

## VISCOSITY OF KF IN MIXED SOLVENT AT DIFFERENT TEMPERATURE

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Ion-solvent interaction has been inferred from the B. Coefficient of Jones-Dole equation for the salt KF in ethanol, methanol, isopropanol, dioxane, glycol and glycerol + water mixture at 10, 20 and 30% (w/w) within temp. ranger 30-40°C.

### 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 KF 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 salt used was of 'E merck' variety. The purification, preparation of solvent, solutions and measurements of viscosity has been described previously [3]. Time of flow is within  $\pm 0.02$  sec's. Concentration range is from 0.1. MI 0.0025 M. The temperature investigation is from 30 to 313  $\pm 0.01$ K.

### DISCUSSION

The change is viscosity with concentration for aqueous and non-aqueous solutions of electrolytes is represented satisfactorily by Jone-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 ranger interionic attraction coefficient and can be calculated theoretically by Folkenhagan and Vernon's expression [4];  $B$  is the 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 viscosity of KF 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 value of  $A$  and  $B$  which are computed on Table-1 to Table-2.

Table 1.  $A \times 10^3 / l^{1/2} \text{ mole}^{1/2}$ 

	Temp. °C	10%	20%	30%
Methanol + water	30	5.6	5.9	6.3
	35	5.6	5.6	6.2
	40	5.5	5.7	6.1
Ethanol + water	30	6.0	6.2	6.5
	25	5.8	6.0	6.4
	40	5.6	5.5	6.3
Isopropanol + water	30	5.4	5.8	6.4
	35	5.4	5.8	6.3
	40	5.5	5.7	6.3
Dioxane + water	30	4.5	4.8	5.1
	35	4.6	4.9	5.2
	40	4.5	4.9	5.3
Glycol + water	30	4.8	4.9	5.2
	35	4.7	5.0	5.3
	40	4.5	4.9	5.2
Glycerol + water	30	4.6	5.1	5.4
	35	4.9	5.2	5.3
	40	4.9	5.3	5.3

Table – 2.  $B/l \text{ mole}^{-1}$ 

	Temp. °C	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	0.028
	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	0.071
	40	0.036	0.061	0.071

**A – Values :**

The different 'A' values (Table-1) indicate ionic interactions. It is also seen that the 'A' values also increase with the increase in organic solvent of the solutions. This may be attributed due 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.

**Table 3.  $\Delta E/\text{KJ mole}^{-1}$** 

	10%	20%	30%
Methanol + water	14.19	15.31	16.12
KF	13.60	14.8	15.4
Ethanol + water	14.07	15.02	15.78
KF	13.1	14.2	14.4
Isopropanol + water	19.52	28.28	20.21
KF	14.8	15.4	14.3
Dioxane + water	17.01	17.38	16.81
KF	16.70	17.19	16.56
Glycol + water	17.1	18.4	18.3
KF	17.0	18.0	18.1
Glycerol + water	17.27	17.57	16.81
KF	14.6	14.3	14.5

**Table 4.  $\Delta G/\text{KJ mole}^{-1}$** 

	10%	20%	30%
Methanol + water	15.78	16.51	17.20
KF	14.1	16.51	17.20
Ethanol + water	15.48	16.31	16.4
KF	14.4	15.4	15.8
Isopropanol + water	10.30	10.67	11.04
KF	8.9	7.6	7.8
Dioxane + water	9.57	10.41	10.78
KF	9.1	9.4	9.8
Glycol + water			
KF			
Glycerol + water	9.67	10.45	10.78
	8.7	8.8	8.9

**Dependence of 'B' on Temperature :**

According to Stokes and Mills [5], the viscosity of a dilute electrolytic solution incorporates that of the solvent plus contribution from other sources. These  $\eta^E$  the positive increase due to increase in shape and size of an ion  $\eta^A$  increase due to alignment or orientation

of the polar molecules by the ionic field and  $\eta^D$ , the decrease in the viscosity arising due to the distortion has been discussed in terms of these viscosity effects at different temperatures.

The positive  $B$  values recorded in Table-2 indicates strong alignment of the solvent molecules with the ions which undoubtedly promotes the structures of the solvent molecules in its immediate vicinity. Thus the net structure breaking or ion-solvent interaction (esser  $B$  values) is found to be of the order: 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 due to large size of the molecules and also through strong association through hydrogen bonding. For larger solvated ions would lead to large value of  $\eta^E$  and  $\eta^A$ . Consequently  $\eta^E + \eta^A > \eta^D$  and hence the  $B$  coefficient becomes larger and larger with the increase in nonaqueous solvent in the mixture.

#### 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 mixtures at 35°C along the data of dioxane + water mixtures have been calculated and tabulated in Table-3 to 5. It is observed that  $\Delta E$ ,  $\Delta G$  and  $\Delta S$  values are less than that of the solvents, indicating a structure breaking effect. Further, the thermodynamic parameter  $\Delta G$  for the above mixtures shows continuous increase with the increase in nonaqueous solvent. The curves *i.e.* plot of vs. % solvent are slightly concave downward showing thereby slight positive deviation from ideal behaviour and hence slight positive deviation in  $\Delta E$  ideal behaviour. Also, slight positive deviation in  $\Delta E$  and  $\Delta S$  is observed as may be the consequence of structure breaking effect of one component on the other [10]. The interaction due to nonaqueous solvents and water in such that the basic 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 not got one -OH group where as water is both an electron donor and acceptor. Hence, 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 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 break down 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 3-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.

**Table – 5.  $\Delta S/\text{KJ mole}^{-1}$**

	10%	20%	30%
Methanol + water	16.12	16.71	17.74
KF	15.4	15.7	16.2
Ethanol + water	15.98	16.51	17.12
KF	14.41	15.24	16.2
Isopropanol + water	24.45	24.84	25.32
KF	20.8	20.6	20.9
Dioxane + water	24.33	22.61	19.56
KF	13.4	21.2	17.4
Glycol + water	25.4	24.9	23.2
KF	23.5	21.2	18.1
Glycerol + water	24.52	23.84	21.52
KF	23.8	26.4	21.6

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