

THERMODYNAMICS OF NaF, NaCl, NaBr AND NaI IN GLYCOL + WATER AND GLYCEROL + WATER MIXTURES FROM VISCOSITY MEASUREMENT AT 30°, 35° AND 40°C.

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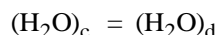
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The ion solvent interaction of NaF, NaCl, NaBr and NaI in Propan-2ol + water and Dioxane + water along with the data of Ethanol and methanol mixtures at 10%, 20% and 30% (w/w) within the temperature range of 30-40°C have been inferred from viscosity measurements. The order is $F > Br > Cl > I^-$ and Ethanol + water > Methanol + water > Dioxane + water > Glycol + water > Glycerol + water.

INTRODUCTION

Water at ordinary temperature has a quasi crystalline structure. A dynamic equilibrium seems to exist between the three dimensional hydrogen bonded clusters and the denser monomers :



Electrolytes which dissolve in water have been classified as structure makers or structure breakers, depending on whether the above equilibrium is shifted to left or right. Frank and Wen gave a picture in which an ion is surrounded by concentric region of water molecules polarized, immobilized and electrostricted by the ion, analogous to a kind of freezing. This they called the region-A. The water molecules in the region-C has the normal three dimensional network as stated above. The centro-symmetric structures imposed by the ion in the region-A is incompatible with the normal structure in the region-C and there is a tendency to resist such order and balance between the two competing forces gives rise to a region-B. Ions with a low charge density has a smaller width of region-A and larger width of region-B are net structure breakers. On the other hand, ions with a high charge density show in opposite behaviour and are net structure makers.

The organic solvents like ethanol, methanol, glycerol and glycol are miscible with water at all solvent compositions and their dielectric constant and dipole moments are very different. Ethanol and methanol are aprotic solvents, where as, water is both an electron donor and an acceptor. Hence, studies of their aqueous mixtures become an interesting field to explore; particularly of the ionic processes accompanying the solutions of the strong electrolytes. It becomes relevant to acquire whether a given mixed solvent will resist the centro-symmetric ordering of the ion more or less than pure water.

From this point of view, the viscosity of NaF, NaCl, NaBr and NaI in Propan-2ol Dioxane 10%, 20% and 30% have been measured at $C \leq 0.1 \text{ mol.L}^{-1}$ at 30°, 40°C and the data have been compared with the data of Ethanol and Methanol [1,2].

EXPERIMENTAL

The change in viscosity with concentrations for aqueous and nonaqueous solution of electrolytes is represented satisfactorily by Jones-Dole [3] equation

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

where η_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 Vemon'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. $C^{1/2}$. 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 . The values thus obtained along with the values in dioxane + water mixture of P.B. Das (D.Sc. thesis) are tabulated in Tables 1 and 2. In the present investigation the viscosity of NaF, NaCl, NaBr and NaI in 10%, 20% and 30% (w/w) of Propan-20l + water and Dioxane + water mixtures were taken at 30°, 35° and 40°C.

DISCUSSION :

The different 'A' values (Tables 1 and 2) indicate the different ionic interactions on the nature of the electrolyte. 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 the change in the dielectric constant of the medium. Positive 'A' values suggest ion-ion interaction, possibility 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 1 : $A \times 10^3/L^{1/2} \text{ mole}^{-1/2}$

		NaF			NaCl			NaBr			NaI		
		10	20	30	10	20	30	10	20	30	10	20	30
I	30	8.7	9.5	9.9	8.4	9.2	9.4	7.7	8.9	10.8	7.1	9.3	10.4
	35	8.4	9.0	9.6	8.0	8.4	8.7	7.6	8.9	10.9	7.3	9.2	11.2
	40	7.9	8.6	9.1	7.8	7.8	7.9	7.6	9.0	10.8	7.2	9.2	11.2
II	30	8.6	9.4	9.8	8.4	9.3	9.3	7.0	7.7	10.0	6.6	8.0	10.0
	35	8.3	8.8	9.3	8.1	8.4	8.7	7.0	7.2	10.0	6.5	7.9	10.2
	40	8.0	8.3	9.0	7.8	7.8	7.9	6.4	6.6	9.5	6.6	7.9	10.1
III	30	8.4	9.5	9.7	8.3	9.0	9.2	6.9	7.8	10.8	6.5	7.9	10.1
	35	8.2	9.0	9.3	7.8	8.1	8.5	6.1	7.0	10.0	6.4	7.8	10.1
	40	7.6	8.8	9.1	7.6	7.5	7.9	5.4	6.0	8.9	6.5	7.7	10.0
IV	30	8.2	9.1	8.9	8.1	8.4	8.9	7.1	7.3	10.4	6.7	8.4	10.3
	35	8.0	8.7	8.6	8.1	8.4	8.0	7.0	7.4	10.2	6.6	8.2	10.2
	40	7.8	8.2	8.2	8.0	8.2	8.8	6.9	7.2	10.1	6.5	8.1	10.2
V	30	8.5	9.0	9.2	8.3	8.6	9.1	7.3	7.5	10.4	6.9	8.2	10.4
	35	8.3	8.6	9.0	8.4	8.6	9.2	7.2	7.6	10.4	6.8	8.2	10.5
	40	8.0	8.2	8.8	8.3	8.5	9.1	7.1	7.4	10.2	6.7	8.1	10.4

Table 2 : B/L Mole⁻¹

		NaF			NaCl			NaBr			NaI		
		10	20	30	10	20	30	10	20	30	10	20	30
I	30	0.93	0.140	0.190	.091	.130	.180	.123	.140	.145	.130	.135	.145
	35	0.95	0.135	0.187	.092	.125	.175	.120	.145	.148	.126	.130	.135
	40	0.97	0.132	0.181	.092	.124	.170	.118	.140	.147	.125	.132	.140
II	30	0.85	0.128	0.181	.082	.120	.170	.110	.140	.170	.097	.100	.110
	35	0.83	0.124	0.178	.080	.110	.170	.120	.130	.180	.090	.110	.120
	40	0.87	0.121	0.176	.090	.120	.190	.110	.130	.180	.090	.110	.140
III	30	0.89	0.101	0.165	.081	.100	.155	.097	.120	.151	.092	.097	.106
	35	0.93	0.121	0.168	.091	.112	.160	.105	.124	.170	.091	.096	.105
	40	0.99	0.129	0.172	.101	.120	.188	.096	.114	.155	.090	.095	.104
IV	30	0.85	0.82	0.92	.080	.085	.086	.079	.083	.085	.083	.085	.089
	35	0.84	0.79	0.91	.080	.084	.086	.078	.082	.084	.082	.084	.088
	40	0.81	0.72	0.89	.089	.083	.084	.777	.081	.083	.081	.082	.088
V	30	0.59	0.58	0.80	.057	.065	.070	.078	.089	.096	.093	.100	.106
	35	0.56	0.56	0.75	.056	.064	.069	.076	.088	.095	.091	.099	.105
	40	0.52	0.52	0.69	.055	.063	.068	.075	.087	.094	.090	.098	.104

DEPENDENCE OF 'B' ON TEMPERATURE :

According to Stokes and Mills [5], the viscosity of dilute electrolytic solution incorporation that of the solvent plus contribution from other sources. These are η^E the positive increase due to the increase in shape and size of an ion, η^A , increase due to alignment or orientation of the polar molecules by the ionic field and η^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 structure of the solvent molecules in its immediate vicinity. Thus, the net structure breaking or ion-solvent interaction (Lesser B values) is found to be of the order $F^- > Br^- > Cl^- > I^-$ and ethyl alcohol + water – methyl alcohol + water > dioxane + water > glycol + water > glycerol + water.

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 of the molecules and also through strong association through hydrogen bonding. For larger solvated ions would lead to large value of η^E and η^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.

EFFECTIVE RIGID MOLAR VOLUME :

The effective rigid molar volume [6] is defined as the volume which a mole of solute particles occupies, when considered purely from hydrodynamics reasons, as rigid microscopic spheres. The B coefficient has been utilized to calculate v_e for all the salts and for all solvent compositions, and are recorded in table 3 (at 40°C only). The plot of B vs. v_e is found to be linear and the equations that fit the data are different for different temperature and for different

nonaqueous solvents. The value of v_e decreases with decrease in nonaqueous solvents. This may be attributed to be due to hydrogen bond better and nonaqueous solvent molecules. As nonaqueous solvent content is increased, more and more hydrogen bonded ethanol, methanol, dioxane, glycol and glycerol molecules are formed resulting in an increase in v_e .

Table 3 : $v_e/L \text{ mol}^{-1} (40^\circ)$

	NaF			NaCl			NaBr			NaI		
	10	20	30	10	20	30	10	20	30	10	20	30
I	0.62	0.68	0.76	.057	.062	.074	.030	.045	.062	.093	.096	.100
II	0.65	0.72	0.84	.060	.070	.090	.030	.050	.070	.090	.090	.094
III	0.72	0.76	0.88	.068	.072	.098	.033	.052	.071	.082	.092	.102
IV	0.75	0.82	0.92	.070	.075	.100	.036	.056	.071	.084	.094	.106
V	0.78	0.86	0.96	.072	.077	.104	.038	.058	.076	.085	.096	.106

ACTIVATION PARAMETERS

Eyring *et al.*, [7] applied the theory of absolute reaction rate to interpret the viscosity of liquids by calculating the energy, free energy and entropy of activation. Nightingale and Benck [8] and Feakins [9] have shown that this theory of reaction rate can be successfully applied to electrolyte solutions. Proceedings in the similar line, ΔE (which does not differ very much from ΔH), ΔG and ΔS for the solvents and salts at 10%, 20% and 30% glycol and glycerol + water mixture at 35° along the data of ethanol, methanol and dioxane + water mixtures have been calculated and tabulated in Tables 4 to 6. It is observed that the ΔE , ΔG and ΔS values are less than that of the solvents, indicating a structure breaking effect and is of the order, $F^- > Br^- > Cl^- > I^-$ for all five nonaqueous solvents. Further, the thermodynamic parameter ΔG for the above mixtures shows continuous increase with the increase in nonaqueous solvent. The curves are slightly concave downward showing thereby slight positive deviation from ideal behaviour. Also, slight positive deviation in ΔE and ΔS is observed and may be the consequence of structure breaking effect of one component on the other [10]. The interaction due to nonaqueous solvents and water is such that the basic geometric structure of both the components will be loosely associated through hydrogen bonding. This loose association of the molecules would give rise to an apparent positive deviation in ΔE and ΔS values as observed. It is of the order ethanol + water \geq methanol + water $>$ dioxane + water $>$ Glycol + water $>$ Glycerol + water. This can be explained as follows :

Table 4 : $\Delta E/kJ \text{ mole}^{-1}$

Solvent	Solvent	NaF			NaCl			NaBr			NaI		
		10	20	30	10	20	30	10	20	30	10	20	30
I	Solvent	18.8	19.2	18.6	17.7	18.5	18.2						
	35	17.3	16.9	17.3	16.7	16.9	17.4	16.8	17.4	17.6	16.9	17.3	17.8
II	Solvent	17.8	18.2	18.1	17.2	17.5	17.5						
	35	16.9	16.9	17.2	16.6	16.8	15.1	16.9	16.9	17.1	16.7	17.1	17.4
III	Solvent	18.2	18.9	18.6	17.07	17.38	17.81						
	35	17.1	17.2	16.4	16.4	16.6	15.8	17.02	17.18	17.19	16.6	17.07	16.7
IV	Solvent	16.4	15.9	17.2	14.19	15.31	16.12						
	35	14.2	14.4	16.8	13.2	14.4	15.4	13.3	14.3	15.3	13.5	14.5	15.2
V	Solvent	15.6	15.8	16.3	14.07	15.02	15.78						
	35	13.3	13.9	14.9	12.8	14.3	14.4	12.8	14.3	14.4	12.7	14.2	14.3

Table 5 : $\Delta G/kJ \text{ mole}^{-1}$

		NaF			NaCl			NaBr			NaI		
		10	20	30	10	20	30	10	20	30	10	20	30
Solvent I	Solvent	12.8	14.6	16.8	11.2	13.4	15.4						
	35	11.2	12.6	14.4	10.6	12.1	14.2	10.4	12.4	14.4	10.6	12.5	14.6
II	Solvent	12.2	12.8	12.2	10.2	11.4	11.7						
	35	10.6	10.9	10.8	9.3	9.6	9.7	9.4	10.2	10.2	9.4	9.8	10.3
III	Solvent	10.2	10.8	10.9	9.57	10.41	10.78						
	35	9.8	10.1	10.6	9.25	9.5	9.8	9.45	10.25	10.13	9.45	9.86	10.27
IV	Solvent	16.4	18.5	17.6	15.78	16.51	17.2						
	35	15.2	17.2	17.1	14.1	15.3	16.1	14.0	15.2	16.1	14.1	15.1	16.2
V	Solvent	17.2	17.8	17.2	15.48	16.31	16.91						
	35	15.8	16.2	16.1	13.3	19.3	15.3	13.3	14.4	15.3	13.3	14.3	15.2

Table 6 : $\Delta S/JK^{-1} \text{ mole}^{-1} 35^{\circ}C$

		NaF			NaCl			NaBr			NaI		
		10	20	30	10	20	30	10	20	30	10	20	30
Solvent I	Solvent	28.1	27.2	25.6	26.8	25.4	24.5						
	35	26.2	25.1	22.8	25.9	24.6	23.4	26.0	24.8	24.0	26.2	29.9	24.1
II	Solvent	26.2	24.2	22.2	25.7	23.5	21.4						
	35	25.1	23.1	21.1	24.0	22.0	19.0	21.0	22.0	19.0	22.0	22.0	18.0
III	Solvent	25.2	24.2	20.4	24.06	22.81	19.56						
	35	23.8	22.6	20.0	23.96	22.4	19.44	21.61	22.03	19.23	22.42	22.13	19.43
IV	Solvent	17.6	18.3	18.9	16.12	16.71	17.74						
	35	15.9	17.5	17.2	15.0	14.98	15.84	14.98	14.78	15.74	15.4	15.91	16.72
V	Solvent	16.8	17.2	17.8	15.98	16.51	17.12						
	35	14.9	15.8	15.1	14.02	14.82	15.78	13.91	14.72	15.44	14.78	15.94	16.42

Ethanol and methanol have got one –OH group, whereas, water is both an electron donor and acceptor. Hence the former 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. 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 + water is less ordered than pure water. It is observed that *E* and *G* increase with increase in dioxane content and hence the three dimensional water structure is broken down through the quanta is less that of ethanol and methanol + water mixtures.

Glycol has got two–OH and glycerol has 3-OH groups. So they should have more tendency to break hydrogen bond more readily than methyl alcohol, but the reverse is seen to be true. 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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