

## **VISCOSITY OF NaF IN MIXED SOLVENT AT DIFFERENT TEMPERATURE**

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Ion-solvent interaction has been inferred from the B. Co. efficient of Jones-Dole equation for the salt NaF in ethanol, methanol, isopropanol dioxane glycol and glycerol + water mixture at 10%, 20% and 30% (w/w) within temperature range 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 NaF 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  $\pm 0.02$  seconds. Concentration range is from 0.1 M to 0.0025 M. The temperature investigation is from 30 to 40  $\pm 0.01$ K.

### **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 Folkenhagan 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

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 NaF 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 by the value of  $A$  and  $B$  which are computed on Table-1 to Table-2.

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

Solvent	Temp.	10%	20%	30%
Methanol	30	7.0	7.2	8.3
+	35	6.9	7.3	8.4
Water	40	6.7	7.2	8.3
Ethanol	30	7.4	7.8	8.6
+	35	7.4	7.8	8.6
Water	40	7.5	7.7	8.6
Isopropanol	30	7.2	7.6	8.7
+	35	7.1	7.6	8.8
Water	40	7.2	7.7	8.9
Dioxane	30	6.4	7.2	8.2
+	35	6.5	7.1	8.4
Water	40	6.2	7.0	8.2
Glycol	35	6.5	7.4	8.2
+	35	6.5	7.5	8.2
Water	40	6.6	7.3	8.4
Glycerol	30	6.5	7.2	8.5
+	35	6.6	7.1	8.6
Water	40	6.5	7.2	8.6

**(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.

**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 and  $\eta^E$  the positive increase due to the 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 decreases in the viscosity arising due to the distortion has been discussed in terms of these viscosity affects at different temperatures.

Table 2.  $B/1 \text{ mol}^{-1}$

Solvent	Temp.	10%	20%	30%
Methanol	30	.075	.080	.082
+	35	.074	.079	.082
Water	40	.073	.078	.081
Ethanol	30	.055	.057	.061
+	35	.054	.056	.060
Water	40	.052	.055	.059
Isopropanol	30	.074	.078	.081
+	35	.073	.079	.082
Water	40	.074	.080	.081
Dioxane	30	.079	.084	.090
+	35	.078	.083	.089
Water	40	.077	.082	.088
Glycol	35	.082	.088	.095
+	35	.080	.090	.097
Water	40	.080	.089	.095
Glycerol	30	.087	.035	.101
+	35	.088	.035	.104
Water	40	.09	.036	.103

Table 3.  $\Delta E/KJ mol^{-1}$ 

Solvent	10%	20%	30%
Methanol + water	14.19	15.31	16.12
NaF	13.2	14.4	15.4
Ethanol + water	14.07	15.02	15.78
NaF	12.9	14.4	14.6
Isopropanol + water	19.52	20.28	20.21
NaF	14.4	14.3	14.7
Dioxane + water	17.01	17.38	16.81
NaF	16.4	16.6	15.8
Glycol + water	17.1	18.4	18.3
NaF	16.6	16.8	15.1
Glycerol + water	17.27	17.57	16.81
NaF	14.5	14.1	14.4

The positive  $B$  values recorded in Table-2 indicates strong alignment of the solvent molecules with the ions which undoubtedly promotes the structure of the solvent molecules in its immediate vicinity. Thus the net structure breaking or ion-solvent interaction (asser  $B$  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 nonaqueous 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 non-aqueous solvent in the mixture.

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

Solvent	10%	20%	30%
Methanol + water	15.78	16.51	17.20
NaF	14.1	15.3	16.2
Ethanol + water	15.48	16.31	16.91
NaF	13.3	14.3	15.3
Isopropanol + water	10.30	10.67	11.04
NaF	8.7	7.7	7.9
Dioxane + water	9.57	10.41	10.78
NaF	9.25	9.5	9.8
Glycol + water	9.7	11.5	12.4
NaF	9.3	9.6	9.7
Glycerol + water	9.67	10.45	10.78
NaF	8.6	8.8	8.9

#### Activation Parameter :

Eyring *at al* [6] applied the theory of absolute reaction rate of interpret the viscosity of liquid by calculating the energy and entropy of activation, Night-n gale and Banck [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 parameters  $\Delta G$  for the above mixtures shows continuous increase with the increase in non-aqueous solvent. The curves *i.e.* plot of vs % solvent are slight concave downward showing thereby slight positive deviation from ideal behaviour. Also, slight positive deviation in  $\Delta E$  and  $\Delta S$  is observed and may be the consequence of structure breaking effect of one component on the other [10]. The interaction due to non-aqueous of both the components will be distorted and 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 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 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 accomodated 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 low ion-solvent dipole interaction energy which is unable to break the strong intermolecular hydrogen bond.

**Table 5.  $\Delta S/JK^{-1} \text{ mol}^{-1}$**

Solvent	10%	20%	30%
Methanol + water	16.12	16.71	17.74
NaF	15.1	15.02	16.04
Ethanol + water	15.98	16.51	17.12
NaF	14.12	15.04	15.98
Isopropanol + water	24.45	24.84	25.32
NaF	20.3	20.5	20.8
Dioxane + water	24.33	22.61	19.56
NaF	23.32	21.4	18.52
Glycol + water	25.4	24.9	23.2
NaF	23.0	21.0	18.0
Glycerol + water	24.52	23.84	21.52
NaF	22.8	20.6	21.3

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