	104.147	-0.65912
0.14431	0.37988	0.97998	1.23982	31.097	-0.49594

**308K**

0.01436	0.11983	0.95229	1.01942	352.945	-1.91543
0.02857	0.16903	0.95732	0.93735	289.063	-1.629324
0.04318	0.20779	0.95936	0.93849	237.16	-1.39895
0.0576	0.24001	0.96412	0.96007	188.934	-1.14319
0.08635	0.29385	0.96895	0.97222	152.456	-0.90231
0.11528	0.33952	0.97116	1.001139	102.256	-0.71672
0.14421	0.37974	0.97303	1.02577	56.934	-0.518453

**313K**

0.01427	0.11945	0.94809	0.91637	342.456	-1.89342
0.02851	0.16882	0.94859	0.86225	287.912	-1.61012
0.04306	0.20751	0.94886	0.891026	264.145	-1.38123
0.05731	0.23939	0.95166	0.91246	235.319	-1.14045
0.08616	0.29353	0.95639	0.93892	198.345	-0.90087
0.11511	0.33926	0.95913	0.95347	161.067	-0.71544
0.14412	0.37963	0.96207	0.95892	123.849	-0.51309

**318K**

0.01409	0.11871	0.94401	0.81811	289.387	-1.83003
0.02833	0.16832	0.94785	0.76193	244.214	-1.60998
0.04285	0.20701	0.94986	0.79321	196.309	-1.29919
0.05708	0.23891	0.95213	0.82532	163.002	-1.0493
0.08605	0.29334	0.95547	0.84325	128.298	-0.82592
0.11501	0.33912	0.95641	0.85011	78.888	-0.70337
0.14352	0.37884	0.95886	0.85505	45.823	-0.480123

**MAGNESIUM SULPHATE**

**303 K**

0.00494	0.07028	0.96987	1.21911	-597.987	-2.87342
0.02472	0.15722	0.97328	0.95822	-489.345	-2.37074
0.03164	0.17787	0.97813	0.96368	-399.342	-2.0723
0.05437	0.23317	0.98718	0.97465	-301.945	-1.55239
0.08897	0.29827	0.99203	0.98841	-210.342	-1.23765
0.11863	0.34442	0.99739	1.04348	-92.567	-0.92013
0.15818	0.39772	1.00462	1.18717	-11.946	-0.56032

**308K**

0.00453	0.0673	0.96392	1.08985	-834.652	-2.61943
0.02432	0.15594	0.97103	0.88636	-712.894	-2.11677
0.03139	0.17717	0.97432	0.89991	-577.786	-1.848009
0.05415	0.2327	0.97915	0.90429	-445.561	-1.51923
0.08834	0.29722	0.98336	0.92768	-261.231	-1.23004
0.11765	0.34301	0.98853	0.96835	-121.432	-0.78166
0.15693	0.39614	0.99905	1.02336	-9.365	-0.57187

**313K**

0.00436	0.06603	0.95731	0.98222	-1001.563	-2.58231
0.02419	0.15553	0.96212	0.79553	-852.618	-2.10987
0.03106	0.17624	0.96891	0.80356	-695.321	-1.83986
0.05401	0.23238	0.97103	0.81203	-459.899	-1.47746
0.08726	0.29539	0.97515	0.82411	-299.999	-1.08002
0.11718	0.34232	0.97913	0.83339	-99.555	-0.88824
0.15568	0.39456	0.98732	0.89517	-8.342	-0.61845

**318K**

0.00425	0.06519	0.94635	0.87216	-1200.453	-2.53897
0.02402	0.15498	0.95233	0.69191	-1033.76	-2.18083
0.03101	0.176082	0.95831	0.70728	-801.654	-1.83596
0.05962	0.23155	0.96313	0.72392	-566.321	-1.43218
0.08703	0.29501	0.96835	0.76692	-354.666	-1.23987
0.11658	0.34144	0.97505	0.79335	-144.495	-0.92165
0.15425	0.39274	0.97615	0.80242	-7.89998	-0.59136

**ALUMINIUM SULPHATE**

**303K**

0.00193	0.04393	0.96335	1.20197	898.956	-4.85234
0.00581	0.07622	0.96556	1.04549	765.298	-4.14099
0.00968	0.09838	0.96919	1.05922	605.398	-3.51845
0.01548	0.12442	0.97743	1.06903	497.321	-2.61987
0.02709	0.16459	0.97813	1.07654	378.645	-1.97342
0.03484	0.18665	0.98115	1.08933	277.639	-1.53709
0.09676	0.31106	0.98322	1.12818	104.876	-0.84057

**308K**

0.00192	0.04392	0.95194	1.01981	6001.348	-5.21923
0.00580	0.07622	0.9543	0.86638	5126.234	-4.52885
0.00958	0.09788	0.95903	0.88326	3946.35	-3.65432
0.01539	0.12405	0.96235	0.89056	2899.012	-2.98453
0.02705	0.16446	0.96886	0.91562	2002.722	-2.32678
0.03431	0.18523	0.97212	0.94015	1169.197	-1.56256
0.09659	0.31078	0.97813	0.94891	201.678	-0.90999

**313K**

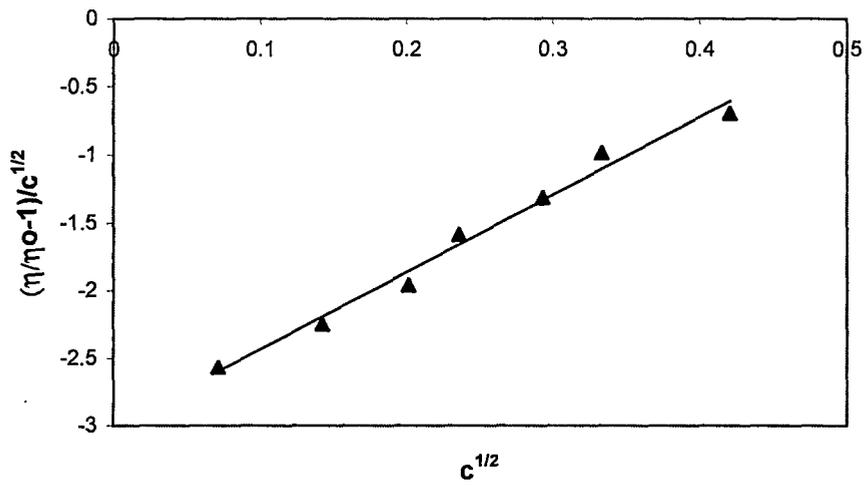
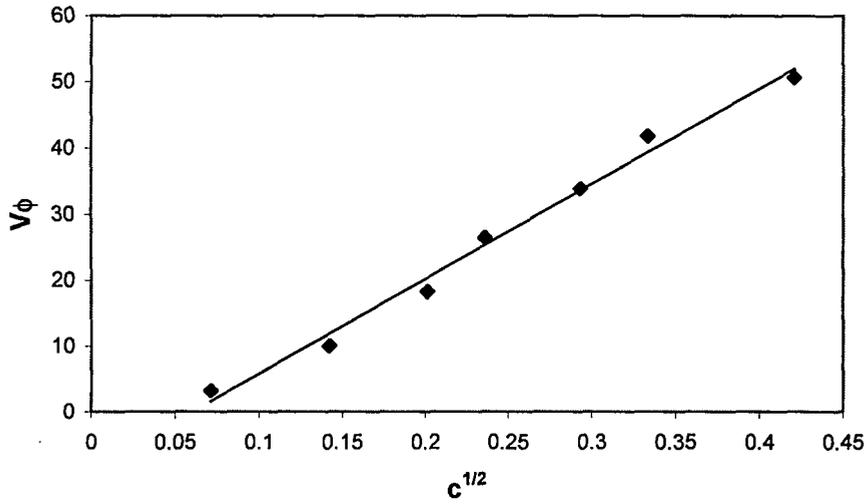
0.00192	0.04382	0.94334	0.90127	6254.652	-5.43871
0.00571	0.07554	0.94813	0.75889	5289.655	-4.75398
0.00945	0.09721	0.95221	0.77932	3998.888	-3.86332
0.01528	0.12361	0.95932	0.78325	3212.932	-2.98123
0.02702	0.164362	0.96132	0.78705	1967.398	-2.32765
0.03415	0.184797	0.96805	0.80339	1068.561	-1.61987
0.09634	0.31038	0.97016	0.86996	232.923	-0.91894

**318K**

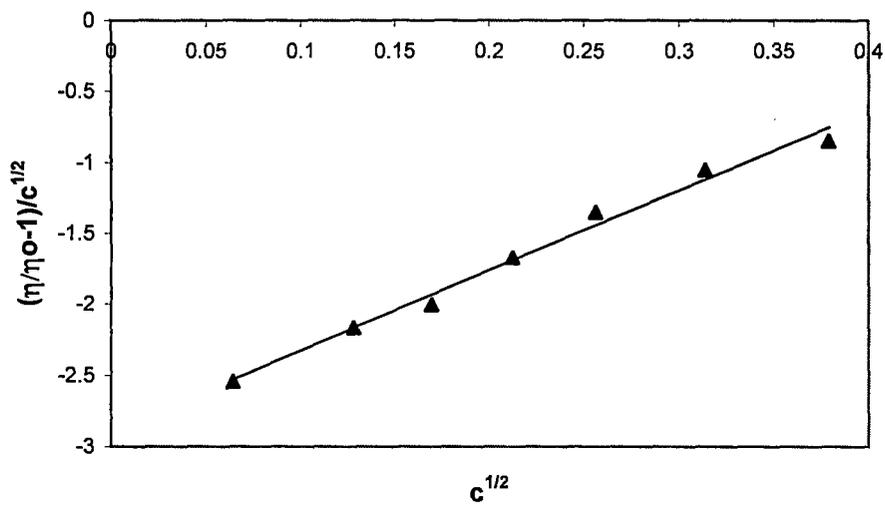
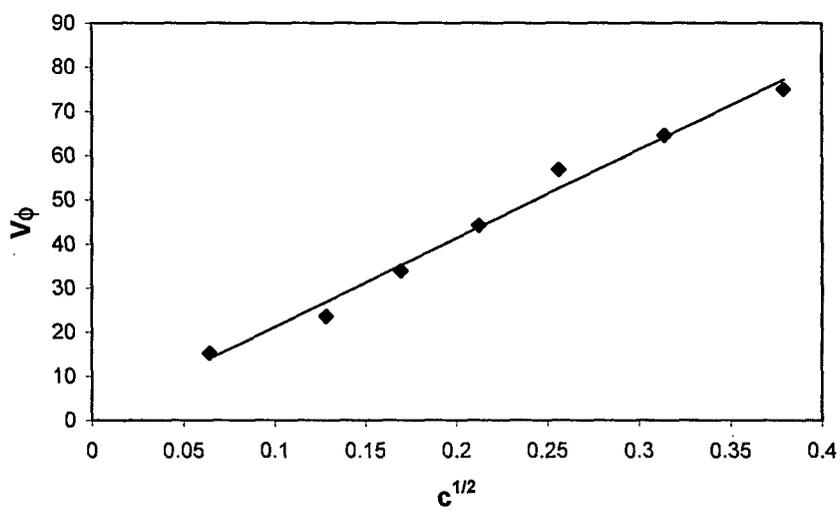
0.00191	0.04362	0.93115	0.78929	8911.867	-5.61237
0.00551	0.07426	0.93817	0.67235	7284.788	-4.9231
0.00932	0.09656	0.94336	0.69311	5467.987	-3.89234
0.01521	0.1233	0.94778	0.72532	3967.876	-3.12876
0.02701	0.16432	0.95245	0.73515	2654.987	-2.32987
0.03401	0.1844	0.95815	0.74732	999.032	-1.62876
0.09611	0.31002	0.96309	0.75844	330.231	-0.95673

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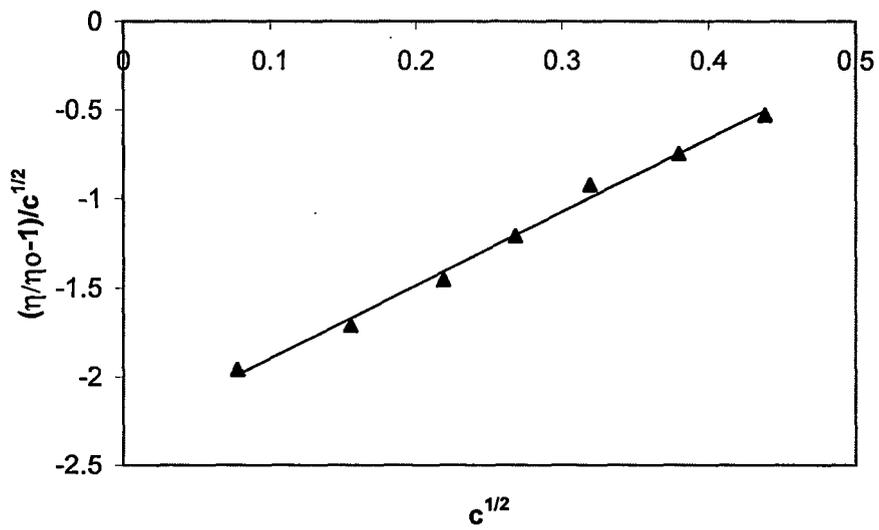
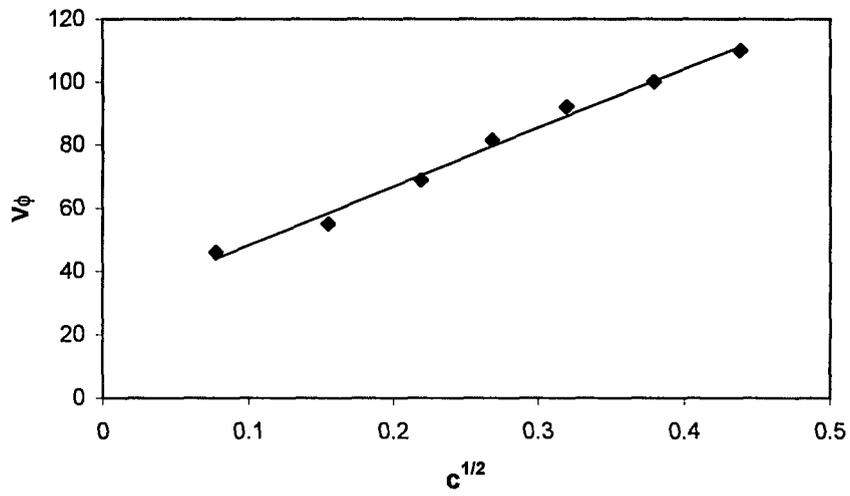
20 mass % THF + water mixture  
Ammonium sulphate



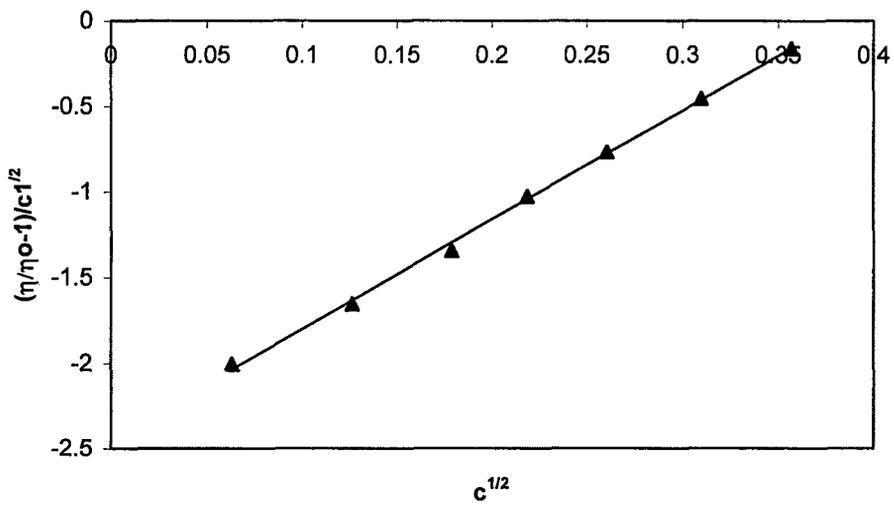
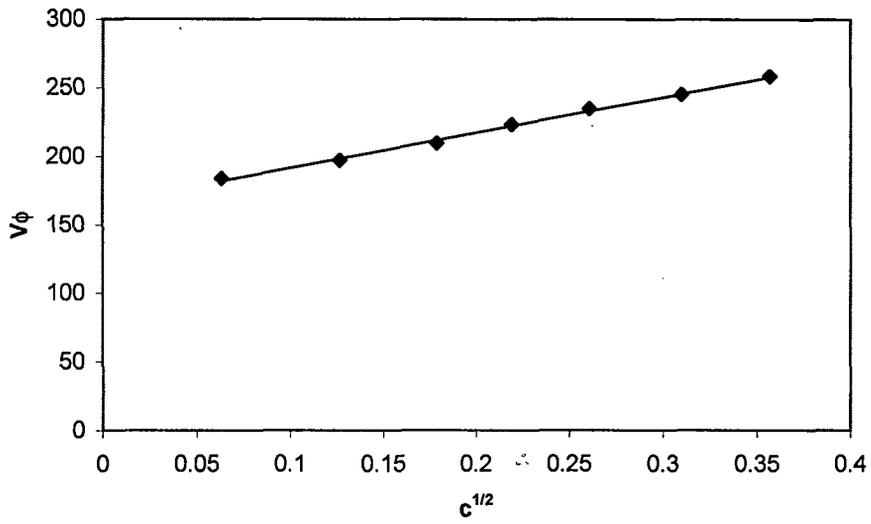
## Sodium sulphate



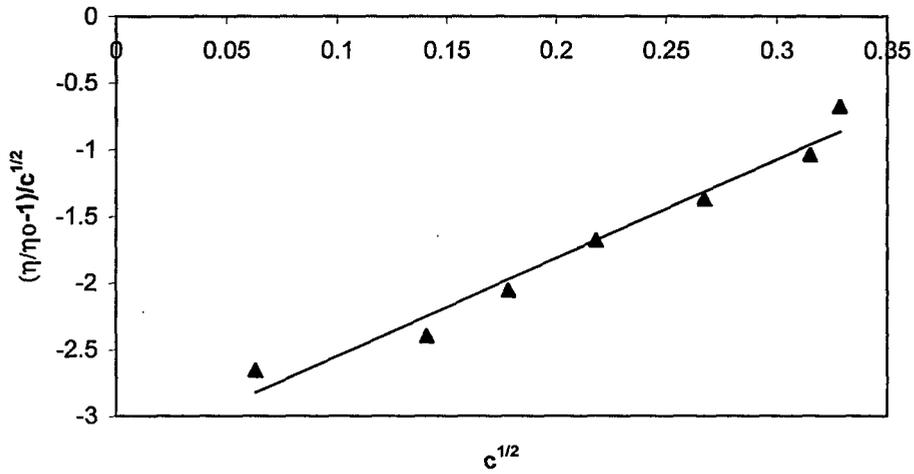
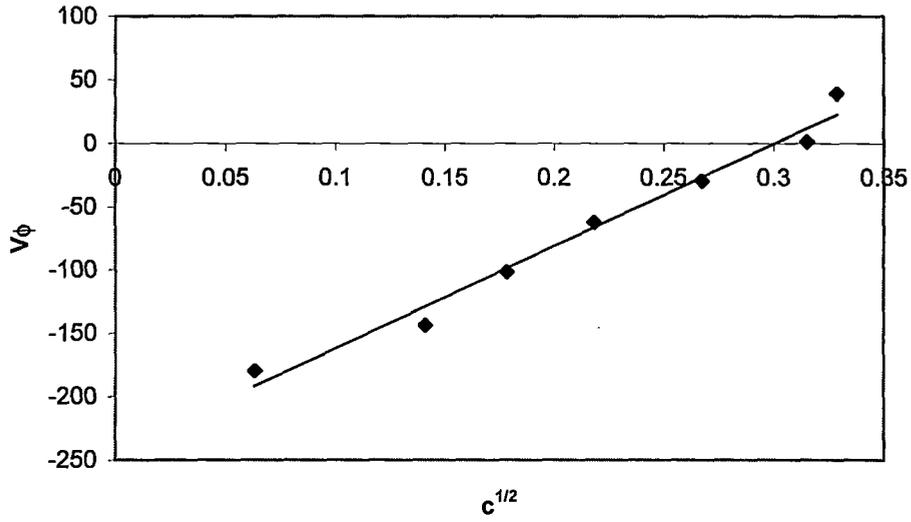
## Magnesium sulphate



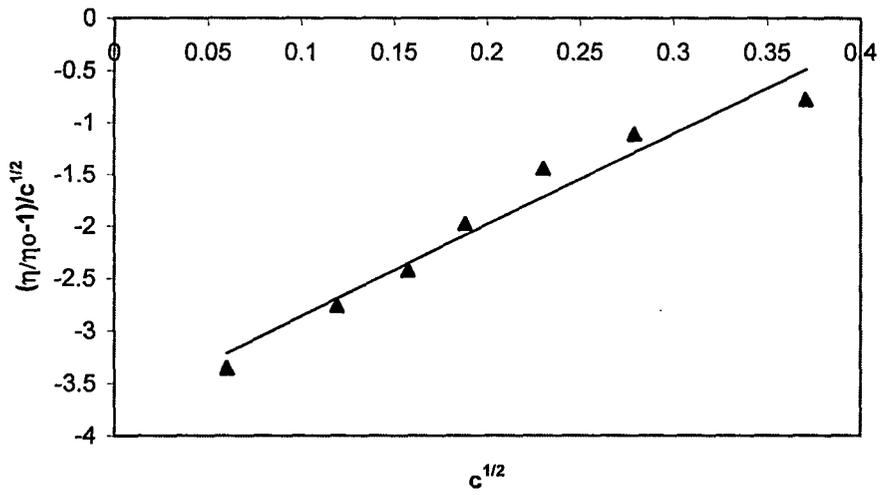
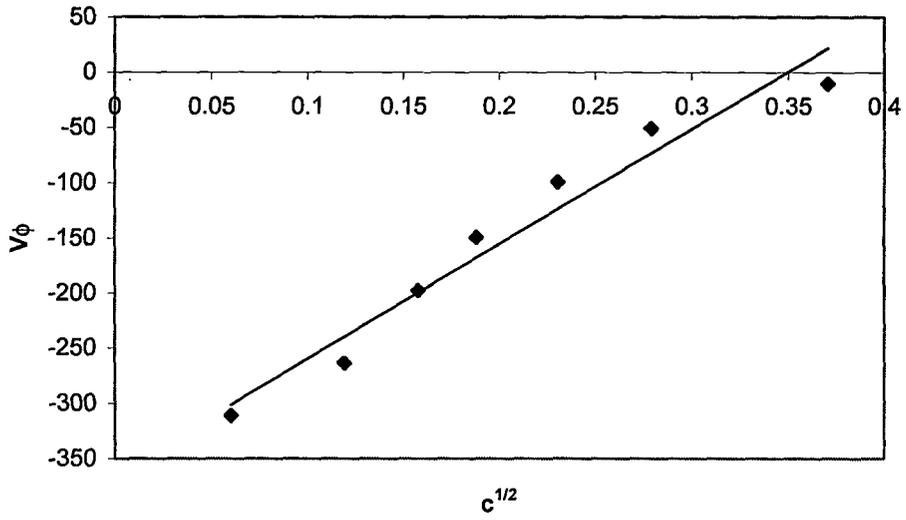
## Aluminium sulphate



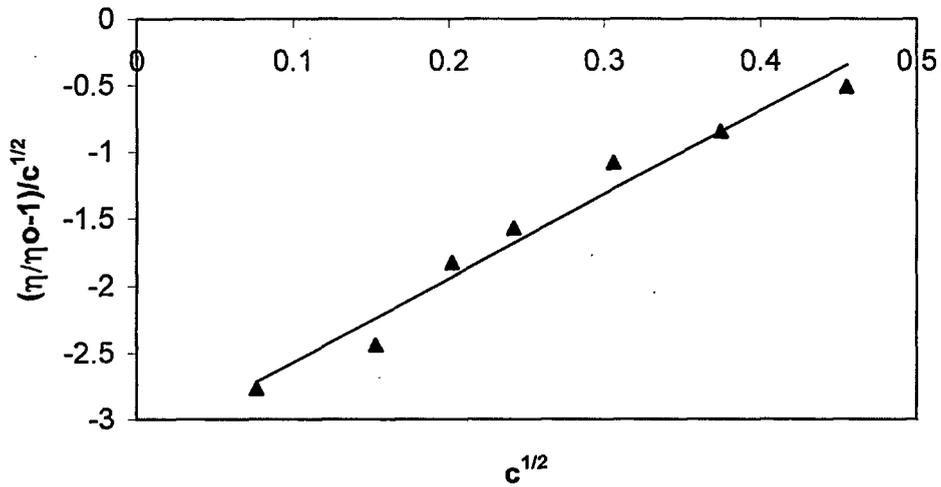
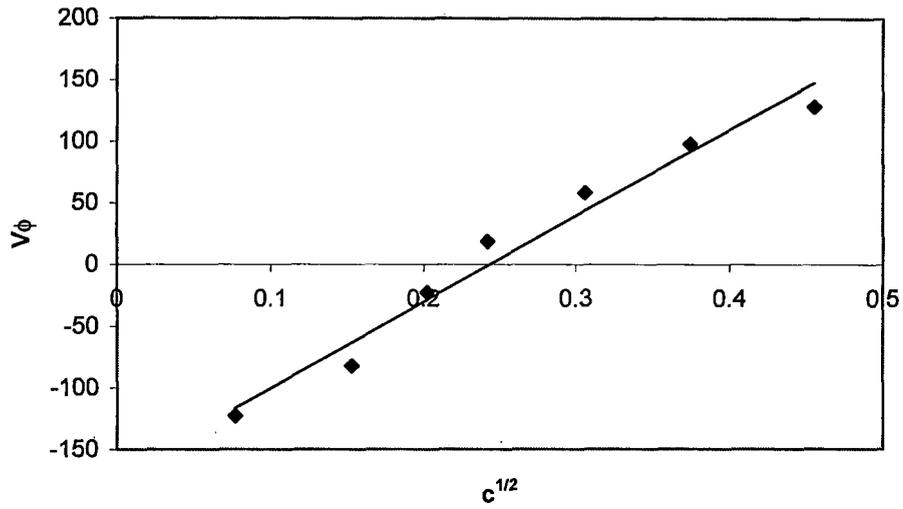
30 mass % THF + water mixture  
Ammonium sulphate



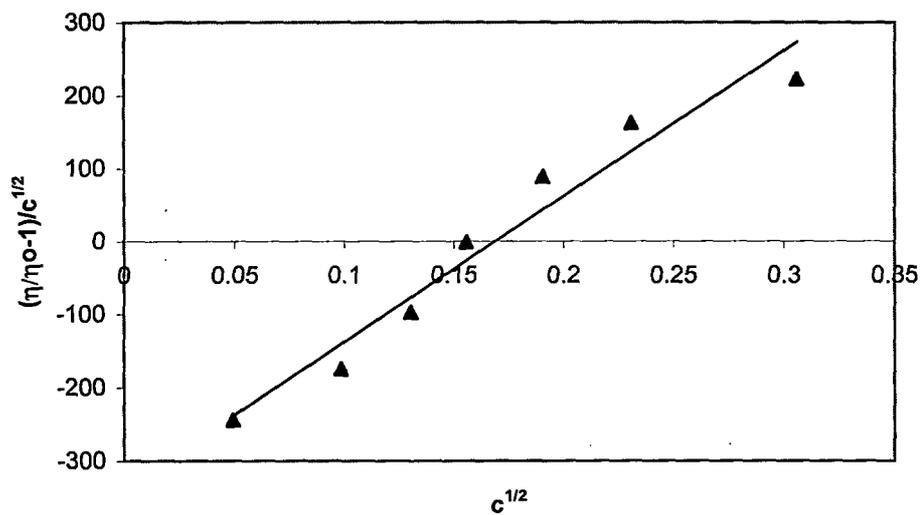
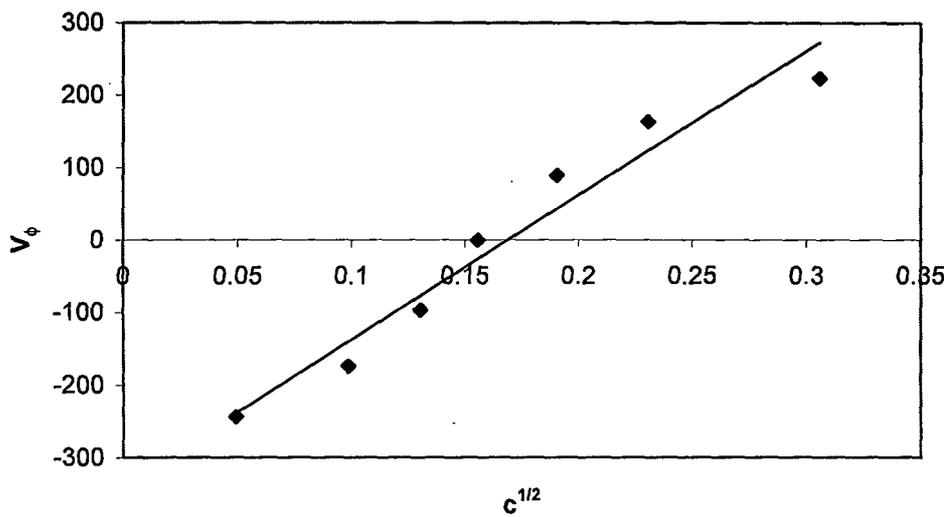
## Sodium sulphate



## Magnesium sulphate



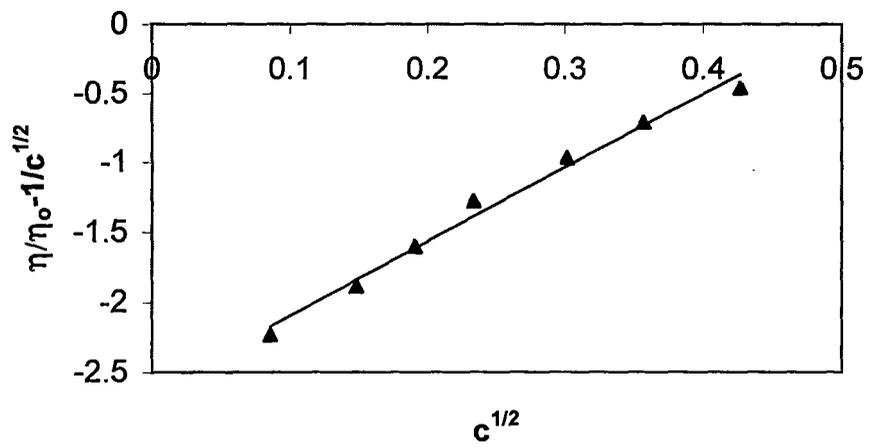
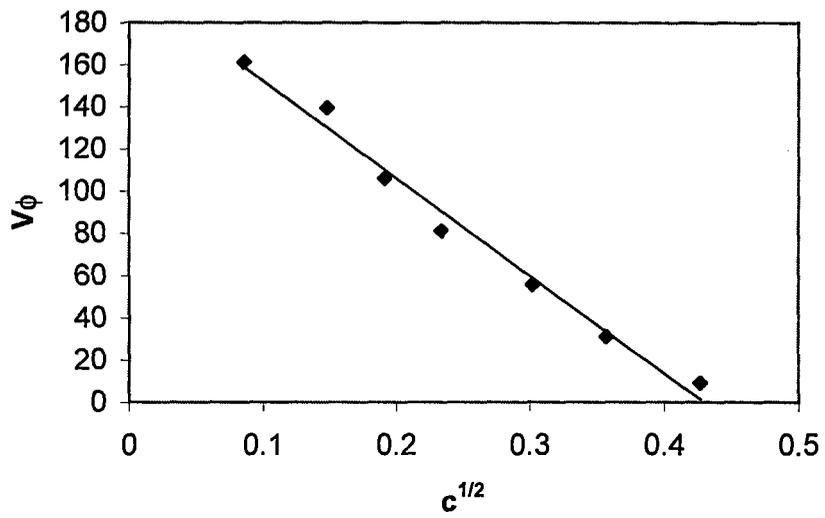
## Aluminium sulphate



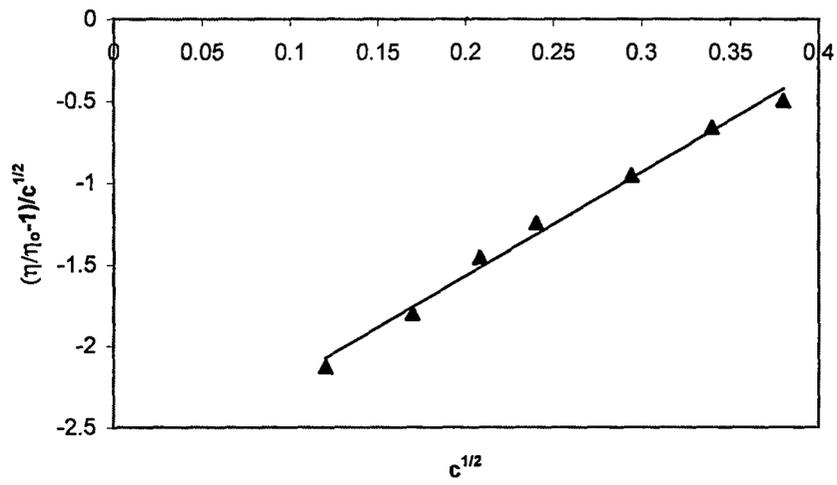
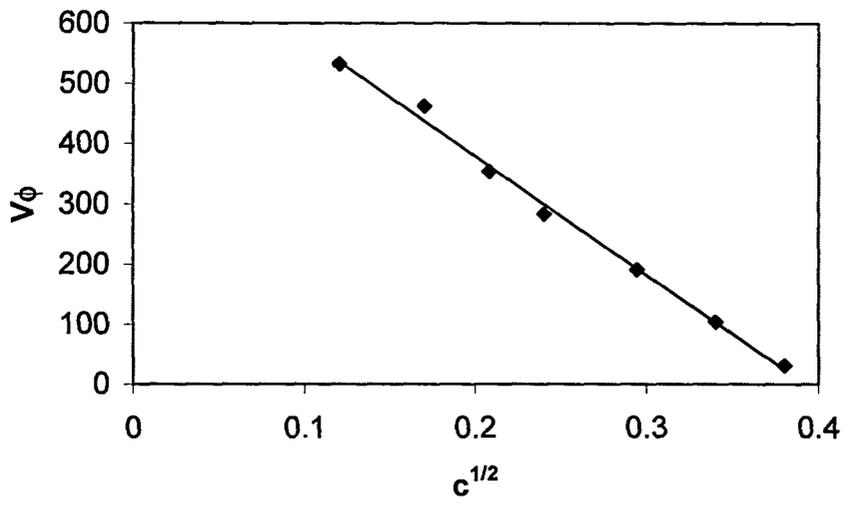
40 mass % THF + water mixture

303K

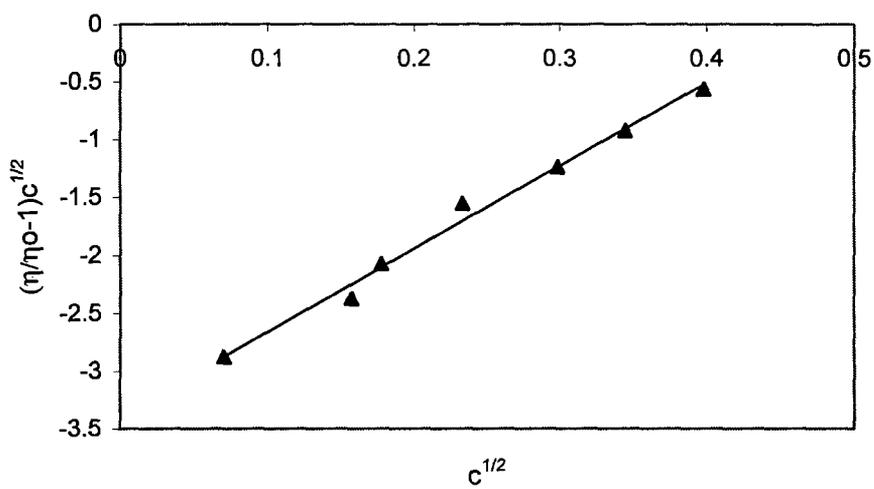
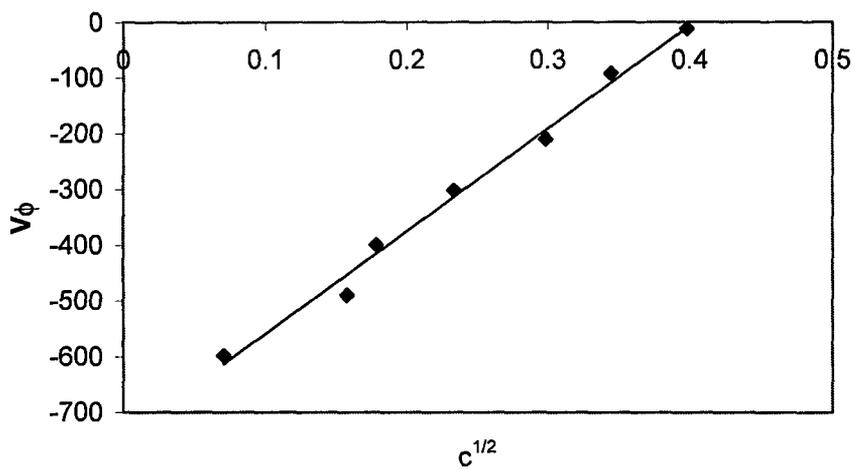
Ammonium sulphate



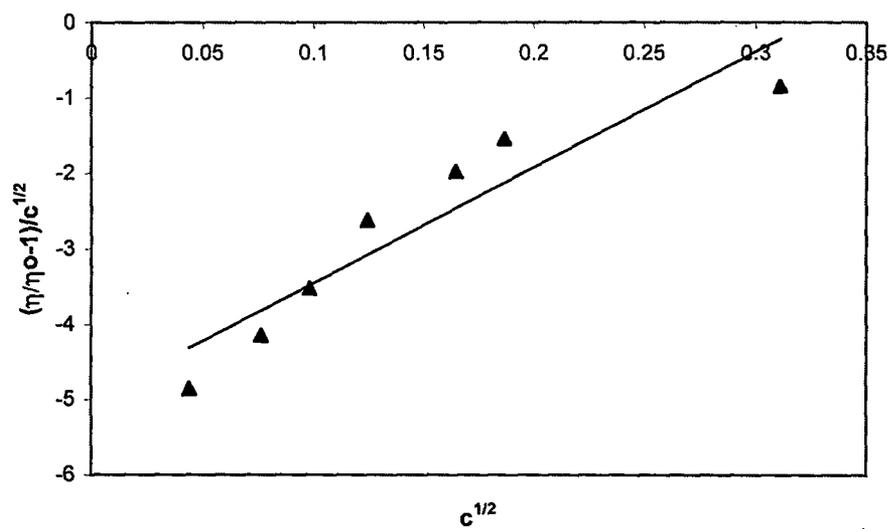
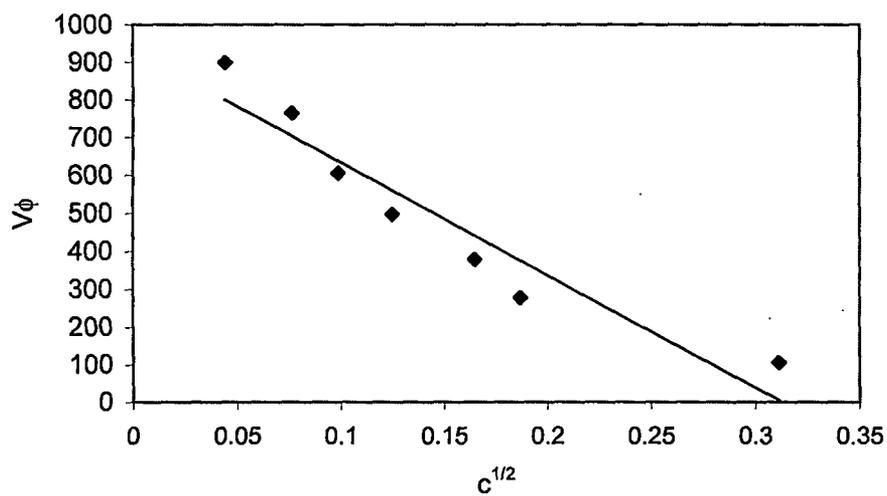
## Sodium sulphate



Magnesium sulphate



## Aluminium sulphate



## CHAPTER VIII

### **Studies on Density and Viscosity of Some Liquid Mixtures of Normal Hexane with Some Polar and Non-Polar Solvents at Different Temperatures.**

#### **Abstract**

Density and viscosity of ternary liquid mixtures of n-hexane with tetrahydrofuran, benzene and isopropanol have been measured as a function of the composition at temperatures 303, 313 and 323K. Various excess thermodynamics functions viz. excess viscosity ( $\eta^E$ ), excess volume ( $V^E$ ), excess Gibbs free energy of activation of flow ( $\Delta G^E$ ) and the values of interaction parameter  $d$  in Grubenberg and Nissn equation have been calculated as a function of composition of ternary mixtures. The results have been interpreted in terms of molecular interactions existing between the components of these mixtures.

#### **8.1 Introduction**

Benzene has a stable structure which contains  $\pi$ -electrons. Tetrahydrofuran (THF) and isopropanol both have lone pair of electrons. The structure of isopropanol is such that if it provides a negative charge on one side, it can provide the positive charge at the other end. Some workers<sup>1,2</sup> have studied the structural behaviour of various solvents in details and have suggested the self-association among its own molecules. Hence it follows that if the unlike molecules want to interact with n-hexane than they have to overcome these weak forces of interaction.

In the light of the above nature of the molecules of polar and non-polar solvents it was thought worthwhile to undertake viscometric studies on the molecular interactions in the ternary liquid mixtures involving n-hexane as the

first component and some polar and non-polar solvents as the second and third component.

## 8.2 Results and Discussion

The values of density ( $\rho$ ), viscosity ( $\eta$ ), molar volume ( $V$ ) and excess thermodynamic functions viz. the excess viscosity ( $\eta^E$ ), the excess molar volume ( $V^E$ ) and the excess Gibbs free energy of activation of flow ( $\Delta G^{\#E}$ ) and the interaction parameter ( $d$ ) have been calculated as a function of composition of the ternary liquid mixtures as discussed below.

The excess viscosity ( $\eta^E$ ) of a given ternary liquid mixture has been evaluated from the observed viscosity of the mixture and that of its pure components using the equation,

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2 + x_3\eta_3) \quad (1)$$

where  $\eta$  is the viscosity of the ternary liquid mixture, and  $\eta_1$ ,  $\eta_2$  and  $\eta_3$  are the viscosities and  $x_1$ ,  $x_2$  and  $x_3$  are the mole fractions of components 1, 2 and 3 respectively. The excess molar volume ( $V^E$ ) of the ternary liquid mixtures has been evaluated from the molar volume of the mixtures ( $V$ ) that of pure components ( $V_1$ ,  $V_2$  and  $V_3$ ) using the equation,

$$V^E = V - (x_1V_1 + x_2V_2 + x_3V_3) \quad (2)$$

The molar volume ( $V$ ) of the ternary liquid mixture has been calculated from the measured density ( $\rho$ ) of the mixture using the equation,

$$V = (x_1M_1 + x_2M_2 + x_3M_3) / \rho \quad (3)$$

where  $x_1$ ,  $x_2$  and  $x_3$  are the mole fractions of the compounds 1, 2 and 3 of the ternary liquid mixtures respectively,  $V_1$  is  $M_1/\rho_1$ ,  $V_2$  is  $M_2/\rho_2$  and  $V_3$  is

$M_3/\rho_3$ ,  $\rho_1$ ,  $\rho_2$  and  $\rho_3$  are the densities of the components 1, 2 and 3 of the ternary liquid mixtures respectively.

The excess Gibbs free energy of activities of flow ( $\Delta G^{\neq E}$ ), for the ternary liquid mixture has been computed from the Eyring equation<sup>3</sup>,

$$\Delta G^{\neq E} = [RT \{ \ln \eta v - (x_1 \ln \eta_1 v_1 + x_2 \ln \eta_2 v_2 + x_3 \ln \eta_3 v_3) \}] \quad (4)$$

where the letters have their usual significance.

Grunberg and Nissan<sup>4</sup> suggested a logarithm relation between the viscosity of a binary liquid mixture and that of its pure components,

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \quad (5)$$

On applying to a ternary liquid mixture, this equation takes up the form,

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_3 \ln \eta_3 + x_1 x_2 x_3 d \quad (6)$$

where  $d$  is a constant regarded as a measure of the strength of molecular interactions between the mixing components.

The density ( $\rho$ ) and viscosity ( $\eta$ ) data of the ternary liquid mixtures at three temperatures (303, 313, 323)K are presented in Table 1 which also includes the values of  $\eta^E$ ,  $V^E$ ,  $\Delta G^{\neq E}$  and  $d$ .

The variation of  $\rho$  and  $\eta$  of the ternary liquid mixtures with their composition has been studied by plotting  $\rho$  and  $\eta$  with mole fraction ( $x_1$ ) of the first component, i.e. n-hexane. The results are shown in figs 1 & 2. It is seen that the plots in each case, are non-linear, indicating the presence of molecular interactions<sup>5-7</sup>. The variations of  $\eta^E$  with the composition of the ternary liquid mixtures are shown in fig. 3 by plotting  $\eta^E$  against the mole fraction ( $x_1$ ) of the first component (n-hexane). The values of  $\eta^E$  are found to

be negative for all the ternary liquid mixtures under study, indicating the dominance of dispersion forces between the unlike molecules<sup>6,8,9</sup> So far as the variation of  $\Delta G^{\neq E}$  with the composition of ternary liquid mixtures is concerned, the ternary liquid mixtures under discussion can be classified in the following two categories; (i) the liquid mixtures with the negative values of  $\Delta G^{\neq E}$ , and (ii) the liquid mixtures in which  $\Delta G^{\neq E}$  changes the sign from positive to negative.

In the ternary liquid mixtures involving THF as a second and benzene as the third component, the values of  $\Delta G^{\neq E}$  have been found to be negative over the entire range of composition. The plots of  $\Delta G^{\neq E}$  vs  $x_1$  are shown in fig 4. The negative values of  $\Delta G^{\neq E}$  in the first ternary mixture may be attributed to the dominance of dispersion forces due to weak intermolecular interactions followed by complex formation between the mixing molecules.<sup>10</sup>

The ternary liquid mixtures involving isopropanol as second and as third component (i e. Ternary-II and ternary-III) show the inversion in the values of  $\Delta G^{\neq E}$  from positive to negative. The positive values of  $\Delta G^{\neq E}$  indicate the presence of strong interactions between the mixing components accompanied by the complex formation. However, as the negative values of  $\Delta G^{\neq E}$  may be attributed to the presence of dispersion forces arising out due to the dissociation of molecular complexes.

A perusal of Table 1 reveals that the values of  $V^E$  vary with the composition. The values of  $V^E$  are found to be negative over the entire range of composition which may be attributed to the formation of intermolecular complexes between the mixing components. The less negative values of  $V^E$  may be ascribed to the dissociation of molecular complexes.

The interaction parameter  $d$  has been calculated (vide eqn. 6) for the ternary liquid mixtures under discussion as a function of the composition of the mixtures and the values are listed in Table 1. It is seen that the values of  $d$  vary greatly in magnitude with the composition, indicating the presence of specific interactions.<sup>8</sup> The positive values of  $d$  indicate the presence of strong molecular interactions due to appreciable dipole-dipole and dipole-induced dipole interactions<sup>11</sup> while the negative values of  $d$  may be attributed to dominance of dispersion type of forces<sup>12,13,14</sup> arising from the breaking of hydrogen bonds in associated components of the ternary mixtures.

### 8.3 Experimental

All the chemicals used in the present study were of A.R. grade. The organic liquids were purified by the standard procedure<sup>15</sup>, and their purities were checked by comparing their density and viscosity with those reported in literature<sup>16</sup> at 303, 313 and 323K which almost agreed with the accuracy of  $\pm 1 \times 10^{-4} \text{ g-cm}^{-3}$  and  $\pm 3 \times 10^{-3} \text{ m pas}$ , respectively.

All the ternary liquid mixtures of known composition were prepared volumetrically<sup>17,18</sup> in stoppered measuring flasks. The densities and viscosities were measured in an Ostwald-Sprengel type Pycnometer and suspended-level Ubbdohde viscometer<sup>15</sup> at 303, 313 and 323K with a precision of  $\pm 3 \times 10^{-5} \text{ g cm}^{-3}$  and 0.05% respectively. The values were in good agreement with the literature values.<sup>19</sup>

### Acknowledgement

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

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**Table 1 : Values of density, viscosity and excess thermodynamics properties for ternary liquid mixture of n-hexane with some polar and non-polar solvents at 303, 313 and 323K.**

303K								
<u>n-hexane(1) + THF(2) + Benzene</u>								
$x_1$	$x_2$	$\rho$ (g.cm-3)	$\eta$ (cp)	$\eta^E$ (cp)	$V$ (cm <sup>3</sup> mol-1)	$V^E$ (cm <sup>3</sup> /mol)	$d$	$\Delta G^{#E}$ (J/mol)
0.0113	0.0000	0.86995	0.55733	0.00000	89.7867	0.0000	0.0000	0.000
0.0000	0.8125	0.90509	0.45870	-0.00818	80.9146	-2.6379	0.0000	-616.043
0.0000	1.0000	0.87828	0.44602	0.00000	82.1036	0.0000	0.0000	0.000
0.0423	0.9109	0.91029	0.43295	-0.01081	80.1788	-4.4121	-10.4436	-642.242
0.0907	0.1084	0.87587	0.45648	-0.06266	89.2660	-3.5470	-13.9158	-1021.67
0.1356	0.2161	0.86962	0.447920	-0.04631	89.5867	-4.3210	-3.7790	-974.284
0.1744	0.7294	0.90078	0.423220	-0.00269	83.4177	-8.2102	1.1490	-682.723
0.2262	0.3245	0.88327	0.449130	-0.00693	88.2951	-8.6416	0.6350	-763.081
0.3171	0.4331	0.90049	0.401220	-0.01658	86.6976	-13.2801	-0.0456	-832.991
0.3581	0.6419	0.89094	0.379190	-0.00356	86.5922	-13.5289	0.0000	-832.811
0.4081	0.5418	0.87858	0.372940	-0.00655	88.9532	-14.0691	1.4203	-913.397
0.6273	0.0000	0.87151	0.365390	-0.01128	95.4347	-21.0949	0.0000	-374.721
0.7803	0.0583	0.88204	0.323350	-0.00270	95.2986	-27.3061	4.8844	-1142.23
1.0000	0.0000	0.65081	0.269340	0.00000	132.4192	0.0000	0.0000	0.000

<u>n-hexane(1) + THF(2) + Isopropanol(3)</u>								
0.0000	0.0000	0.78914	1.71568	0.00000	76.1588	0.0000	0.0000	0.000
0.0000	0.7692	0.90487	0.71058	-0.02820	76.6022	-4.1961	0.0000	258.422

0.0000	1.0000	0.87738	0.44566	0.00000	82.1878	0.0000	0.0000	0.000
0.0418	0.8983	0.88532	0.51046	-0.00390	81.2957	-2.6385	33.8796	125.565
0.0732	0.0874	0.86644	1.42353	-0.07520	72.7791	-8.0365	12.4632	-64.756
0.1135	0.1809	0.87493	1.30976	-0.01170	74.5507	-9.0939	12.7357	218.846
0.1695	0.7809	0.89583	0.55889	-0.01120	81.5135	-8.4809	10.1572	172.201
0.1994	0.2859	0.87241	1.00079	-0.06320	78.7273	-10.4028	7.3701	295.041
0.2949	0.4028	0.88122	0.76323	-0.01410	82.4183	-12.8029	-6.2672	415.281
0.3581	0.6419	0.88731	0.35925	-0.02290	86.4546	-13.7728	0.0000	-389.409
0.4021	0.5338	0.88439	0.44623	-0.00950	87.0558	-14.9847	8.6313	-27.918
0.5643	0.0000	0.86949	0.88095	-0.01810	86.0469	-21.9396	0.0000	477.427
0.7443	0.0556	0.85623	0.54679	-0.02110	93.6421	-24.8317	37.6906	257.009
1.0000	0.0000	0.65011	0.26843	0.00000	132.5622	0.0000	0.0000	0.000

**n-hexane(1) + Isopropanol(2) + Benzene(3)**

0.0000	0.0000	0.86721	0.55702	0.00000	90.0704	0.0000	0.0000	0.000
0.0000	0.8386	0.87021	1.44323	-0.08490	72.3952	-6.1518	0.0000	-177.491
0.0000	1.0000	0.78726	1.71515	0.00000	76.3475	0.0000	0.0000	0.000
0.0373	0.9627	0.86226	1.53236	-0.15180	74.5609	-7.6035	-13.1609	-627.879
0.0888	0.1273	0.79225	0.63715	-0.04170	96.6042	4.4503	6.3084	282.883
0.1299	0.2485	0.80115	0.78114	-0.02620	93.2195	0.9562	-16.3062	448.014
0.1522	0.7638	0.84725	1.29236	-0.10530	77.3967	-8.7447	9.5751	22.614
0.2125	0.3656	0.81324	0.86835	-0.05080	90.0601	-4.1595	5.7224	415.376
0.2918	0.4782	0.83011	0.98428	-0.04210	86.5671	-9.5374	7.6181	424.145
0.3174	0.6826	0.82903	1.18121	-0.07490	82.4792	-11.9145	0.0000	291.621
0.3682	0.5866	0.81813	0.98325	-0.14710	86.1924	-11.7113	18.0968	215.594
0.6273	0.0000	0.74309	0.35329	-0.02290	111.9172	-5.2118	0.0000	-66.679
0.7713	0.0691	0.72412	0.40105	-0.01390	114.7461	-7.6567	23.9962	392.433
1.0000	0.0000	0.64688	0.26891	0.00000	133.2241	0.0000	0.0000	0.000

313K

**n-hexane(1) + THF(2) + Benzene(3)**

0.0000	0.0000	0.86371	0.45365	0.00000	90.4354	0.0000	0.0000	0.000
0.0000	0.8125	0.90051	0.37512	-0.01110	81.3262	-18.5063	0.0000	-164.014
0.0000	1.0000	0.86801	0.37062	0.00000	83.0751	0.0000	0.0000	0.000
0.0423	0.9109	0.90699	0.35426	-0.01280	80.4705	-19.4838	-15.1219	-218.889
0.0907	0.1084	0.87038	0.42233	-0.00120	89.8272	-16.7559	3.4608	-18.783
0.1356	0.2161	0.86411	0.39552	-0.00500	90.1595	-27.7767	1.1374	-49.374
0.1744	0.7294	0.89334	0.33745	-0.01030	84.1124	-25.9821	-0.0403	-215.764
0.2262	0.3245	0.87732	0.35621	-0.01180	88.8939	-30.0565	0.4763	-174.711
0.3171	0.4331	0.89388	0.32798	-0.00740	87.3388	-32.0838	0.9391	-251.151
0.3581	0.6419	0.88334	0.30012	-0.00730	87.3372	-34.0717	0.0000	-279.677
0.4081	0.5418	0.86911	0.29278	-0.01010	89.9225	-37.3332	1.6130	-294.887
0.6273	0.0000	0.86181	0.30244	-0.01160	96.5099	-47.6831	0.0000	-173.506
0.7803	0.0583	0.87617	0.24289	-0.01350	95.9372	-52.0489	6.6878	-542.306
1.0000	0.0000	0.63114	0.19421	0.00000	136.5465	0.0000	0.0000	0.000

**n-hexane(1) + THF(2) + Isopropanol(3)**

0.0000	0.0000	0.76638	1.27737	0.00000	78.4336	0.0000	0.0000	0
0.0000	0.7692	0.88644	0.56226	-0.01530	78.1948	-4.3427	0.0000	218.459
0.0000	1.0000	0.86077	0.36754	0.00000	83.7738	0.0000	0.0000	0.000
0.0418	0.8983	0.87339	0.40023	-0.04510	81.9933	-3.3244	15.2812	46.372
0.0732	0.0874	0.85419	1.10862	-0.00930	73.8218	-9.4698	20.1935	1.359
0.1135	0.1809	0.85891	0.95923	-0.02940	75.8591	-10.3436	10.9064	126.619
0.1695	0.7809	0.88123	0.40925	-0.03810	82.8641	-9.5283	4.9256	-41.849
0.1994	0.2859	0.85785	0.77326	-0.02630	80.0635	-11.8652	8.1458	331.663
0.2949	0.4028	0.86832	0.55309	-0.03570	83.6381	-14.6487	6.5122	270.563
0.3581	0.6419	0.87219	0.29236	-0.00990	88.4537	-15.0011	0.0000	-284.787
0.4021	0.5338	0.87023	0.34551	-0.00720	88.4797	-11.9155	9.6469	-25.376
0.5643	0.0000	0.85621	0.64235	-0.01880	87.3815	-24.9291	0.0000	416.829
0.7443	0.0556	0.84123	0.39923	-0.01480	95.2879	-28.1267	41.3744	307.357
1.0000	0.0000	0.62236	0.18544	0.00000	138.4726	0.0000	0.0000	0.000

**n-hexane(1)+Isopropanol(2)+Benzene(3)**

0.0000	0.0000	0.85025	0.45402	0.00000	91.8671	0.0000	0.0000	0.000
0.0000	0.8386	0.85324	1.10998	-0.02940	73.8351	-7.0401	0.0000	-152.757
0.0000	1.0000	0.76302	1.27135	0.00000	78.7659	0.0000	0.0000	0.000
0.0373	0.9627	0.84725	1.16818	-0.08130	75.8818	-8.9287	13.3635	-585.703
0.0888	0.1273	0.76752	0.50618	-0.02810	99.7064	-5.2975	6.4704	317.094
0.1299	0.2485	0.78623	0.59318	-0.02910	94.9885	0.2224	6.3757	378.702
0.1522	0.7638	0.83113	0.99313	-0.04420	78.8978	-10.1647	13.6061	91.478
0.2125	0.3656	0.80823	0.65511	-0.04050	90.6183	-6.5284	5.5174	351.337
0.2918	0.4782	0.81903	0.74712	-0.01930	87.7383	-11.6991	8.3328	451.002
0.3174	0.6826	0.81525	0.87819	-0.04830	83.8732	-14.0899	0.0000	321.554
0.3682	0.5866	0.80236	0.80613	-0.02830	87.8866	-13.7405	30.7717	502.817
0.6273	0.0000	0.72896	0.26881	-0.01640	114.0865	-7.4895	0.0000	-13.672
0.7713	0.0691	0.71098	0.29011	-0.01290	116.8667	-10.6345	20.3298	269.316
1.0000	0.0000	0.61891	0.81512	0.00000	139.2448	0.0000	0.0000	0.000

**323K**

**n-hexane(1)+THF(2)+Benzene(3)**

0.0000	0.0000	0.84478	0.34457	0.00000	65.9857	-26.4762	0.0000	0.000
0.0000	0.8125	0.88318	0.32517	-0.01990	64.6796	-21.3978	0.0000	-486.661
0.0000	1.0000	0.85233	0.28232	0.00000	61.4615	-23.1405	0.0000	0.000
0.0423	0.9109	0.88362	0.31818	-0.01480	64.4918	-22.7806	77.8407	-419.524
0.0907	0.1084	0.86221	0.26531	-0.01070	67.4108	-28.4104	-19.9734	-1343.097
0.1356	0.2161	0.85025	0.26633	-0.00690	66.241	-30.8326	-4.1974	-1206.613
0.1744	0.7294	0.87589	0.29112	-0.01150	65.8152	-29.0312	11.0882	-565.435
0.2262	0.3245	0.86345	0.26023	-0.00970	67.3391	-33.0986	-0.3019	-1048.391
0.3171	0.4331	0.87669	0.25316	-0.01050	68.4435	-35.3705	1.9522	-871.651
0.3581	0.6419	0.86562	0.26011	-0.00320	66.7812	-37.2989	0.0000	-648.225
0.4081	0.5418	0.85851	0.24495	-0.01260	67.0939	-40.1004	12.5098	-806.567
0.6273	0.0000	0.85288	0.22951	-0.03740	70.9361	-50.7159	0.0000	-954.611
0.7803	0.0583	0.86795	0.20252	-0.02870	72.9574	-55.3562	26.0374	-963.125
1.0000	0.0000	0.62002	0.13853	0.00000	53.4333	-85.5617	0.0000	0.000

**n-hexane(1)+THF(2)+Isopropanol(3)**

0.0000	0.0000	0.74681	1.02563	0.00000	80.4756	0.0000	0.0000	0.000
0.0000	0.7692	0.86997	0.43393	-0.02120	79.7017	-4.0858	0.0000	208.816
0.0000	1.0000	0.85056	0.28401	0.00000	84.7794	0.0000	0.0000	0.000
0.0418	0.8983	0.85522	0.29112	-0.01140	83.5485	-3.2721	-9.5473	-144.697
0.0732	0.0874	0.83675	0.86623	-0.02940	75.2612	-9.9339	16.9631	-56.122
0.1135	0.1809	0.84187	0.85029	-0.02290	77.3945	-10.5836	18.9116	438.344
0.1695	0.7809	0.86484	0.34188	-0.01710	84.4344	-9.1418	10.5302	191.678
0.1994	0.2859	0.83919	0.61009	-0.02620	81.8439	-11.6861	8.5275	381.562
0.2949	0.4028	0.85247	0.44123	-0.02340	85.1932	-14.5005	8.3844	382.054
0.3581	0.6419	0.86142	0.21025	-0.00310	89.5596	-14.8048	0.0000	-434.324
0.4021	0.5338	0.85764	0.26818	-0.00390	89.7711	-16.8407	11.3245	41.227
0.5643	0.0000	0.84563	0.50325	-0.02040	88.4233	-25.5084	0.0000	558.996
0.7443	0.0556	0.83236	0.31856	-0.00380	96.3034	-28.5403	22.1191	458.109
1.0000	0.0000	0.61661	0.13621	0.00000	139.7642	0.0000	0.0000	0.000

**n-hexane(1)+Isoprpanol(2)+Benzene(3)**

0.0000	0.0000	0.83825	0.34432	0.00000	93.1822	0.0000	0.0000	0.000
0.0000	0.8386	0.84013	0.89123	-0.02370	74.9873	-7.6841	0.0000	-159.861
0.0000	1.0000	0.74512	1.02486	0.00000	80.6582	0.0000	0.0000	0.000
0.0373	0.9627	0.83216	0.97814	-0.02780	77.2578	-9.5012	48.9479	-479.081
0.0888	0.1273	0.75016	0.38856	-0.02390	102.0245	6.1696	7.2302	365.693
0.1299	0.2485	0.77213	0.44632	-0.04020	96.7231	0.4102	5.4041	342.582
0.1522	0.7638	0.81523	0.78116	-0.05130	80.4366	-10.4875	12.9818	72.239
0.2125	0.3656	0.79215	0.50919	-0.03980	92.4577	-6.3598	5.7603	396.026
0.2918	0.4782	0.80317	0.55113	-0.05810	89.4708	-11.7583	6.8782	325.168
0.3174	0.6826	0.80106	0.72615	-0.01680	85.3591	-14.5323	0.0000	466.427
0.3682	0.5866	0.79711	0.63476	-0.03230	88.4654	-15.0697	31.9627	514.491
0.6273	0.0000	0.71532	0.20188	-0.01220	116.2765	-7.0443	0.0000	17.475
0.7713	0.0691	0.70023	0.21313	-0.01810	118.6608	-10.7304	18.5262	237.487
1.0000	0.0000	0.61011	0.13668	0.00000	141.2532	0.0000	0.0000	0.000

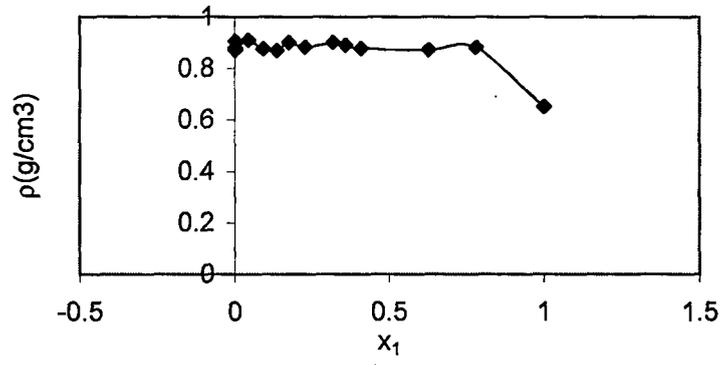


Fig. 1(a)

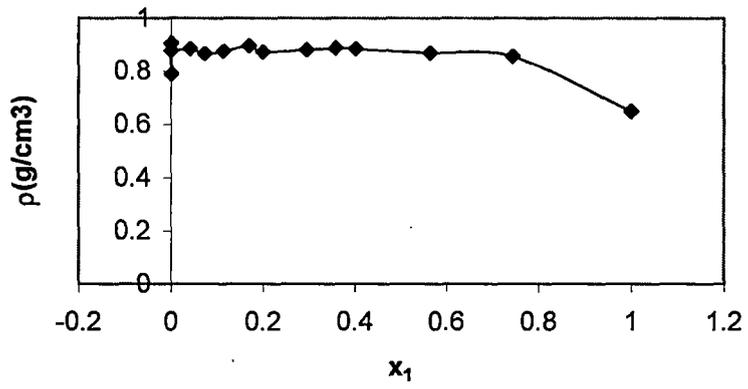


Fig. 1(b)

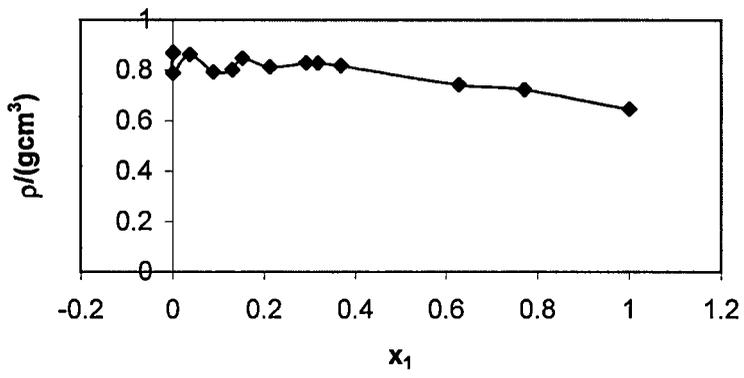


Fig. 1(c)

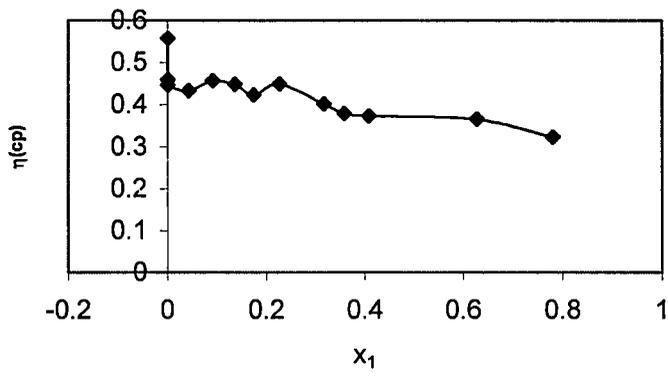


Fig. 2(a)

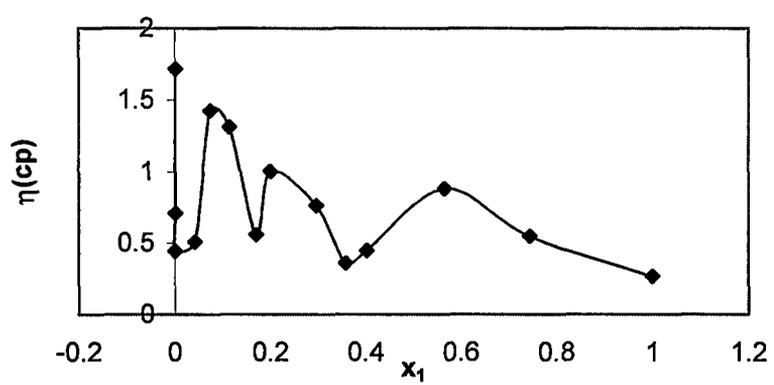


Fig. 2(b) at 303K

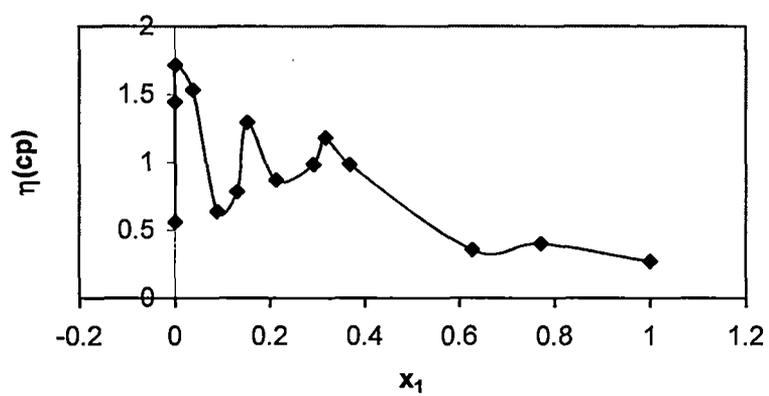


Fig. 2(c) at 303K

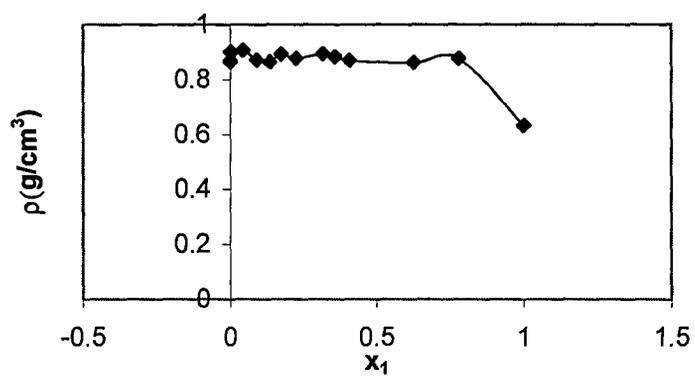


Fig. 1(a) at 313K

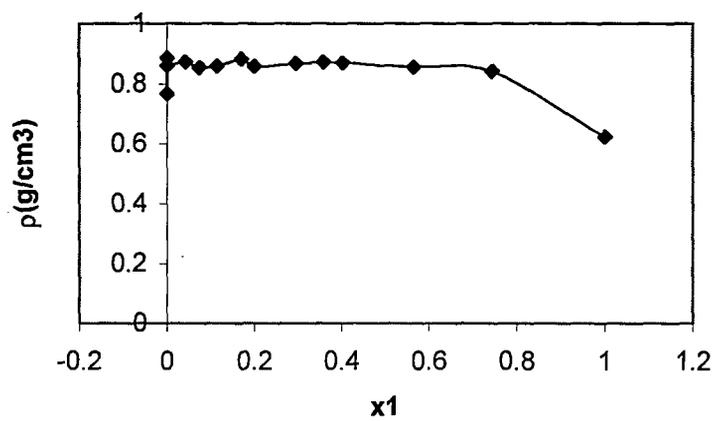


Fig. 1(b) at 313K

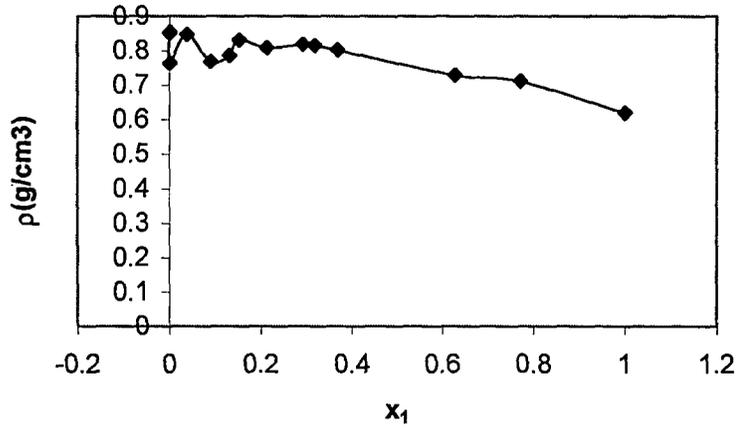


Fig. 1(c) at 313K

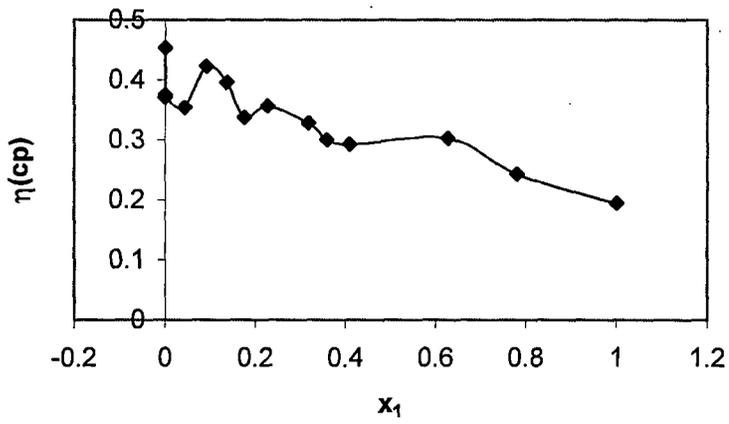


Fig. 2(a) at 313K

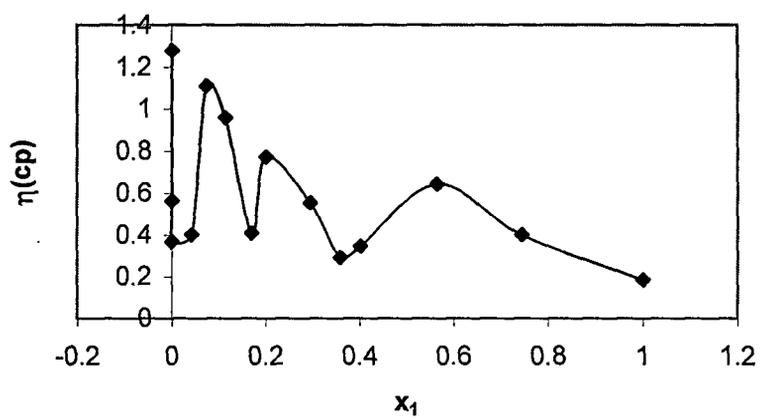


Fig. 2(b) at 313K

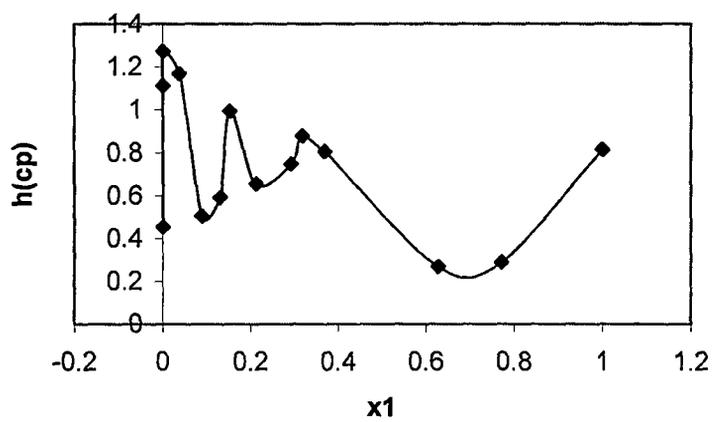


Fig. 2(c) at 313K

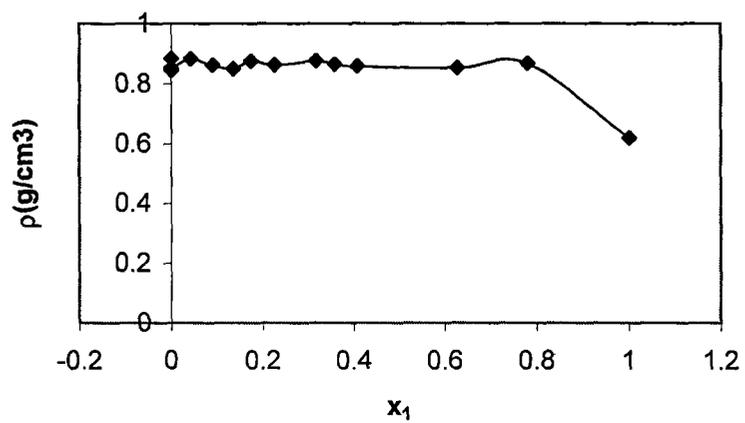


Fig. 1(a) at 323K

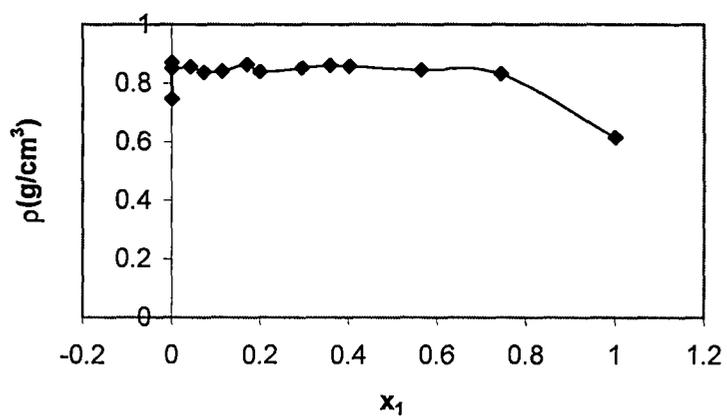


Fig. 1(b) at 323K

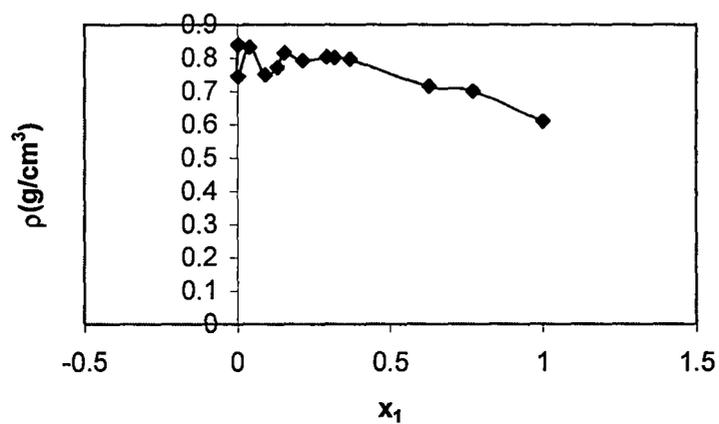


Fig. 1(c) at 323K

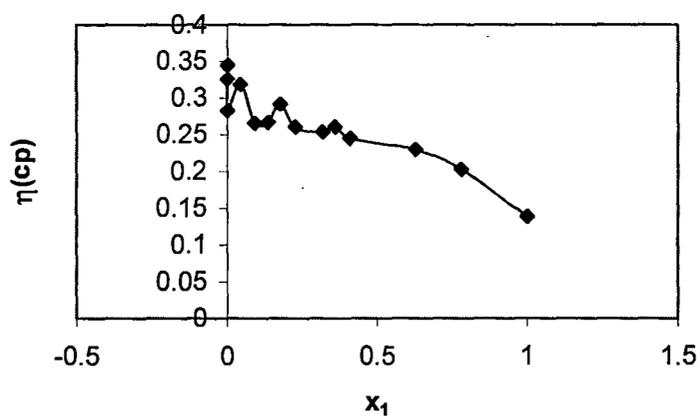


Fig. 2(a) at 323K

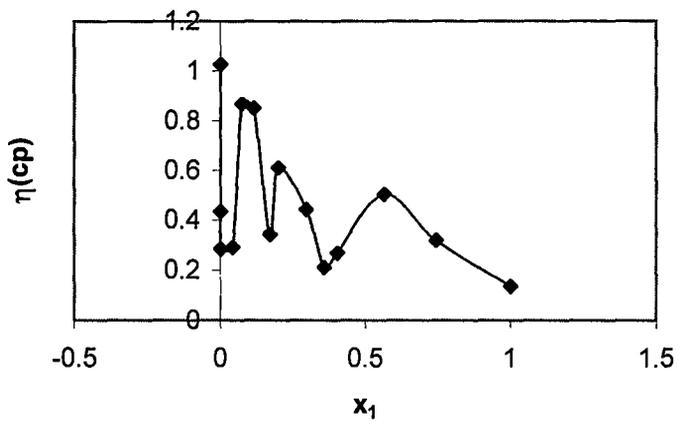


Fig. 2(b) at 323K

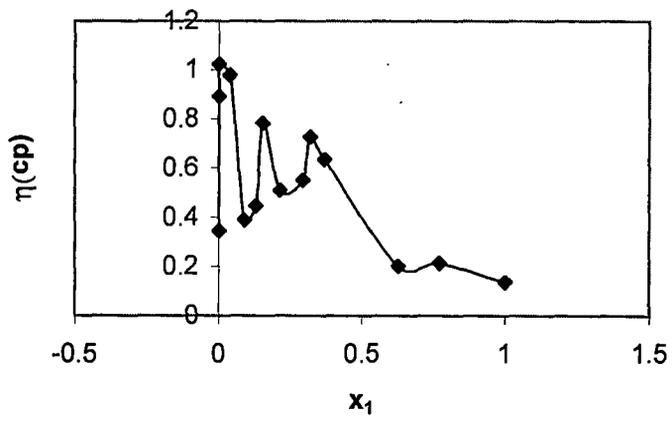


Fig. 2(c) at 323K

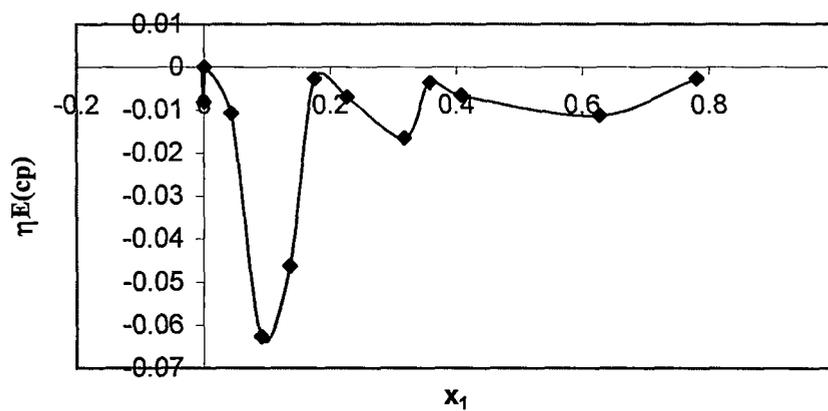


Fig. 3(a) at 303K

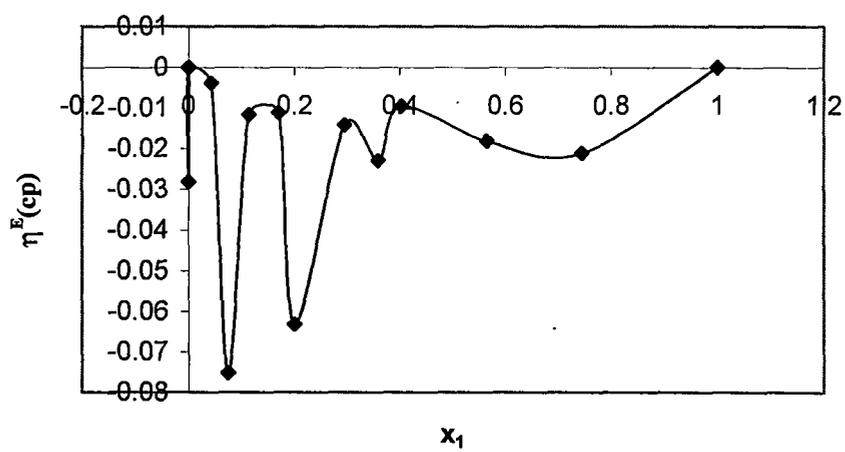


Fig. 3(b) at 303K

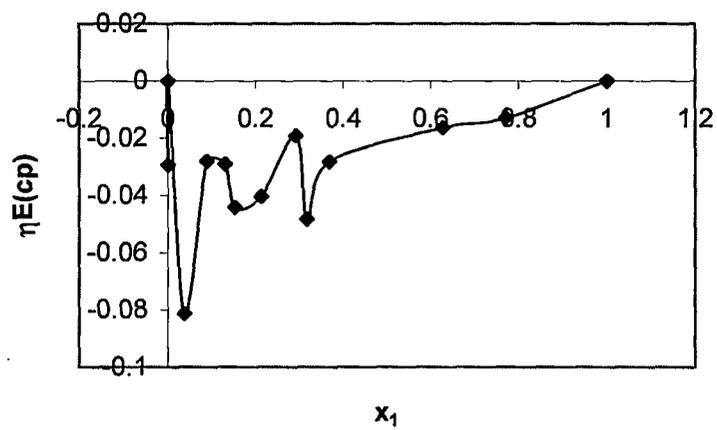


Fig. 3(c) at 303K

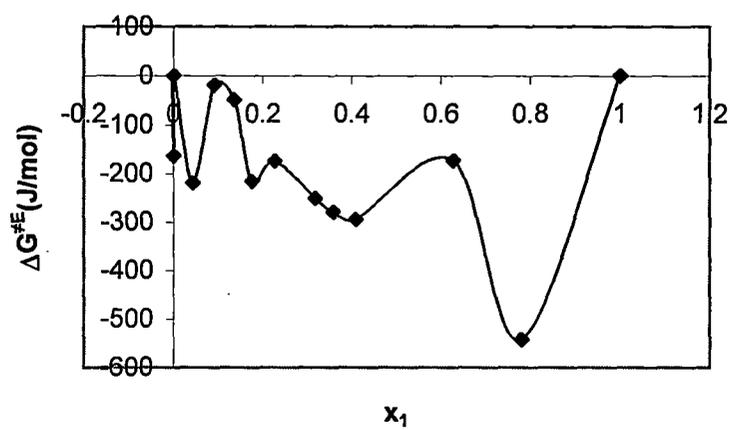


Fig. 4(a) at 303K

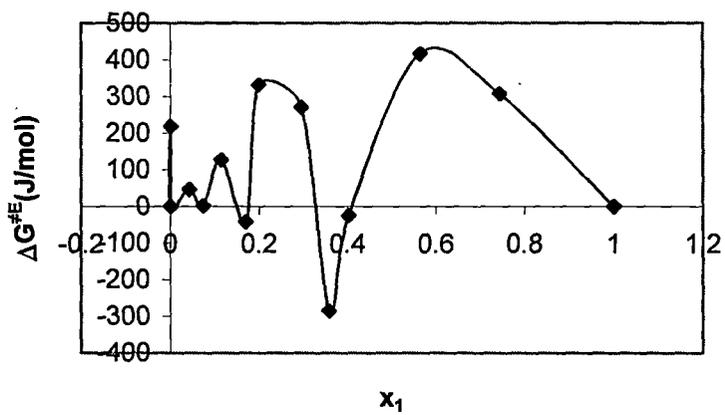


Fig. 4(b) at 303K

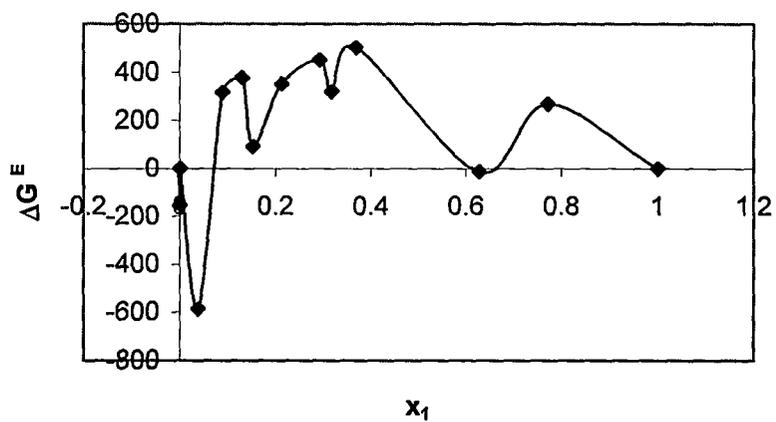


Fig. 4(c) at 303K

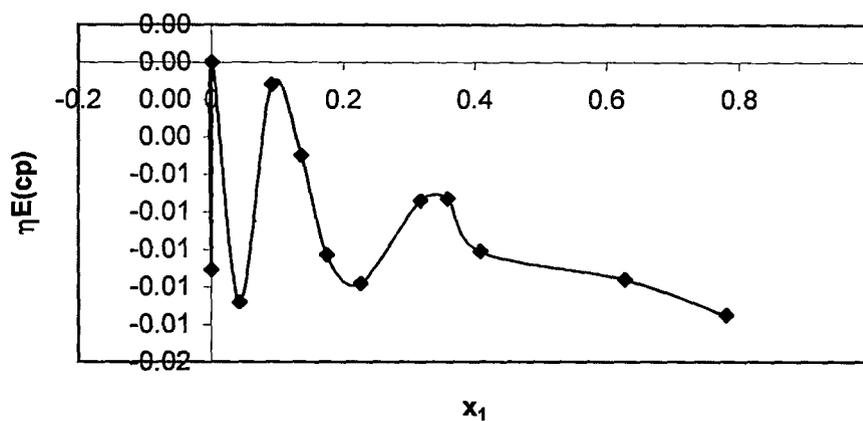


Fig. 3(a) at 313K

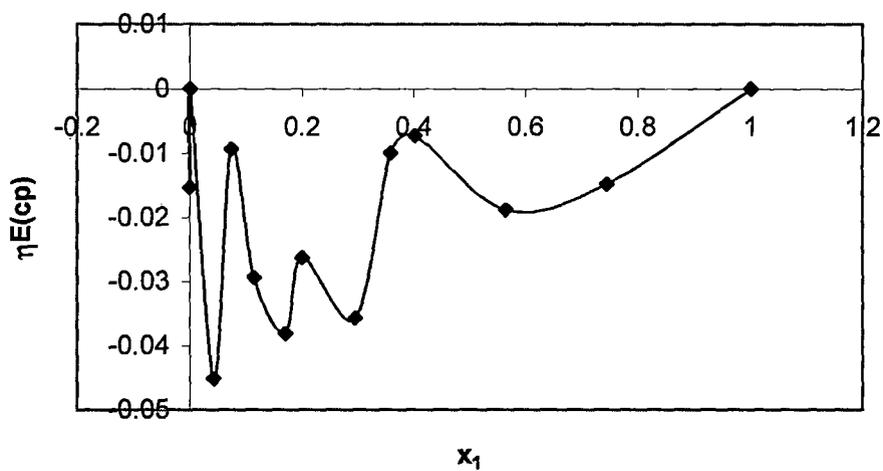


Fig. 3(b) at 313K

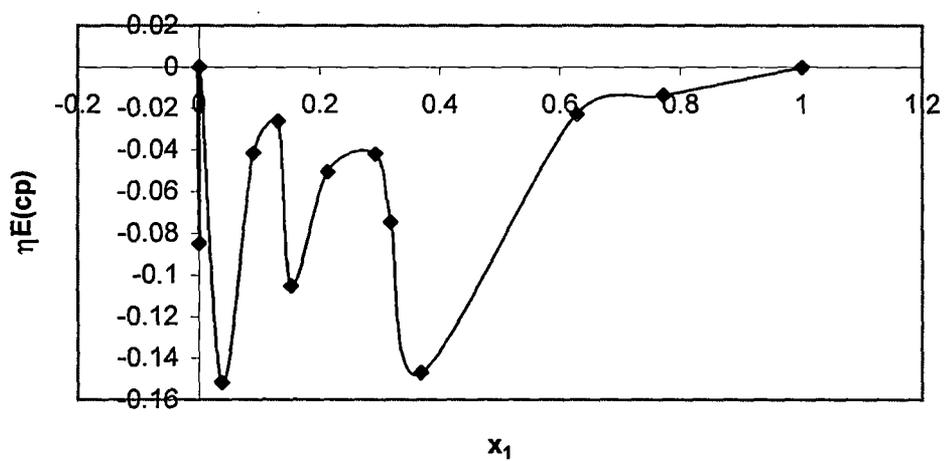


Fig. 3(c) at 313K

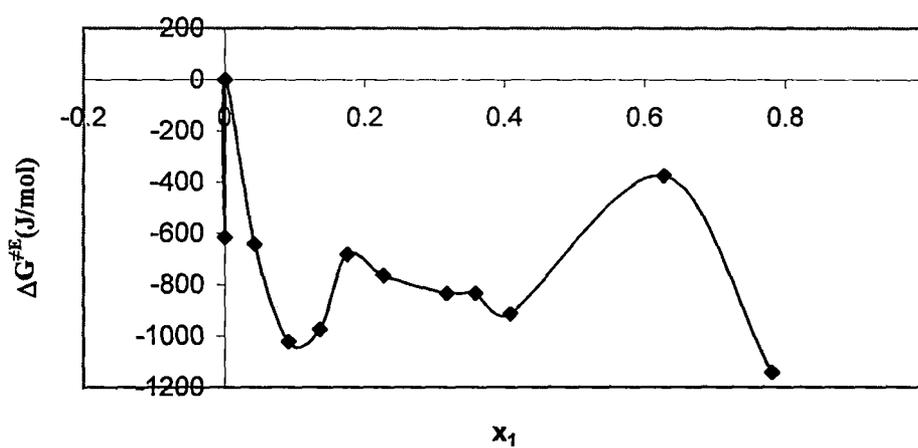


Fig. 4(a) at 313K

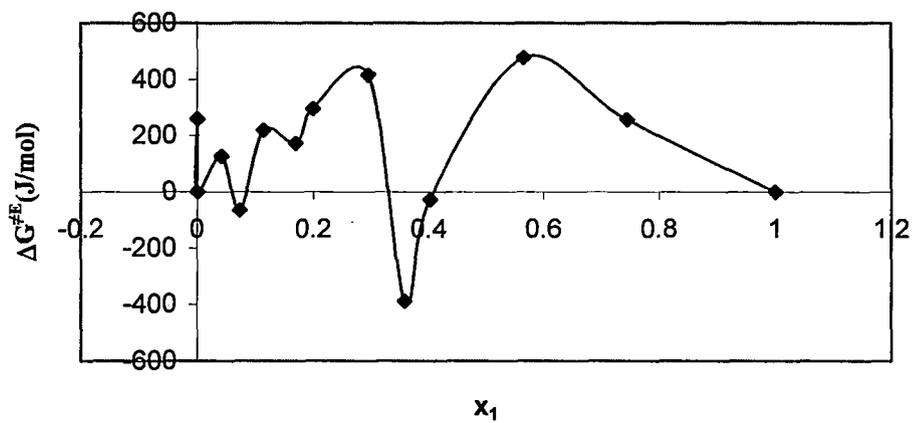


Fig. 4(b) at 313K

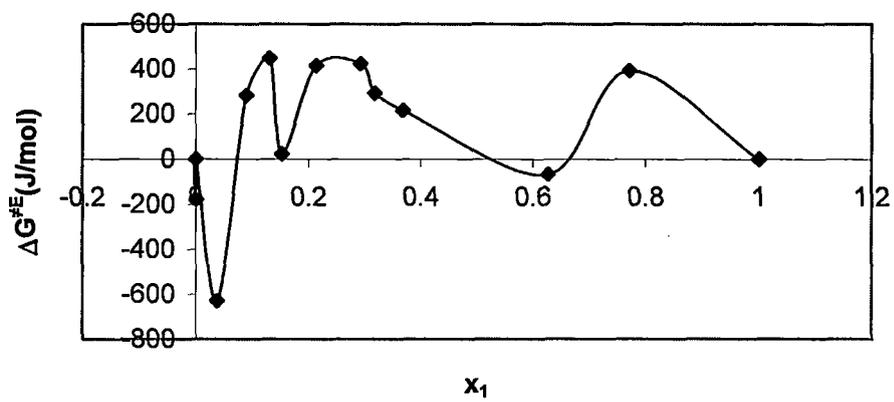


Fig. 4(c) at 313K

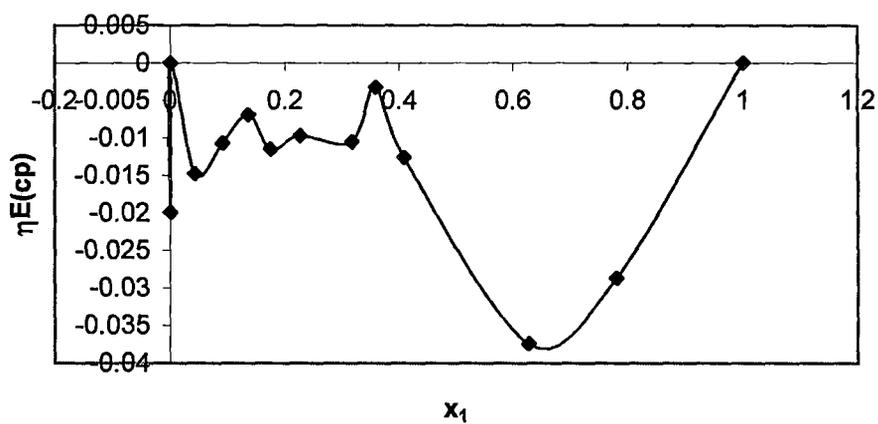


Fig. 3(a) at 323K

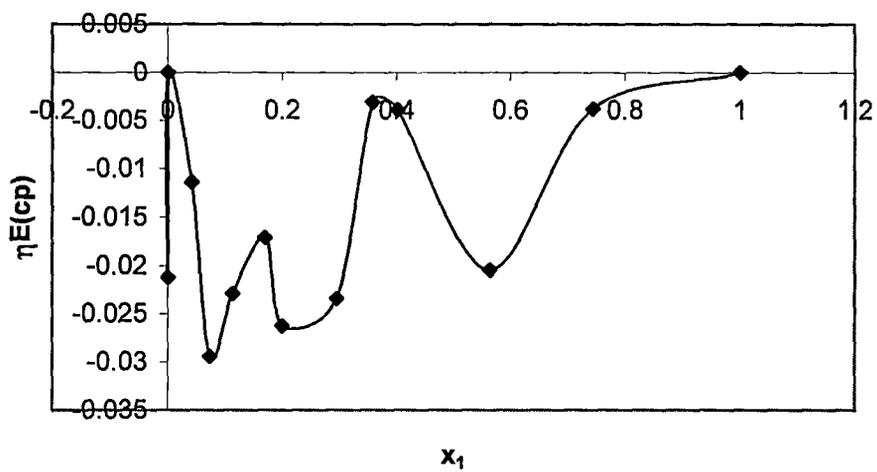


Fig. 3(b) at 323K

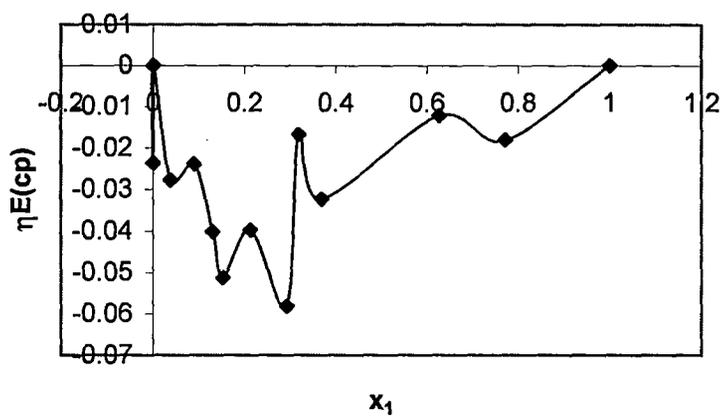


Fig. 3(c) at 323K

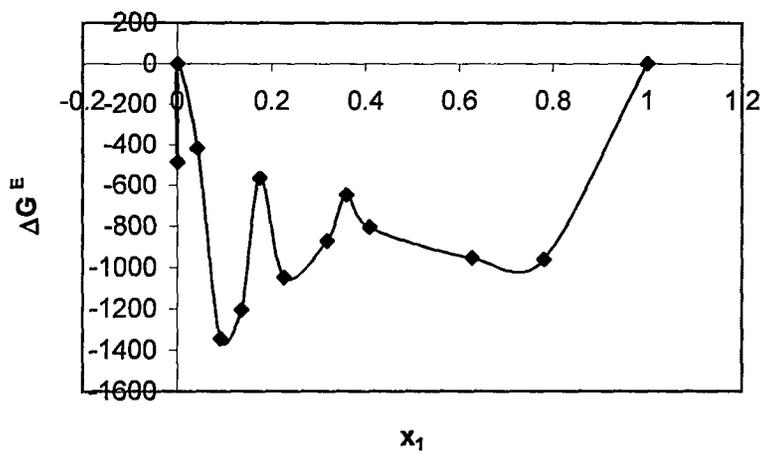


Fig. 4(a) at 323K

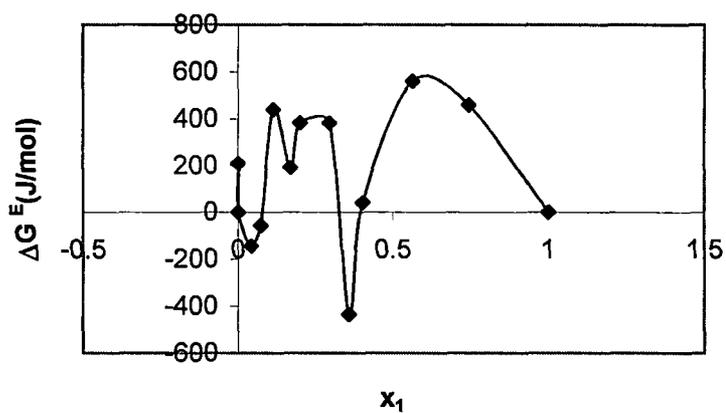


Fig. 4(b) at 323K

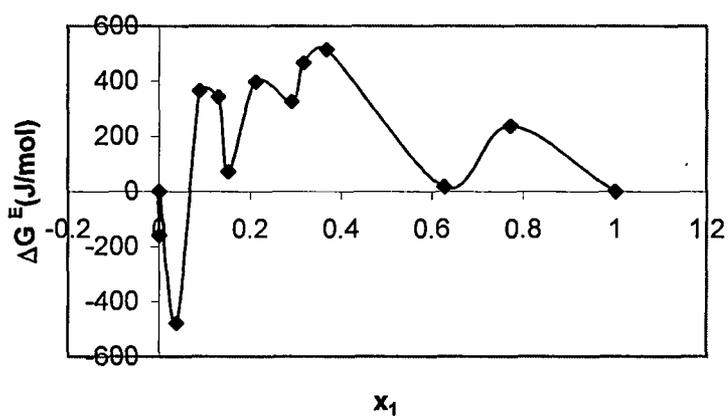


Fig. 4(c) at 323K

- a → n-hexane (1) + THF (2) + benzene (3)  
 b → n-hexane (1) + THF (2) + isopropanol (3)  
 c → n-hexane(1) + isopropanol (2) + benzene(3)

## CHAPTER IX

### **Ion-Solvent and Ion-Ion Interactions of Resorcinol in Mixed 1,4-Dioxane+Water Systems at Different Temperatures**

#### **ABSTRACT**

The densities, viscosities and ultrasonic speeds of resorcinol in various mass % of 1,4-dioxane + water mixtures and pure 1,4-dioxane have been measured at 303.15, 313.15 and 323.15 K. Apparent molar volumes ( $V_\phi$ ) and viscosity B-coefficient of that compound are obtained from those data supplemented with densities and viscosities respectively. The limiting apparent molar volumes ( $V_\phi^0$ ) and experimental slopes ( $S_v^*$ ) derived 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 and the derived parameters B and A have also been interpreted in terms of ion-solvent and ion-ion interactions respectively. The structure making/breaking capacities of resorcinol in the studied solvent systems have been discussed. The compressibilities obtained from the data supplemented with their ultrasonic speeds indicate the electrostriction of the solvent molecules around the ions.

#### **9.1 Introduction**

Studies on densities, viscosities and ultrasonic speeds of electrolytic solutions are of great help in characterizing the structure and properties of solutions. Various types of interactions exist between the ions in solutions and of these ion-ion and ion-solvent interactions are of current interest in all branches of Chemistry. These interactions help in better understanding of the nature of the solute and solvent, i.e. whether the solute modifies or distorts the structure of the solvent.

1,4-dioxane and its aqueous mixtures are very important solvents widely used in various industries. It is a good industrial solvent and figures

prominently in the high-energy battery technology and has also found its application in the organic synthesis as manifested from the physico-chemical studies in these media<sup>1-8</sup> In the present work, an attempt has been made to provide an unequivocal interpretation of ion-solvent and ion-ion interactions prevailing in the studied electrolytic solutions. Several workers have reported volumetric, viscometric and ultrasonic studies of this compound in aqueous solutions<sup>9-13</sup> but such studies in pure 1,4-dioxane and its aqueous mixtures are still scanty.

## 9.2 EXPERIMENTAL

1,4-dioxane, Merck, India, was kept several days over Potassium hydroxide (KOH), refluxed for 24 hours and distilled over lithium aluminium hydride ( $\text{LiAlH}_4$ ) described earlier<sup>1</sup>. Resorcinol (A.R.) was purified by the reported procedure<sup>14</sup> and the compound was dried and stored in a vacuum desiccator.

The density ( $\rho$ ) and viscosity ( $\eta$ ) of resorcinol in pure 1,4-dioxane and different mass % of 1,4-dioxane + water mixtures at various temperatures were determined by a Sprengel type pycnometer and suspended-level Ubbelohde<sup>15</sup> viscometer respectively described in detail earlier<sup>16</sup>.

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, described in detail elsewhere<sup>17,18</sup>. The various salt solutions studied here were made by mass and the conversion of molality in molarity was done<sup>19</sup>.

The experimental values of concentrations(c), densities ( $\rho$ ), viscosities ( $\eta$ ) and derived parameters of various temperatures are recorded in table 1.

### 9.3 Results & Discussion

The apparent molar volumes ( $V_\phi$ ) were determined from the solution densities using the following equation:

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

Where  $M$  is the molecular weight of the solute,  $c$  the molarity of the solution and the other symbols have their usual significance.

The limiting apparent molar volumes ( $V_\phi^0$ ) were calculated using the least square treatment to the plots of  $V_\phi$  vs.  $c^{1/2}$  using the following Masson equation [20],

$$V_\phi = V_\phi^0 + S_v^* \sqrt{c} \quad (2)$$

Where  $V_\phi^0$  is the partial molar volume at infinite dilution and  $S_v^*$  the experimental slope. The plots of  $V_\phi$  against root of molar concentration ( $c^{1/2}$ ) were found to be linear with negative slopes. The values of  $V_\phi^0$  and  $S_v^*$  along with the standard errors were recorded in table 2.

As the investigation systems are characterized by hydrogen bond, the ion-solvent and ion-ion interactions can be interpreted in terms of structural changes, which arise due to hydrogen bond interactions present between various components of the solvent and solution systems.

To examine the ion-solvent interactions, the  $V_\phi^0$  can be used. Table 2 reveals that the  $V_\phi^0$  values are positive and increase with rise in temperature and decrease with increase in mass % of 1,4-dioxane in the mixtures. This indicates the presence of strong ion-solvent interaction and these interactions are strengthened with rise in temperature and weakened with increase in the amount of 1,4-dioxane in the mixed solvent under investigation, suggesting larger electrostriction at higher temperature and lower mass % of 1,4-dioxane

in the mixture. Similar results were obtained for some 1:1 electrolytes in aqueous DMF<sup>21</sup> and aqueous THF (1).

It is evident from table 2 that the  $S_v^*$  values are negative for all temperatures for aqueous mixtures of 1,4-dioxane but positive for pure 1,4-dioxane. Since  $S_v^*$  is a measure of ion-ion interactions, the results indicate the presence of weak ion-ion interactions. These interactions, however, decrease with rise in temperature, which is attributed to more violent thermal agitation at higher temperature, resulting in diminishing the force of ion-ion interactions (ionic dissociation)<sup>22</sup>. The  $S_v^*$  values increase with increase in mass% of 1,4-dioxane in the mixture which is caused to the decrease in solvation of ions, i.e., more and more solute is accommodated in the void space left in the packing of large associated solvent molecules with the addition of 1,4-dioxane to the mixture.

The variation of  $V_\phi^0$  with temperature of resorcinol in solvent mixtures follows the polynomial-

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

Over the temperature range under investigation, where T is the temperature in degree kelvin.

Values of coefficients of the above equation for resorcinol for different mass% of 1,4-dioxane + water mixtures and recorded in Table 3.

From the values of coefficients the following equations are obtained:

10 mass% 1,4-dioxane + Water mixture.

$$V_\phi^0 = -1123.388 / \text{cm}^3 \text{ mol}^{-1} + 7.229 T / \text{cm}^3 \text{ mol}^{-1} \text{ K}^{-1} - 0.010 T^2 / \text{cm}^3 \text{ mol}^{-1} \text{ K}^{-2} \quad (4)$$

20 mass% 1,4-dioxane + Water mixture.

$$V_\phi^0 = -74.863 / \text{cm}^3 \text{ mol}^{-1} + 1.018 T / \text{cm}^3 \text{ mol}^{-1} \text{ K}^{-1} - 0.001 T^2 / \text{cm}^3 \text{ mol}^{-1} \text{ K}^{-2} \quad (5)$$

30 mass% 1,4-dioxane + Water mixture.

$$V_{\phi}^0 = -216.274 / \text{cm}^3 \text{mol}^{-1} + 1.894 T / \text{cm}^3 \text{mol}^{-1} \text{K}^{-1} - 0.002 T^2 / \text{cm}^3 \text{mol}^{-1} \text{K}^{-2} \quad (6)$$

100 mass% 1,4-dioxane + Water mixture.

$$V_{\phi}^0 = -500.304 / \text{cm}^3 \text{mol}^{-1} + 3.298 T / \text{cm}^3 \text{mol}^{-1} \text{K}^{-1} - 0.005 T^2 / \text{cm}^3 \text{mol}^{-1} \text{K}^{-2} \quad (7)$$

The apparent molar expansibilities ( $\Phi_E^0$ ) can be obtained by the following equation.

$$\Phi_E^0 = (\delta V_{\phi}^0 / \delta T)_P = a_1 + 2a_2 T \quad (8)$$

The values of  $\Phi_E^0$  of the studied compound at 303.15, 313.15 and 323.15K are determined and reported in Table 4.

It is found from Table 4 that the values of  $\Phi_E^0$  decrease with rise in temperature as well as with increase in mass% of 1,4-dioxane in the mixture, which can be ascribed to the absence of caging or packing effect<sup>23</sup>.

During the past few years it has been emphasized by different workers that  $S_v^*$  is not the sole criterion for determining the structure-making or breaking nature of any solute. Hepler<sup>24</sup> developed a technique of examining the sign of  $(\delta^2 V_{\phi}^0 / \delta T^2)_P$  for solute in terms of long range structure-making and breaking capacity of the solute in the mixed solvent systems using the general thermodynamic expression,

$$(\delta c_P / \delta P)_T = - (\delta^2 V_{\phi}^0 / \delta T^2)_P \quad (9)$$

On the basis of this expression, it has been deduced that the structure making solutes should have positive value, whereas structure-breaking solutes negative values. In our present investigation, it is evident from Table 4 that the  $(\delta^2 V_{\phi}^0 / \delta T^2)_P$  values are negative for resorcinol and for all mass% of 1,4-dioxane + water mixtures investigated here, suggesting thereby that resorcinol acts as structure breaker in these solvent mixtures.

The viscosity data of solutions for resorcinol in 10, 20, 30 mass% of 1,4-dioxane + water mixture and pure 1,4-dioxane have been analyzed using the Jones-Dole<sup>25</sup> equation.

$$\eta / \eta_0 = 1 + A c^{1/2} + B c \quad (10)$$

$$(\eta / \eta_0 - 1) / c^{1/2} = A + B c^{1/2}, \text{ where } \eta = (k t - L / t) \rho$$

Where  $\eta_0$  and  $\eta$  are the viscosities of solvent/solvent mixtures and solution respectively. K and L are the constants for a particular viscometer. The values of A and B are estimated by computerized least squares method and recorded in Table 5.

A perusal of Table 5 shows that the values of the A coefficients are negative for 10 and 20 mass% of 1,4-dioxane and positive for 30 and 100 mass% of 1,4-dioxane for all temperatures. These results indicate the presence of weak ion-ion interactions and these interactions increase with the increase of 1,4-dioxane to the mixture.

It is also observed from Table 5 that the values of B-coefficient of resorcinol in the studied solvent systems are positive thereby suggesting the presence of strong ion-solvent interactions and these type of interactions are strengthened with rise in temperature and weakened with increase of mass% of 1,4-dioxane in the mixture. These conclusions are excellent agreement with that drawn from  $V_\phi^0$  values discussed earlier.

It has been reported by a number of workers that  $dB/dT$  is a better criterion<sup>26,27</sup> for determining the structure making/breaking nature of any solute rather than simply the value of B-coefficient. It is found from Table 5 that the values of B-coefficient increase with rise in temperature (Positive  $dB/dT$ ) suggesting structure-breaking tendency of resorcinol in the solvent systems. A similar result was reported by some workers<sup>28</sup> in the case of viscosity of some salts in propionic acid + ethanol mixtures.

Adiabatic compressibility ( $\beta$ ) was calculated from the following relation:

$$\beta = 1/u^2 \rho \quad (11)$$

Where  $\rho$  is the solution density and  $u$  is the sound velocity in the solution. The apparent molal adiabatic compressibility ( $\Phi_K$ ) of the liquid solutions was determined from the relation,

$$\Phi_K = M \beta / \rho_0 + 1000 (\beta \rho_0 - \beta_0 \rho) / m \rho \rho_0 \quad (12)$$

The limiting apparent molal adiabatic compressibility ( $\Phi_K^0$ ) was obtained by extrapolating the plots of  $\Phi_K$  versus the square root of molal concentration of the solute to zero concentration by the computerized least squares method.

$$\Phi_K = \Phi_K^0 + S_K^* m^{1/2} \quad (13)$$

where  $S_K^*$  is the experimental slope.

The values of  $u$ ,  $\beta$ ,  $\Phi_K$ ,  $\Phi_K^0$  and  $S_K^*$  are recorded in Table 6.

A perusal of table 6 shows that the  $\Phi_K^0$  values increase whereas  $S_K^*$  values decrease with the increase of mass% of 1,4-dioxane in the mixtures for the salt studied here. Since the values of  $V_\phi^0$  and  $S_v^*$  are measure of ion-solvent and ion-ion interactions respectively, the results are in good agreement with that drawn from the conclusion based on the values of  $\Phi_K^0$  and  $S_K^*$  explained here earlier. The same result was obtained by us<sup>29</sup> in case of studies on sound velocity of some salts in different mass% of tetrahydrofuran (THF) + water mixtures.

## 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.

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**Table 1: Concentration(c), Density ( $\rho$ ), Viscosity ( $\eta$ ), Apparent Molar Volume ( $V_\phi$ ) and  $(\eta/\eta_0 - 1)/\sqrt{c}$  of Resorcinol in pure 1,4-dioxane and different mass % of 1,4-dioxane + water mixture at different temperature.**

<u>10% mass of 1,4-dioxane + Water</u>				
$c / \text{mol cm}^{-3}$	$\rho / \text{g.cm}^{-3}$	$\eta/c_p$	$V_\phi / \text{cm}^3 \text{mol}^{-1}$	$(\eta / \eta_0 - 1) / \sqrt{c}$
<u>T = 303.15K</u>				
0.00696	1.00769	1.03758	115.98421	-0.14432
0.04872	1.00758	1.02551	112.58358	-0.10662
0.09048	1.00824	1.03581	103.84121	-0.04564
0.13224	1.00912	1.05069	98.94112	0.00123
0.17400	1.01037	1.07889	94.29936	0.06542
0.21575	1.01186	1.10903	90.34211	0.12054
T = 313.15K				
0.00694	1.00125	0.94077	123.54652	-1.00021
0.04851	1.00093	0.83336	118.51121	-0.85342
0.09014	1.00109	0.82462	112.78923	-0.65441
0.13168	1.00186	0.83508	106.02315	-0.51338
0.17331	1.00302	0.86198	100.31120	-0.38453
0.21502	1.00501	0.92907	92.90543	-0.20423
T = 323.15K				
0.00689	0.99751	0.68339	130.02543	-0.72798
0.04818	0.99706	0.69393	122.54321	-0.20922
0.08946	0.99722	0.76091	115.12037	0.15437
0.13074	0.99787	0.89312	108.67535	0.63042

0.17242	0.99911	1.07930	101.87342	1.16540
0.21397	1.00095	1.23543	94.87523	1.51023

**20% mass of 1,4-dioxane + Water**

T = 303.15K

0.00712	1.01637	1.22046	114.98541	-0.05432
0.04981	1.01629	1.21797	110.88871	-0.02961
0.09251	1.01647	1.22654	107.78321	0.00124
0.13519	1.01717	1.23913	102.87120	0.02897
0.17789	1.01868	1.25629	95.80971	0.05843
0.22059	1.02075	1.26989	89.00087	0.07609

T = 313.15K

0.00707	1.00995	0.94893	118.05435	0.00113
0.04951	1.00981	0.96814	112.98431	0.09142
0.09186	1.01005	0.99395	108.56321	0.15689
0.13432	1.01065	1.02309	104.28711	0.21354
0.17679	1.01185	1.06479	98.73584	0.29065
0.21967	1.01416	1.11135	90.33200	0.36543

T = 323.15K

0.00703	1.00354	0.85946	121.00652	-0.51652
0.04932	1.00342	0.81889	113.89012	-0.39836
0.09122	1.00359	0.81979	109.99872	-0.28966
0.13396	1.00412	0.85545	106.00067	-0.13055
0.17589	1.00541	0.90459	99.57092	0.01651
0.21793	1.00749	0.94864	91.99642	0.11985

**30% mass of 1,4-dioxane + Water**

T = 303.15K

0.00702	1.02019	1.43758	103.65571	0.10065
0.04913	1.02078	1.46349	95.56437	0.12001
0.91246	1.02177	1.48054	90.58478	0.12766
0.13336	1.02291	1.49722	87.67532	0.13765
0.17548	1.02415	1.51775	85.62294	0.15437
0.21758	1.02666	1.53258	78.65435	0.16094

T = 313.15K

0.00698	1.01628	1.28547	105.09876	0.10154
0.04895	1.01679	1.30914	97.68765	0.12226
0.09097	1.01769	1.32596	92.89043	0.13343
0.13284	1.01888	1.34016	88.98760	0.14098
0.17481	1.02024	1.36022	85.94978	0.16054
0.21672	1.02258	1.37875	79.65439	0.17542

T = 323.15K

0.00693	1.01063	1.10758	106.51690	0.10171
0.04859	1.01107	1.12788	99.60034	0.12224
0.09025	1.011886	1.14450	95.00654	0.14007
0.13184	1.013185	1.16071	89.65432	0.15654
0.17359	1.01431	1.17628	87.89543	0.17045
0.21493	1.01669	1.18991	80.99765	0.17995

**100% mass of 1,4-dioxane**

T = 303.15K

0.00694	1.02031	1.11085	47.45322	0.25399
0.04850	1.02259	1.15145	53.00011	0.26554
0.09025	1.02452	1.17821	57.55432	0.27654
0.13189	1.02608	1.20005	61.87762	0.28405
0.17356	1.02784	1.22222	62.98762	0.29654
0.21521	1.02921	1.24614	65.44322	0.31369

**T = 313.15K**

0.00691	1.01468	0.99899	49.49872	0.25445
0.04800	1.01689	1.03616	54.76542	0.26999
0.08939	1.01863	1.05918	60.47652	0.27654
0.13078	1.02019	1.08088	63.87651	0.28998
0.17206	1.02187	1.10407	64.99980	0.30996
0.21337	1.02334	1.12243	66.62787	0.31898

**T = 323.15K**

0.00682	1.00365	0.86213	50.65425	0.25506
0.04752	1.00581	0.89419	55.97865	0.27087
0.08839	1.00749	0.91465	61.88796	0.28007
0.12929	1.00908	0.93471	64.78313	0.29765
0.17021	1.01075	0.95499	65.81603	0.31765
0.21105	1.01219	0.97384	67.53009	0.33387

**Table 2: Limiting apparent molar volume ( $V_{\phi}^0$ ) and experimental slope ( $S_v^*$ ) for resorcinol in different mass% of 1,4-dioxane at different temperature.**

<u>Mass%</u>	$V_{\phi}^0 / \text{cm}^3 \text{mol}^{-1}$			$S_v^* / \text{cm}^2 \text{dm}^{1/2} \text{mol}^{-3/2}$		
	<u>303.15K</u>	<u>313.15K</u>	<u>323.15K</u>	<u>303.15K</u>	<u>313.15K</u>	<u>323.15K</u>
<u>of 1,4-dioxane</u>						
10	124.51048 ( $\pm 0.05$ )	133.52268 ( $\pm 0.02$ )	140.48141 ( $\pm 0.04$ )	-70.84036 ( $\pm 0.02$ )	-79.62990 ( $\pm 0.01$ )	-92.22016 ( $\pm 0.04$ )
20	123.77328 ( $\pm 0.01$ )	126.57666 ( $\pm 0.03$ )	129.14059 ( $\pm 0.02$ )	-64.83818 ( $\pm 0.04$ )	-67.81811 ( $\pm 0.03$ )	-71.16413 ( $\pm 0.02$ )
30	109.06017 ( $\pm 0.01$ )	111.31093 ( $\pm 0.05$ )	113.02003 ( $\pm 0.02$ )	-60.60275 ( $\pm 0.03$ )	-63.41065 ( $\pm 0.01$ )	-64.11416 ( $\pm 0.02$ )
100	43.10334 ( $\pm 0.01$ )	45.47524 ( $\pm 0.02$ )	46.85378 ( $\pm 0.01$ )	48.54575 ( $\pm 0.02$ )	47.50699 ( $\pm 0.04$ )	46.75033 ( $\pm 0.01$ )

(Standard errors are given in parenthesis.)

**Table 3: Values of various coefficients for resorcinol in different mass% of 1,4-dioxane + water mixtures.**

<u>Mass% of 1,4-dioxane</u>	$a_0 / \text{cm}^3 \text{mol}^{-1}$	$a_1 / \text{cm}^3 \text{mol}^{-1} \text{K}^{-1}$	$a_2 / \text{cm}^3 \text{mol}^{-1} \text{K}^{-2}$
10	-1123.388	7.229	-0.010
20	-74.863	1.018	-0.001
30	-216.274	1.894	-0.002
100	-500.304	3.298	-0.005

**Table 4: Limiting apparent molar expansibilities ( $\Phi_E^0$ ) for resorcinol in various mass% of 1,4-dioxane at different temperatures.**

Mass% of 1,4-dioxane	$\Phi_E^0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$			$(\delta\Phi_E^0 / \delta T)_P$
	<u>303.15K</u>	<u>313.15K</u>	<u>323.15K</u>	
10	1.00389	0.79854	0.59319	Negative
20	0.29231	0.26836	0.24442	Negative
30	0.24813	0.19393	0.13973	Negative
100	0.28686	0.18752	0.08819	Negative

**Table 5: Values of A and B parameters for resorcinol in different mass% of 1,4-dioxane at different temperatures.**

Mass% of 1,4-dioxane	A / $\text{cm}^{3/2} \text{ mol}^{-1/2}$			B / $\text{cm}^3 \text{ mol}^{-1}$		
	<u>303.15K</u>	<u>313.15K</u>	<u>323.15K</u>	<u>303.15</u>	<u>313.15K</u>	<u>323.15K</u>
10	-0.23358 ( $\pm 0.01$ )	-1.24201 ( $\pm 0.02$ )	-1.40559 ( $\pm 0.01$ )	0.69835 ( $\pm 0.01$ )	2.08046 ( $\pm 0.02$ )	5.95159 ( $\pm 0.02$ )
20	-0.09598 ( $\pm 0.01$ )	-0.10096 ( $\pm 0.02$ )	-0.72622 ( $\pm 0.02$ )	0.35102 ( $\pm 0.01$ )	0.92467 ( $\pm 0.02$ )	1.69798 ( $\pm 0.01$ )
30	0.08489 ( $\pm 0.01$ )	0.08193 ( $\pm 0.01$ )	0.07996 ( $\pm 0.02$ )	0.15712 ( $\pm 0.01$ )	0.18473 ( $\pm 0.02$ )	0.21173 ( $\pm 0.02$ )
100	0.23615 ( $\pm 0.02$ )	0.23437 ( $\pm 0.01$ )	0.22969 ( $\pm 0.01$ )	0.14799 ( $\pm 0.02$ )	0.17052 ( $\pm 0.02$ )	0.20609 ( $\pm 0.01$ )

(Standard errors are given in parenthesis.)

**Table 6: Mass% of 1,4-dioxane, Molality (m), Density ( $\rho$ ), Sound velocity (u), Adiabatic compressibility ( $\beta$ ), Apparent molaladiabatic compressibility ( $\Phi_K$ ), Limiting apparent adiabatic compressibility ( $\Phi_K^0$ ) and Experimental slope ( $S_K^*$ ) of resorcinol at 303.15K.**

Mass% of 1,4- dioxane	m / mol.Kg <sup>-1</sup>	$\rho$ / Kg.m <sup>-3</sup>	u /msec <sup>-1</sup>	$\beta \times 10^{10}$ / Pa <sup>-1</sup>	$\Phi_K \times 10^{10}$ / m <sup>3</sup> mol <sup>-1</sup> Pa <sup>-1</sup>	$\Phi_K^0 \times$ 10 <sup>10</sup> / m <sup>3</sup> mol <sup>-1</sup> Pa <sup>-1</sup>	$S_K^* \times 10^{10}$ m <sup>3</sup> mol <sup>-3/2</sup> Pa <sup>-1</sup> Kg <sup>1/2</sup>
10	0.00691	1.00769	1576.73	3.99168	1.050		
	0.04861	1.00758	1572.70	4.01262	0.963		
	0.09064	1.00824	1570.36	4.02194	0.794	1.307	-2.020
	0.13296	1.00912	1573.30	4.00343	0.515	( $\pm 0.02$ )	( $\pm 0.04$ )
	0.17555	1.01037	1573.09	3.99957	0.446		
	0.21835	1.01186	1575.75	3.98003	0.327		
20	0.00701	1.01637	1590.39	3.88993	1.440		
	0.04928	1.01629	1584.30	3.92019	1.180		
	0.09193	1.01647	1586.07	3.91075	0.720	1.813	-3.579
	0.13488	1.01717	1590.98	3.88397	0.408	( $\pm 0.03$ )	( $\pm 0.05$ )
	0.17805	1.01868	1593.76	3.86472	0.271		
	0.22137	1.02075	1596.57	3.84330	0.168		
30	0.00687	1.02019	1590.07	3.87045	2.850		
	0.04839	1.02078	1580.33	3.92260	1.910		
	0.09019	1.02178	1583.03	3.90540	0.991	3.472	-7.627
	0.13227	1.02291	1584.14	3.89559	0.704	( $\pm 0.02$ )	( $\pm 0.03$ )
	0.17463	1.02415	1595.59	3.83525	0.265		
	0.21699	1.02666	1605.11	3.78063	0.0009		

(Standard errors are given in parenthesis.)

## CHAPTER X

### Ion Association and Ion-Solvent Interactions of Some Ammonium and Tetraalkylammonium Salts in Binary Mixtures Containing Tetrahydrofuran and Water at 298.15 K Using Conductometric Technique

#### Abstract

Precise conductance measurements are reported for ammonium fluoride ( $\text{NH}_4\text{F}$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ), ammonium bromide ( $\text{NH}_4\text{Br}$ ), sodium iodide (NAI), tetramethyl ammonium chloride ( $\text{Me}_4\text{NCl}$ ) and tetrabutyl ammonium iodide ( $\text{Bu}_4\text{NI}$ ) in different mass% of tetrahydrofuran (THF) [10,20,30] + water mixtures at 298.15K. The limiting molar conductivity ( $\Lambda^\circ$ ) the association constant ( $K_A$ ) and association distance ( $R$ ) in the solvent mixtures have been evaluated using the Fuoss conductance equation (1978). The results have been interpreted in terms of Ion-ion, ion association and ion-solvent interactions.

#### 10.1 Introduction

Physico-chemical studies on ion Association and ion-solvent interaction of some ammonium and tetraalkyl ammonium salts in solvents of low permitivity are very few. Such studies have been assumed importance because of their applications in modern technology.<sup>1</sup> Tetrahydrofuran (THF), a solvent of low permitivity ( $\epsilon=7.58$ ), has also been found its probability of applications in high energy batteries and organics synthesizes as manifested from the physico chemical studies in this medium.<sup>2,3</sup> Renard and Justice<sup>4</sup> studied the conductances of CsCl in THF + water mixtures to reveal the nature of ionic association and mobility of ions in the different mass% of THF + water mixture systems. In the present communication, an attempt has been made to ascertain the complete nature of solute-solvent interactions of

ammonium and tetraalkylammonium halides in THF + H<sub>2</sub>O mixtures through the measurements of their conductances.

## 10.2 Results and Discussion

The solvent properties of THF + H<sub>2</sub>O mixtures are given in Table 1 and the data are presented by figs 1 and 2 where  $\epsilon$  is the dielectric constant,  $d_0$  the density (gcm<sup>-3</sup>),  $\eta_0$  the viscosity (cp),  $L_0$  specific conductance ( $\Omega^{-1}\text{cm}^{-1}$ ),  $w$  the weight percent of THF in the aqueous mixtures and  $x_2$  the corresponding mole fraction. Dielectric constants of solvent mixtures were obtained by extrapolation of  $\epsilon$  versus  $w\%$  plots, the original values were taken from the work of Renard and Justice.<sup>4</sup> The equivalent conductance at infinite dilution ( $\Lambda^\circ$ ) and the association constant ( $K_A$ ) were calculated using the Fuoss conductance equation<sup>5</sup>,

$$\Lambda = P[\Lambda^\circ(1 + R_x) + E_L] \quad (1)$$

$$P = [1 - \alpha(1 - \gamma)] \quad (2)$$

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

$$-\ln f = \beta k / 2(1 + \kappa R) \quad (4)$$

$$\beta = e^2 / DKT \quad (5)$$

where the terms have their usual significance. The parameters  $K_A$  and  $R$  were obtained from the above equations by finding the values of  $\Lambda^\circ$  and  $\alpha$  which minimize

$$\sigma^2 = \sum_j [\Lambda_j(\text{cal}) - \Lambda_j(\text{obs})]^2 / (n-2) \quad (6)$$

for a sequence of  $R$  values. Initial  $\Lambda^\circ$  values for the interaction procedure was taken from Shedlovsky extrapolations of the data.

A scan using unit increment of R values has been done considering the appropriate values.

Shedlovsky method<sup>6</sup> involves the linear extrapolation equation (7),

$$\frac{1}{\wedge S_{(z)}} = \frac{1}{\wedge_0} + \frac{K_A}{\wedge_0^2} (C \wedge f_{\pm}^2 S_{(z)}) \quad (7)$$

where  $\wedge$  is the equivalent conductance at a concentration  $C(\text{moldm}^{-3})$ ,  $\wedge^0$  the limiting equivalent conductance and  $K_A$  the observed association constant. The other symbols are given by

$$S_{(z)} = (Z/2 + \sqrt{1 + (Z/2)^2})^2, \quad Z = [(\alpha \wedge_0 + \beta) / \wedge_0^{3/2}] (C \wedge)^{1/2} \quad (8)$$

$$\alpha = \frac{0.8204 \times 10^6}{(DT)^{3/2}}, \quad \beta = \frac{82.501}{\eta(DT)^{1/2}}$$

where D is the dielectric constant, and  $\eta$  the viscosity of the medium. The degree of dissociation ( $\tau$ ) is related to  $S_{(z)}$  by

$$\tau = \wedge S_{(z)} / \wedge^0$$

$f_{\pm}$  the mean activity coefficient of the free ions was calculated using equation (8)

$$-\log f_{\pm} = \frac{A(\tau e)^{1/2}}{1 + BR(\tau c)^{1/2}} \quad (9)$$

$$\text{where } A = \frac{1.8246 \times 10^6}{(DT)^{3/2}}, \quad B = \frac{0.5029 \times 10^{10}}{(DT)^{3/2}}$$

R is the maximum center to center distance between the ions in the solvent separated ion-pair.

The computations in these cases were carried out from arbitrarily presetting<sup>5</sup> of R values at  $R = a + d$ . Here a is the sum of the crystallographic radii of the ions and d the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by

$$d(A^\circ) = (M/N_p)^{1/3} = 1.183(M/\rho)^{1/3} \quad (10)$$

Where M is the molecular weight of solvent and r is its density. For mixed solvents, M is replaced by the mole fraction average molecular weight ( $M_{\text{aver}}$ ) which is given by

$$M_{\text{aver.}} = M_1M_2/(W_1M_2 + W_2M_1) \quad (11)$$

Where  $W_1$  is the weight fraction of the first component of molecular weight  $M_1$ . Though this is an over simplification which ignores possible selective solvation, it at least provides a self-consistent way to obtain an acceptable value for the parameter when a broad range of R values fit the data. The values of  $\wedge$ ,  $K_A$  and R obtained by this procedure are recorded in Table 2.

It is observed from Table 1 that the viscosity ( $\eta_o$ ) of the solvent mixture (THF + H<sub>2</sub>O) increases rapidly to a maximum at about 0.143 mole fraction or 40 mass% of THF thereafter decreases. Such characteristic in the viscosity versus composition curve is a manifestation of strong specific interaction<sup>7</sup> between unlike molecules predominated by hydrogen bonding interaction.

From Table 2, it is found that the values of  $\wedge^\circ$  for ammonium halides e.g. NH<sub>4</sub>F, NH<sub>4</sub>Cl and NH<sub>4</sub>Br increase as the sizes of the anion increase in any mole fraction of the mixed solvent system but  $\wedge^\circ$  value for NaI lies between the  $\wedge^\circ$  values of NH<sub>4</sub>F and NH<sub>4</sub>Br. For tetraalkylammonium salt  $\wedge^\circ$  values decrease as the size of cation and anion increases. However, for any particular salt  $\wedge^\circ$  value continuously decreases with the addition of THF to the solvent mixture but Walden product increases with the addition of THF and the

viscosity of the solvent-mixture follows the opposite trend compared with the trend in  $\wedge^\circ$  value.

A perusal of Table 2 shows that the  $\wedge^\circ$  values of ammonium halides common cation follow the sequence ;  $\text{Br}^- > \text{Cl}^- > \text{F}^-$  and for tetraalkyl-ammonium halide :  $\text{Me}_4\text{N}^+ > \text{Bu}_4\text{N}^+$  . the trend of variation of  $\wedge^\circ$  values also indicates the relative actual sizes of these ions as they exist in solution, follow as following order :  $\text{F}^- > \text{Cl}^- > \text{Br}^-$  and  $\text{Bu}_4\text{N}^+ > \text{Me}_4\text{N}^+$ .

It is found from Table 2 that the value of association constant ( $K_A$ ) is very low for all electrolytes and increase with the addition of THF to the mixture in all cases (except  $\text{NH}_4\text{Cl}$  at 20 mass% of THF). This indicates that all these electrolytes almost remain unassociated in all composition of the solvent mixtures and the association increases with increasing THF to the solvent-mixture as well as the increasing anionic sizes in case of ammonium halides. Further the  $K_A$  value for the tetraalkylammonium salts are greater than those for the ammonium salts indicating the higher association for tetraalkylammonium salts. D' Aprano and Fuoss<sup>8</sup> found similar trends for many of the salts in dioxane-water mixtures.

The Walden products ( $\wedge^\circ\eta_o$ ) for all studied salts increases with increasing mass% of THF to the mixtures in all cases. Though the variation of the Walden product with the solvent composition is difficult to explain quantitatively, still its variation with the solvent composition can be interpreted in view of preferential solvation<sup>9,10</sup> of the studied ions by water and THF molecules respectively. At low mass% of THF, these ions are preferentially solvated by water than THF and the viscosity of the solvent in the vicinity of these ions is lower than that of the bulk solvent shown in Table 1. The preferential solvation can also be explained on the basis of association constant ( $K_A$ ) discussed earlier here.

It may be observed from Table 2 that for all electrolytes ionic association increases slowly with increasing tetrahydrofuran (THF) content in the solvent-mixtures. This is quite expected due to the gradual decrease in the dielectric constant of the medium with increasing amount of THF in the binary solvent mixtures (THF + H<sub>2</sub>O). Exactly the same conclusion regarding the ion-association behavior of some alkali metal halides in THF + water mixtures has been drawn from our conductometric Studies.<sup>12</sup>

### 10.3 Experimental Section

Tetrahydrofuran (Merck) was kept several days over KOH, then refluxed for 24 hours and distilled over LiAlH<sub>4</sub>. Its boiling point, density and viscosity compared well with the literature values.<sup>11</sup> The purities as checked by gas chromatography were found to be better than 99.8% for tetrahydrofuran. The specific conductance of THF was Ca.  $0.81 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$  l at 25°C. Triple distilled water was used for this purpose and specific conductance of used water was  $1.01 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$ .

Tetraalkylammonium salts were of Purum or Puriss grade (Fluke) and were purified as described earlier.<sup>12</sup> Alkali metal salts (Fluka, Purum or Puriss grade) were purified as described earlier.<sup>13,14</sup> A stock solution for each salt (~0.1M) in the appropriate solvent mixture was prepared (by weight) and the working solutions were obtained by weight dilution. The molar concentration of the solution was calculated from molality and density values. The mixed solvents of THF were prepared by mixing the requisite amounts of THF and water (by weights).

Density and viscosity of solvent mixtures were measured in an Ostwald-Sprengel type Pycnometer and suspended-level Ubbdohde viscometer<sup>15</sup> at  $(298.15 \pm 0.01)\text{K}$  with a Precision of  $\pm 3 \times 10^5 \text{ gcm}^{-3}$  and

0.05% respectively. The values were in good agreement with the literature values.<sup>11</sup>

Conductance measurements were carried out on a systronic 306 conductivity bridge (accuracy  $\pm 0.1\%$ ) with a dip-type immersion conductivity cell and the conductance was measured at  $298.15 \pm 0.01\text{K}$ . the cell was calibrated by the method of Lind and coworkers<sup>16</sup> using aqueous potassium chloride solution. The measurements were made in a water bath maintained at  $298.15 \pm 0.01\text{K}$  as described earlier<sup>17,18,19</sup>. Several independent solutions were prepared and runs were performed to ensure the reproducibilities of the results. All data were corrected at  $298.15\text{K}$  with the specific conductance of the solvent and in good agreement with the literature values.<sup>11</sup> The molar concentration and equivalent conductances for various electrolytes in different mass% of THF + water mixture at  $298.15\text{K}$  are reordered in Table 3.

### **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.

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**Table 1 : Physical Properties of THF + water mixtures at 298.15K**

W%	X <sub>1</sub>	ε	d <sub>0</sub> /g cm <sup>-3</sup>	η <sub>0</sub> /cp
00	0.000	78.54	0.99707	0.8903
10	0.027	63.00	0.98999	1.2014
20	0.059	57.25	0.98668	1.4900
30	0.097	51.25	0.97833	1.6798
40	0.143	44.50	0.96640	1.7321
60	0.273	32.00	0.9460	1.4904
80	0.500	19.50	0.91592	0.9237
100	1.000	7.58	0.88072	0.4630

**Table 2 : Derived conductivity parameters for ammonium and tetraalkyl ammonium halides in tetrahydrofuran(1) + water (2) mixtures at 298.15K.**

Salt -NH <sub>4</sub> F						
mass%	mole fraction(X <sub>1</sub> )	Λ° /S.cm <sup>2</sup> mol <sup>-1</sup>	K <sub>A</sub> /dm <sup>-3</sup> mol <sup>-1</sup>	R/A°	Λ°η°	σ
10	0.03	117.96 ±0.35	2.81779	3.995	1.417	0.35
20	0.06	117.14±0.64	3.92083	3.890	1.745	0.64
30	0.10	111.31±0.50	5.2933	3.8825	1.869	0.50
Salt - NH <sub>4</sub> Cl						
10	0.03	125.22±0.41	3.18302	4.465	1.504	0.41
20	0.06	119.84±0.42	0.76722	4.3599	1.785	0.42
30	0.10	118.41±0.56	3.29167	4.3525	1.988	0.56

**Salt – NH<sub>4</sub>Br**

10	0.03	130.87±0.48	3.10985	4.6051	1.572	0.48
20	0.06	125.51±0.60	3.20096	4.4999	1.870	0.60
30	0.10	118.287±0.55	3.36746	4.4925	1.986	0.55

**Salt – NaI**

10	0.03	119.55±0.47	0.45796	4.305	1.436	0.47
20	0.06	112.17±0.41	1.94869	4.1994	1.671	0.41
30	0.10	107.71±0.41	6.08424	4.1920	1.809	0.41

**Salt – Me<sub>4</sub>NCl**

10	0.03	118.59±0.34	4.43	6.45	1.425	0.34
20	0.06	111.44±0.14	5.47	6.39	1.661	0.14
30	0.10	107.91±.13	10.10	6.34	1.813	0.13

**Salt – (Bu)<sub>4</sub>NI**

10	0.03	96.71±0.26	6.92	8.28	1.162	0.26
20	0.06	93.07±0.18	10.04	8.22	1.386	0.18
30	0.10	88.14±0.13	14.05	8.17	1.481	0.13

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**Table 3 : Molar conductances ( $\Lambda$ ) and corresponding molarities( c) of ammonium and tetraalkyl ammonium halides in tetrahydrofuran (1) + water(2) at 298.15K.**

$X_1 = 0.027$			$X_1 = 0.059$		
Ammonium fluoride					
$C \times 10^4 /$ $\text{mol.dm}^{-3}$	$\sqrt{c}$ $/(\text{mol.dm}^{-3})^{1/2}$	$\Lambda / \text{S.cm}^2.$ $\text{mol}^{-1}$	$C \times 10^4$ $\text{mol.dm}^{-3}$	$\sqrt{C}$ $/(\text{mol.dm}^{-3})^{1/2}$	$\Lambda$ $\text{mol}^{-1}$
53.63	0.0732	110.31	60.22	0.0771	108.31
78.93	0.0888	109.42	116.66	0.1082	105.80
103.290	0.1016	108.40	169.69	0.1302	104.22
126.76	0.1125	107.31	266.66	0.1632	100.63
149.40	0.1222	106.30	219.61	0.1481	102.80
171.31	0.1308	105.22	311.12	0.1763	99.71
192.33	0.1386	104.71	334.89	0.1831	98.83
212.71	0.1458	103.52	361.29	0.193	97.90
232.41	0.1524	102.43	377.31	0.1946	97.11
251.45	0.1585	101.72	392.98	0.1981	96.40
Ammonium Chloride					
60.15	0.0772	116.72	46.83	0.0684	113.41
88.53	0.0940	115.60	90.73	0.0952	112.30
115.86	0.1073	114.40	131.98	0.1148	111.12
142.19	0.1191	113.53	170.80	0.1306	110.20
167.58	0.1293	112.32	207.41	0.1440	109.52
192.08	0.1381	111.14	241.97	0.1555	108.81

215.74	0.1462	110.81	261.81	0.1618	108.35
238.59	0.1543	109.72	281.01	0.1676	107.72
260.68	0.1611	108.93	299.58	0.1731	107.14
282.05	0.1672	107.73	317.59	0.1782	106.82

**Ammonium Bromide**

69.57	0.0833	120.33	56.44	0.0751	117.11
91.06	0.0951	119.21	109.36	0.1045	114.82
111.74	0.1053	118.42	159.07	0.1261	113.43
131.70	0.1141	117.30	187.48	0.1369	112.50
150.96	0.1220	116.51	217.43	0.1474	111.53
169.55	0.1304	115.42	244.16	0.1563	110.45
187.51	0.1373	114.53	269.97	0.1643	109.70
204.87	0.1432	113.30	294.92	0.1717	108.72
221.66	0.1483	112.31	319.02	0.1786	107.61
237.92	0.1544	111.46	342.23	0.1850	106.82

**Sodium Iodide**

59.52	0.0771	112.42	42.69	0.0653	106.01
115.32	0.1073	111.20	82.72	0.0909	104.13
167.74	0.1295	110.13	120.32	0.1096	102.87
217.07	0.1473	109.42	155.72	0.1248	102.02
263.59	0.1623	108.64	189.08	0.1375	101.13
307.53	0.1753	107.83	220.60	0.1485	100.40
349.08	0.1868	107.11	238.68	0.1545	99.77
388.45	0.1971	106.46	256.18	0.1601	98.91
461.28	0.2147	105.32	273.12	0.1653	98.62
527.18	0.2296	104.73	289.54	0.1702	97.81

**Tetra methyl ammonium chloride**

61.29	0.0782	110.20	41.76	0.0646	104.82
90.21	0.0949	108.70	61.45	0.0783	103.50
118.05	0.1086	107.80	80.42	0.0896	102.41
144.87	0.1203	106.7	98.71	0.0994	101.52
170.74	0.1306	105.4	116.33	0.1078	100.65
195.71	0.1398	104.5	133.33	0.1155	99.72
219.81	0.1482	103.6	149.6	0.1223	98.82
243.09	0.1559	102.8	165.63	0.1286	98.11
265.61	0.1629	101.7	180.96	0.1345	97.60
287.37	0.1695	100.9	195.79	0.1399	97.25

**Tetra butyl ammonium Iodide**

54.38	0.0737	89.20	40.34	0.0635	86.40
80.03	0.0894	87.63	59.37	0.0771	84.72
104.73	0.1023	86.41	77.70	0.0882	83.83
128.53	0.1133	85.70	95.36	0.0976	82.54
151.48	0.1230	84.5	112.39	0.1061	81.35
173.63	0.1317	83.4	128.82	0.1135	80.21
195.01	0.1396	82.5	144.69	0.1203	79.43
215.67	0.1468	81.7	160.02	0.1264	78.90
235.64	0.1535	80.8	174.83	0.1322	78.31
254.95	0.1596	81.13	189.41	0.1376	77.72

$X_1=0.097$

$C \times 10^4$ mol.dm <sup>-3</sup>	$\sqrt{C}$ /(mol.dm <sup>-3</sup> ) <sup>1/2</sup>	$\Lambda/S.cm^2$ mol <sup>-1</sup>	$C \times 10^4$ mol.dm <sup>-3</sup>	$\sqrt{C}$ /(mol.dm <sup>-3</sup> ) <sup>1/2</sup>	$\Lambda/S.cm^2$ mol <sup>-1</sup>
<b>Ammonium Fluoride</b>			<b>Ammonium Chloride</b>		
35.45	0.0596	104.31	39.019	0.0626	111.21
68.68	0.0828	101.72	75.94	0.0871	109.50
99.91	0.0999	100.20	110.45	0.1051	108.20
129.29	0.1137	99.34	142.29	0.1195	107.15
146.11	0.1208	98.40	161.53	0.1270	106.40
162.34	0.1274	97.52	179.48	0.1339	105.10
183.16	0.1353	96.30	196.84	0.1403	104.70
207.92	0.1442	95.42	213.63	0.1462	104.13
231.36	0.1521	94.43	229.86	0.1516	103.53
253.61	0.1593	93.10	245.85	0.1567	102.36
<b>Ammonium Bromide</b>			<b>Sodium Iodide</b>		
51.64	0.0718	110.20	30.43	0.0552	101.61
100.05	0.1001	108.34	58.96	0.0767	98.83
145.53	0.1206	106.53	85.76	0.0926	97.24
188.33	0.1372	105.43	110.98	0.1053	96.11
212.82	0.1458	104.71	134.76	0.1161	95.14
228.69	0.1512	103.73	157.22	0.1254	94.16
244.19	0.1562	103.33	178.46	0.1335	93.2
259.34	0.1610	102.63	190.67	0.1381	92.31
274.17	0.1655	102.11	202.49	0.1423	91.5
288.67	0.1699	101.21	213.95	0.1463	90.81
<b>Tetra methyl ammonium chloride</b>			<b>Tetra butyl ammonium iodide</b>		
29.71	0.0545	101.31	27.77	0.0526	82.44
43.72	0.0661	99.72	40.87	0.0639	80.53
57.21	0.0756	98.6	53.48	0.0733	79.41
70.22	0.0837	97.63	65.64	0.081	78.52
82.75	0.0909	96.52	77.36	0.0879	77.62
94.85	0.0973	95.3	88.67	0.0942	76.81
106.54	0.1032	94.71	99.59	0.0997	75.92
117.82	0.1085	93.93	110.15	0.1049	75.23
128.73	0.1134	93.42	120.34	0.1141	74.13
139.28	0.118	92.75	130.21	0.1182	74.15

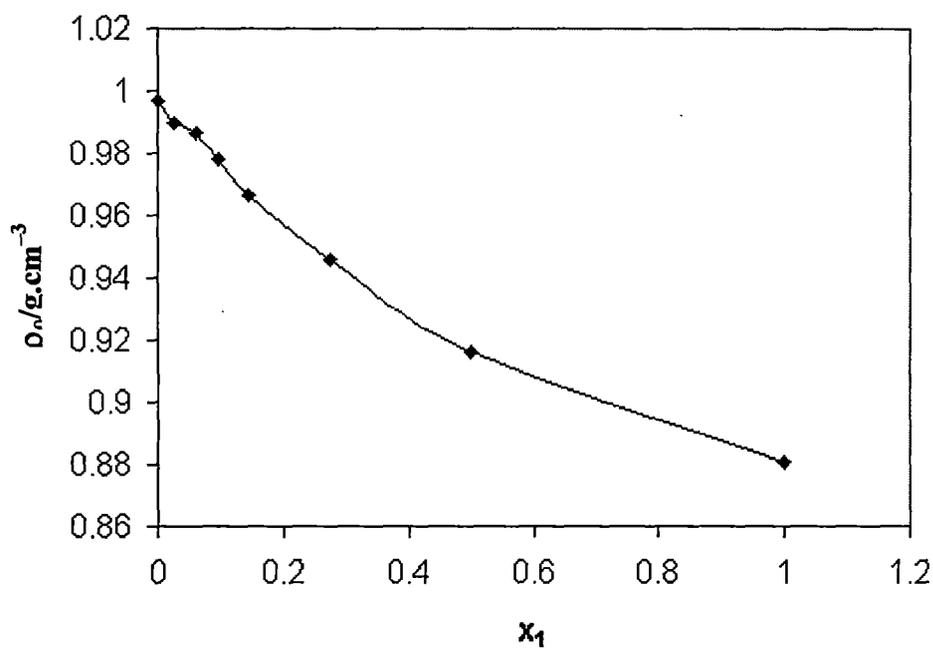


Fig. 1 : Plot of density ( $\rho_0$ ) versus different mole fraction ( $x_1$ )  
of THF + water mixtures at 298.15K

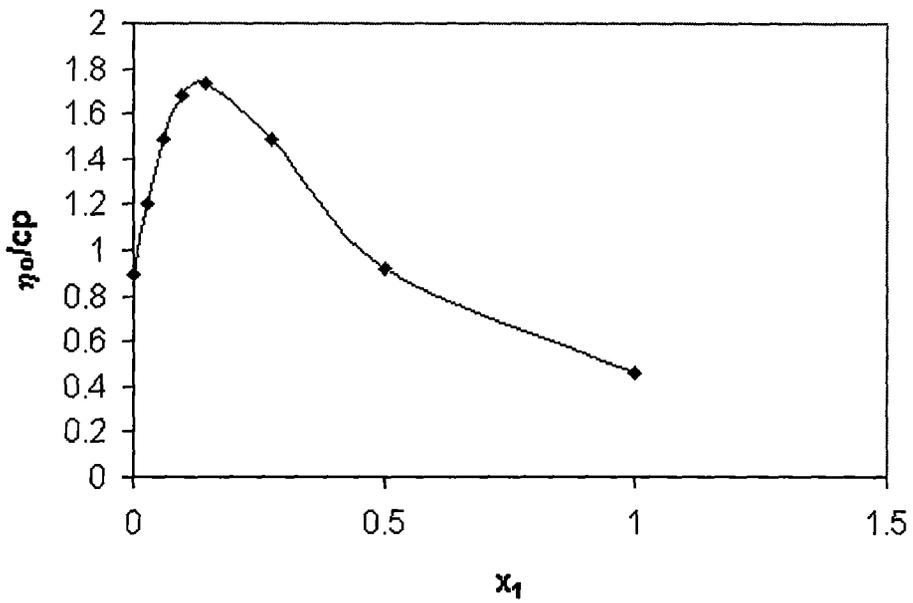


Fig.2 : Plot of viscosity ( $\eta_0$ ) versus different mole fraction ( $x_1$ ) of THF + water mixtures at 298.15K.

## **CHAPTER XI**

### **CONCLUDING REMARKS**

At the present work we have tried to investigate the various interactions of some metal and tetraalkyl ammonium salts in different solvent media and some useful conclusion of them have been derived. Tetrahydrofuran and its aqueous and non aqueous mixtures are very important solvents widely used in various industries including the manufacture of pharmaceuticals and cosmetic products and modern battery technology.

Rheology is the branch of science that studies material deformation and flow and is increasingly applied to analyze the viscous behavior of many pharmaceutical products and to establish their stability and even bioavailability since it has been firmly established that viscosity influences drug absorption rate in the body.

The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics and industrial products etc. is essential for confirming that their viscosity is appropriate for the contemplated use of the products.

Alkali metal and symmetrical tetraalkylammonium salts show numerous interesting properties that are now being actively investigated in many laboratories. Most of the present day knowledge on non-aqueous solutions have come from studies on various thermodynamic properties e.g. apparent molar volumes, adiabatic compressibilities, heat capacities etc. as well as on transport properties, e.g. conductance, viscosity and transference numbers. So, we determined the thermodynamic and transport properties of some alkali metal and tetraalkyl ammonium salts in tetrahydrofuran and water mixtures from the measurements of their viscosities, conductances apparent

molar volumes and adiabatic compressibilities. In addition to this, we also investigated the interactions between the binary mixtures tetrahydrofuran (THF) + benzene and tetrahydrofuran + n-hexane and among the ternary mixtures n-hexane + tetrahydrofuran + benzene, n-hexane + tetrahydrofuran + isopropanol and n-hexane + isopropanol + benzene at different temperatures.

The apparent molar volumes ( $V_\phi$ ) of the solutes and the apparent molal adiabatic compressibilities ( $\phi_k$ ) of the liquid solution were calculated from the following relations.

$$V_\phi = M / \rho_o - 1000(r - \rho_o) / c \rho_o$$

$$\phi_k = \beta M / \rho_o + 1000 (\beta r - \beta^o \rho) / m \rho \rho_o$$

where the symbols have their usual significances.

The determination of apparent molar volumes and apparent molal adiabatic compressibilities of electrolyte solutions is useful as a guide to the structural properties of solutions, particularly in the study of ion-solvent, ion-ion and solvent-solvent interactions. The concentrations dependence of these properties can be used to study ion-ion interactions. The relative magnitude of the limiting apparent molar volumes,  $V_\phi^o$  and the limiting apparent molar adiabatic compressibilities  $V_k^o$ , would enable us to provide information about the strengths of interactions between ions and solvent molecules. Measurements of the apparent molar volumes as a function of temperature can give an indication of electrostriction or concentration of solvent molecules around an ion.

The excess thermodynamic properties of binary and ternary liquid mixtures are also very useful as a guide to the structural properties of solutions mainly in the study of complex formation between the mixing molecules due

to intermolecular interactions, dispersion forces arising out due to the dissociation of molecular complexes strong molecular interactions due to appreciable dipole-dipole and dipole induced dipole interactions etc based on the following equations

$$\begin{array}{l} V^E = V - (x_1v_1 + x_2v_2) \\ \eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \end{array} \quad \left| \begin{array}{l} \\ \end{array} \right. \begin{array}{l} \text{(binary liquid mixtures)} \\ \end{array}$$

$$\begin{array}{l} V^E = V - (x_1v_1 + x_2v_2 + x_3v_3) \\ \eta^E = \eta - (x_1\eta_1 + x_2\eta_2 + x_3\eta_3) \end{array} \quad \left| \begin{array}{l} \\ \end{array} \right. \begin{array}{l} \text{(ternary liquid mixture)} \\ \end{array}$$

(symbols have their usual significance)

Another important parameters is the excess Gibbs free energy of activities of flow ( $\Delta G^{\neq E}$ ) which computed from the Eyring equation for ternary liquid mixture.

$$\Delta G^{\neq E} = [RT \{ \ln\eta^E - (x_1\ln\eta_1v_1 + x_2\ln\eta_2v_2 + x_3\ln\eta_3v_3) \}]$$

where the letters have their usual significance which may be attributed to the dominance of dispersion forces due to weak intermolecular interactions. Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolytic solutions. The measurements can be made in a variety of solvents over wide ranges of temperature and pressure and in dilute solutions where interionic interaction theories are not applicable. Recent development of experimental techniques provides an accuracy to the extent of 0.01% or even more. Conductance measurements together with transference number determinations provide an unequivocal method of obtaining single ion values.

The conductance method primarily depends on the mobility of ion so, it can be suitably utilized to determined the dissociation constant of weak acids

and association constants of electrolytes in aqueous and non-aqueous solvents. The limiting equivalent conductance ( $\Lambda^\circ$ ) and the solute-association constant ( $K_A$ ) will be evaluated using Shedlovsky equation. The results will be discussed in terms of solute-solute, solute-solvent and solvent-solvent interactions. Thermodynamics parameters will be evaluated to understand the change of the association constants with solvent composition. The conductance data can also be analyzed with Fuoss 1978 equation and Fuoss Kraus equation which is still one of widely used equations for the simultaneous evaluation of  $K_A$  and  $\Lambda^\circ$ .

Viscosity is one of the most important transport properties used for the determination of ion-solvent interactions. It is not a thermodynamics quantity, but viscosity of an electrolytic solution together with the thermodynamic property,  $\bar{V}_2$ , the partial molar volume gives much information and insight regarding ion-solvent interactions and the structures of the electrolytic solution. The viscosity B-coefficients give us quantitative values of the ion-solvent interactions.

The proper understanding of the ion-solvent interactions would form the basis of explaining quantitatively the influence of the solvent and the extent of interactions of the ions in solvents and have the way for the real understanding of the different phenomenon associated with the solution chemistry.

However, it is necessary to remember that ion-solvent interactions are very complex in nature. There are strong electrical forces between the ions and between the ions and solvents, and it is not really possible to separate them all. Nevertheless, if careful judgement is used, valid conclusions can be drawn in many cases from viscosity, conductivity, apparent molar volume and apparent molal adiabatic compressibility measurements relating to degree of structure and order of the system.

More extensive studies of the different thermodynamic and transport properties of the electrolytes will be of sufficient help in understanding the nature of the ion-solvent interactions and the role of solvents in different chemical processes.

