

## NOTE

**Ultrasonic Velocity, Viscosity and Density of LiCl in Aqueous Solutions of Alcohols at 303.15 K**

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Densities ( $\rho$ ), ultrasonic velocities (U) and relative viscosity ( $\eta_r$ ) of lithium chloride in 20% ethanol + water mixtures have been measured as a function of electrolyte concentration at 303.15 K temperature. The experimental values of  $\rho$  and U are used to calculate isentropic compressibility ( $\phi_k$ ), intermolecular free length ( $L_f$ ), relative association ( $R_A$ ), and apparent molar volume ( $\phi_v$ ). The derived parameters have been used to interpret the solvent-solvent, ion-solvent and solute-solvent interactions.

Aqueous solutions of alcohols have been of considerable interest to a wide range of scientists and technologists. A low cost and miscibility with water of the lower members of the homologous series renders such mixtures useful as industrial solvent media for a variety of chemical reactions and for small and large scale separation processes. In particular, aqueous solutions of alcohols are often employed in the extraction and manipulation of labile materials such as proteins<sup>1</sup>.

It is generally observed that there is a loss in volume of alcohols on dissolution in water, *i.e.*, the limiting partial molar volume ( $\phi_{v_0}$ ) is smaller than the volume of the pure liquid at the same temperature<sup>2</sup>. Considering these facts of alcohol mixtures an attempt has been made to study the change in thermodynamic properties of aqueous solutions of alcohols in presence of simple uniunivalent electrolytes like lithium chloride.

Lithium chloride (purity 99.8%) was of AR grade and used without further purification. Ethanol was purified by standard procedure<sup>3</sup> and stored in a closely tight bottle (teflon tape and aluminium foils are used) to check the absorption of humidity. Redistillation of the alcohol was carried out prior to the actual measurements. Triply distilled water was used for the required dilution. The purity of these two solvents was checked by measuring their individual densities and time flow, which were further compared with literature values<sup>4</sup>.

Solution of ethanol + water (20% composition) and different concentrations of salt solutions were prepared by (w/w) concept. Weighing was done with Mettler balance. Solutions were allowed to achieve thermal equilibrium before going to actual measurements by keeping them in a thermostat for 15-20 min.

Ultrasonic velocity measurements, viscosity measurements and density measurements were carried out by using ultrasonic interferometer, model MX<sub>4</sub>

(supplied by Mittal Enterprises, New Delhi) of variable frequency, Schott Gerate AVS350 Viscometer, made in Germany and single arm pycnometer of 5 cm<sup>3</sup> capacity respectively. Temperature was controlled by circulating water through an ultrathermostat F25 Julabo water bath made in Germany, which has an accuracy  $\pm 0.02^\circ\text{C}$ . Experiments were generally performed at least on five replicates for each solution and the results were averaged. The experimental reproducibility of the viscosity measurements for each solution at 303.15 K was  $\pm 0.2\%$  and for ultrasonic velocity and density measurements were  $\pm 2 \text{ m s}^{-1}$  and  $\pm 0.00001 \text{ g cm}^{-3}$  respectively. Details regarding the mathematical equations are already given in the earlier publication<sup>5</sup>.

Water-ethanol-lithium chloride is a ternary system. The effect of addition of ethanol to water is well established<sup>6</sup>. Lithium chloride is known to be water structure maker<sup>7</sup>. Patil *et al.*<sup>8</sup> have reported that alcohol molecules which are associated with each other in liquid state get dissociated on the first addition of water, resulting in a minima, which results in decrease in limiting partial molar volume ( $\phi_{v_0}$ ) as observed in this system (Table-2). The probable reason for this is the decrease in hydrogen bonding between alcohol molecules, —OH—OH— interaction or hydrogen bond between alcohol and water molecule.

TABLE-1  
DENSITY ( $\rho$ ), ULTRASONIC VELOCITY (U), RELATIVE VISCOSITY  
OF LITHIUM CHLORIDE IN 20% ETHANOL AT 303.15 K

Conc.	Density ( $\rho$ ) ( $\text{g cm}^{-3}$ )	Ultrasound velocity (U) ( $\text{m s}^{-1}$ )	Relative viscosity
0.0	0.96395	1610.00	
0.2	0.96927	1624.12	1.08498
0.4	0.97440	1633.75	1.15942
0.6	0.97931	1643.48	1.20650
0.8	0.98403	1653.11	1.24712
1.0	0.98854	1662.51	1.28274

It is evident from Table-1 and 2 that the ultrasonic velocity, relative viscosity, apparent molar volume, apparent molar isentropic compressibility and acoustic impedance values are increasing with increasing concentration which clearly indicates that there are strong solute-solvent, solvent-solvent and ion-solvent interactions<sup>9</sup>. The decrease in  $\phi_{v_0}$  may be attributed to the increase in electrostriction. Thus the electrostriction effect, which brings about shrinkage in the volume of solvent is enhanced in mixed solvent as compared with that in pure liquids. Since electrostriction primarily reflects electrolyte-solvent interactions, it can be inferred that electrolyte-solvent interaction increases with increase in solute concentration. It is also clear from the values of  $S_v$ ,  $S_k$  and  $B/\phi_{v_0}$ , *i.e.*, 2.2743, 1.5073 and 23.774 respectively which are positive and large showing the presence of strong solute-solute and solute-solvent interactions.

In general, ultrasonic velocity and intermolecular free length have been reported to vary inversely with each other with concentration<sup>10-12</sup> as in the present case, which indicates significant interaction between solute-solvent molecules in

solution. Acoustic impedance,  $Z$ , increases with the concentration<sup>13, 14</sup> suggesting strong solute-solvent interaction in the present system.

TABLE-2  
APPARENT MOLAR VOLUME ( $\phi_v$ ), APPARENT MOLAR ISENTROPIC COMPRESSIBILITY ( $\phi_k$ ), INTERMOLECULAR FREE LENGTH ( $L_f$ ), RELATIVE ASSOCIATION ( $R_A$ ) AND ACOUSTIC IMPEDANCE ( $Z$ ) IN 20% ETHANOL AND WATER AT 309.15 K

$\phi_v$ (cm <sup>3</sup> /mole)	$\phi_k$ (cm <sup>2</sup> /dyne/mole)	$L_f$ (Å)	$R_A$	$Z$ (gm cm <sup>2</sup> /sec)
15.25	$-4.2733 \times 10^{-3}$	$3.94628 \times 10^{-6}$	1.0025965	1574.2108
15.70	$-4.1163 \times 10^{-3}$	$3.91268 \times 10^{-6}$	1.0059187	1591.9260
16.17	$-3.4737 \times 10^{-3}$	$3.87975 \times 10^{-6}$	1.0089884	1609.4764
16.62	$-3.0581 \times 10^{-3}$	$3.84789 \times 10^{-6}$	1.0118789	1626.7098
17.07	$-2.9248 \times 10^{-3}$	$3.81739 \times 10^{-6}$	1.0145991	1643.4576

$$\phi_{v0} = 14.80; \quad \phi_{k0} = -4.396 \times 10^{-3}$$

In the present study relative association ( $R_A$ ) is increased with increasing concentration suggesting that again solute-solvent interaction dominates<sup>15</sup>. The relative association ( $R_A$ ) values are influenced by two factors:

- (i) Breaking up of the solvent molecule upon addition of electrolyte.
- (ii) Subsequent solvation of the solute.

### REFERENCES

1. F. Franks, *Water Science Reviews*, 1st Edn., Cambridge University Press (1985).
2. P.S. Nikam and A.R. Hiray, *Asian J. Chem.*, **4**, 176 (1992).
3. A.I. Vogel, *A Text Book of Practical Organic Chemistry*, 4th Edn., Longman, London (1978).
4. J.A. Riddick and W.B. Bunger, *Wiley-Interscience*, New York, 2nd Edn. (1955).
5. D.V. Jahagirdar, *J. Molecular Liquids*, **85**, 361 (2000).
6. J.S. Rowlinson, *Liquid and Liquid*, Butterworths Scientific Publications, London (1962).
7. B. Behra and R.K. Mishra, *Indian J. Chem.*, **17A**, 445 (1979).
8. K.J. Patil, *Indian J. Chem.*, **33A**, 1069 (1995).
9. M.L. Parmar and S. Sharma, *Indian J. Chem.*, **37A**, 718 (1999).
10. A. Ali, A.K. Nain and M. Kamil, *Thermochim. Acta*, **274**, 209 (1996).
11. A. Ali and A.K. Nain, *Acoustic Letters*, **19**, 181 (1996).
12. —————, *Indian J. Pure and Appl. Phys.*, **35**, 729 (1997).
13. M. Iqbal and R.E. Verall, *Can. J. Chem.*, **67**, 727 (1989).
14. C. Sharma, *Ind. J. Pure and Applied Physics*, **27**, 32 (1989).
15. A. Ali, S. Hyder and A.K. Nain, *J. Pure and Applied Ultrason.*, **21**, 127 (1999).
16. H. Eyring and J.F. Kincaid, *J. Chem. Phys.*, **6**, 728 (1977).