

## **VISCOSITY OF LITHIUM FLUORIDE IN MIXED SOLVENT AT DIFFERENT TEMPERATURES**

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Ion-solvent interaction has been inferred from the B coefficient of Jones-Dole equation for lithium fluoride in ethanol, methanol, isopropanol, dioxane, glycol and glycerol + water mixture at 10.20 and 30% (w/w) within the temperature range 30-40°C.

**KEY WORDS** : Viscosity, Mixed solvents, Potassium fluoride, Jones-Dole equation.

### **INTRODUCTION**

Ion-solvent interaction has been a subject of interest among physical chemists for the last two decades [1, 2]. The inference regarding the interaction is derived either from viscosity or molar volume and conductance measurements. In the present study, the viscosity of lithium fluoride in ethanol, methanol, isopropanol, dioxane, glycol, glycerol+water mixture at 10, 20 and 30% (w/w) at 30, 35 and 40°C has been measured. Ion-solvent interaction has been inferred from the B-coefficient of Jones-Dole equation.

### **EXPERIMENTAL**

The solvents and chemicals were purchased from E. Merck, India. The purification, preparation of solvent, solutions and measurements of viscosity were performed as described previously [3]. The temperature ranged from 30 to 313 ± 0.01K during the study.

### **RESULTS AND DISCUSSION**

The change in viscosity with concentration for aqueous and non-aqueous solutions of electrolytes is represented satisfactorily by Jones-Dole equation.

$$\eta_r = 1 + A\sqrt{C} + BC \quad \dots(1)$$

where  $\eta_r$  is the relative viscosity and  $A$  and  $B$  are constants. The constant  $A$  is long range interionic attraction coefficient and can be calculated theoretically by Falkenhagen and Vernon's expression [4];  $B$  is a measure of solute-solvent interaction and  $C$  is the concentration in moles per litre. The procedure to see the validity of the above equation is to first see that a straight line is obtained by plotting  $\eta_r - 1/C^{1/2}$  vs.  $C^{1/2}$ . In the present investigation, the viscosities of Lithium fluoride in 10, 20 and 30% (w/w) of ethyl alcohol, methyl alcohol, isopropanol, dioxane, glycol and glycerol + water mixture have been studied at 30, 35 and 40°C and in all the cases the above plots are found to be linear. The intercept and

the slope of the above plot gave respectively the values of  $A$  and  $B$  which are computed in Table-1 and Table-2.

Table – 1.  $A \times 10^3/L^{1/2} \text{ mol}^{1/2}$

	Temperature (°C)	Composition (%)		
		10	20	30
<b>Methanol + water</b>	30	5.6	5.9	6.3
	35	5.6	5.6	6.2
	40	5.5	5.7	6.1
<b>Ethanol + water</b>	30	6.0	6.2	6.5
	35	5.8	6.0	6.4
	40	5.6	5.5	6.3
<b>Isopropanol + water</b>	30	5.4	5.8	6.4
	35	5.4	5.8	6.3
	40	5.5	5.7	6.3
<b>Dioxane + water</b>	30	4.5	4.8	5.1
	35	4.6	4.9	5.2
	40	4.5	4.9	5.2
<b>Glycol + water</b>	30	4.8	4.9	5.2
	35	4.7	5.0	5.3
	40	4.5	4.9	5.2
<b>Glycerol + water</b>	30	4.6	5.1	5.4
	35	4.9	5.2	5.3
	40	4.9	5.3	5.3

#### 'A' Values

The different ' $A$ ' values (Table-1) indicate the ionic interactions. It is also seen that the ' $A$ ' values increase with the increase in organic solvent of the solutions. This may be attributed to the change in the mobility of the ions with a change in the dielectric constant of the medium. Positive ' $A$ ' values suggest ion-ion interaction, possibly due to cation-cation and cation- anion penetration. It may also be noted that ' $A$ ' decreases with the rise in temperature for all the salts in all solvents, which one would expect in view of the thermal agitation at higher temperature and reduction of attractive forces.

**Dependence of 'B' on temperature** : The positive  $B$  values (Table-2) indicate the strong alignment of the solvent molecules with the ions which undoubtedly promotes the structure of the solvent molecules in its immediate vicinity [5]. Thus, the net structure breaking or ion-solvent interaction (lesser  $B$  values) is found to be ethyl alcohol + water > methyl alcohol + water > isopropanol + water > dioxane + water > glycol + water > glycerol + water. It is also seen that it is differing slightly with temperature.

**Dependence of 'B' on organic solvent** : The increase in  $B$  coefficient with the increase in non-aqueous solvents (Table-2) may be attributed to the large size of the molecules and strong association through hydrogen bonding. For larger solvated ions would lead to large value of  $\eta^E + \eta^A > \eta^D$  and hence the  $B$  coefficient becomes larger and larger with the increase in non-aqueous solvent in the mixture.

Table – 2.  $B/L \text{ mol}^{1/2}$ 

	Temperature (°C)	Composition (%)		
		10	20	30
Methanol + water	30	0.018	0.022	0.026
	35	0.017	0.021	0.025
	40	0.016	0.020	0.024
Ethanol + water	30	0.018	0.022	0.027
	35	0.018	0.022	0.027
	40	0.017	0.021	0.026
Isopropanol + water	30	0.018	0.022	0.027
	35	0.018	0.023	0.028
	40	0.017	0.022	0.028
Dioxane + water	30	0.027	0.046	0.058
	35	0.024	0.046	0.057
	40	0.026	0.045	0.057
Glycol + water	30	0.030	0.051	0.062
	35	0.027	0.052	0.061
	40	0.028	0.051	0.060
Glycerol + water	30	0.035	0.059	0.069
	35	0.035	0.060	0.072
	40	0.036	0.061	0.071

**Activation parameter :** Eyring *et al* [6] applied the theory of absolute reaction rate to interpret the viscosity of liquid by calculating the energy and entropy of activation. Nightingale Benck [7] and Feakins [8] have shown that this theory of reaction rate can be successfully applied to electrolytic solutions. Proceeding in the similar line,  $\Delta E$  (which does not differ very much from  $\Delta H$ ),  $\Delta G$  and  $\Delta S$  for the solvents and salts at 10, 20 and 30% ethanol and methanol + water mixture at 35°C along the data of dioxane + water mixture have been calculated and tabulated in Table 3-5.

Table – 3.  $\Delta E \text{ kJ mol}^{-1}$ 

	Composition (%)		
	10	20	30
Methanol + water	14.18	15.34	16.13
Lithium fluoride	13.65	14.85	15.42
Ethanol + water	14.08	15.03	15.79
Lithium fluoride	13.14	14.24	14.42
Isopropanol + water	10.53	28.29	20.24
Lithium fluoride	14.84	15.14	14.32
Dioxane + water	17.00	17.39	16.84
Lithium fluoride	16.00	17.15	16.55
Glycol + water	17.13	18.43	18.34
Lithium fluoride	17.01	18.00	18.19
Glycerol + water	17.23	17.56	16.84
Lithium fluoride	14.63	14.36	14.50

Table – 4.  $\Delta G$  kJ mol<sup>-1</sup>

	Composition (%)		
	10	20	30
Methanol + water	15.78	16.54	17.29
Lithium fluoride	14.15	16.54	17.29
Ethanol + water	15.45	16.35	16.45
Lithium fluoride	14.43	15.49	15.84
Isopropanol + water	10.39	10.65	11.05
Lithium fluoride	8.95	7.65	7.85
Dioxane + water	9.54	10.43	10.75
Lithium fluoride	9.12	9.43	9.84
Glycol + water	-	-	-
Lithium fluoride	-	-	-
Glycerol + water	9.62	10.46	10.74
Lithium fluoride	8.71	8.85	8.93

Table – 5.  $\Delta S$  JK<sup>-1</sup> mol<sup>-1</sup>

	Composition (%)		
	10	20	30
Methanol + water	16.13	16.74	17.75
Lithium fluoride	15.49	15.75	16.29
Ethanol + water	16.00	16.54	17.13
Lithium fluoride	14.45	15.25	16.25
Isopropanol + water	24.40	24.85	25.33
Lithium fluoride	20.80	20.69	20.95
Dioxane + water	24.39	22.64	19.55
Lithium fluoride	13.49	21.23	17.45
Glycol + water	25.45	24.93	23.23
Lithium fluoride	23.55	21.29	18.14
Glycerol + water	24.53	23.85	21.53
Lithium fluoride	23.80	26.45	21.65

It is observed that  $\Delta E$ ,  $\Delta G$  and  $\Delta S$  values are less than those of the solvents, indicating a structure breaking effect. Further, the thermodynamic parameter  $\Delta G$  for the above mixture shows continuous increase with the increase in non-aqueous solvent. The curves, *i.e.*, plot of salt-solvent mixture vs. composition % solvent are slightly concave downward showing thereby slight positive deviation from ideal behaviour and hence slight positive derivation in  $\Delta E$  ideal behaviour. Also slight positive deviation in  $\Delta E$  and  $\Delta S$  is observed and might be the consequence of structure breaking effect of one component on the other [10]. The interaction due to non-aqueous solvents and water in such that the basis geometric structure of both the components will be distorted and then the individual ethanol, methanol, isopropanol, dioxane, glycol and glycerol-water molecules will be loosely associated through hydrogen bonding. This loose association of the molecules would give rise to an apparent slight positive deviation

in  $\Delta E$  and  $\Delta S$  values as observed. It is of the order ethanol + water > methanol + water > isopropanol + water > dioxane + water > glycol + water > glycerol + water. This can be explained as follows :

Ethanol, methanol and isopropanol have got one –OH group whereas water is both an electron donor and acceptor. The former being hydrophobic in nature could accept a proton from water and hence the three-dimensional water structure is easily broken down.

The addition of a small amount of dioxane to water may give rise to two effects: if the dioxane is accommodated in the solvent structure, it may strengthen the water structure because dioxane is a proton acceptor or if it cannot be accommodated because of its bulky size then it may cause a breakdown in three-dimensional water structure. Several authors have observed that dioxane in water is less ordered than pure water. It is observed that  $\Delta E$  and  $\Delta G$  increase with increase in dioxane content and hence the three-dimensional water structure is broken down though the quanta is less than that of ethanol and methanol + water mixture.

Glycol has got two –OH groups and glycerol has got three –OH groups, so it should have more tendency to break hydrogen bond more readily than methyl alcohol and ethyl alcohol but the reverse is seen to be true and this is probably due to the low ion-solvent dipole interaction energy which is unable to break the strong intermolecular hydrogen bond.

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