VISCOSITY OF Na$_2$CO$_3$ IN MIXED SOLVENTS

L K NAYAK[1], C R DAS[2], P K DASH[3] AND S SHARMA[4]

1. Department of Chemistry, Bhadrak Auto College, Bhadrak, Odisha.

2. Department of Chemistry, Choudwar College, Cuttack, Odisha.

3. Asso .Professor of Chemistry and Dy.Controller of Examination, CHSE, Odisha, Bhubaneswar.

4. PG Department of Chemistry, Paher University, Udaipur, Rajasthan.

The viscosity data of Na$_2$CO$_3$ in methanol, ethanol, isopropanol, dioxane, glycol and glycerol + water at different composition and at temperature between 30-40°C have been computed and ion solvent interaction have been inferred.

INTRODUCTION

Numerous studies have shown that viscosity measurements are very useful in providing information regarding ion-solvent interactions and particularly as regards to the modifications induced by ions on the solvent structure [1-6]. Viscosity of electrolytic solution in aquo organic solvents have been studied of Na$_2$CO$_3$ in methanol, ethanol, isopropanol, dioxane, glycol and glycerol + water mixtures (10, 20 and 30% w/w) at 30, 35 and 40^{0}C have been studied and attempt has been made to deal with the ion solvent interaction and hydrogen bonding.

EXPERIMENTAL

All the salts used were E. Merck 'Extrapure' variety. The apparatus, technique and preparation of solvents and solution were the same as reported earlier [3]. The concentration of visocity was from 0.1 -0.0025 mol dm^3. The time of flow did not exceed 0.2 sec. in 15 minute. The density data being accurate upto $\pm$0.002 gm.

DISCUSSION

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

$$\eta_r = 1 + A\sqrt{c} + BC \qquad \qquad \text{...(1)}$$

where 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 Folkenhaan and Vernon's expression [4]; *B* is a measure of solute-solvent interaction, and *C* is the concentration is mols 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 NaCl 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 40^0C 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 and Table-2.

Table 1 : $A \times 10^3/1^{1/2}$ mole$^{-1/2}$

	Temp.^{0}C	10%	20%	30%
Methanol + water	30	7.0	7.2	8.3
	35	6.9	7.3	8.4
	40	6.7	7.2	8.3
Ethanol + water	30	7.4	7.8	8.6
	35	7.4	7.8	8.6
	40	7.5	7.7	8.5
Isopropanol + water	30	7.2	7.6	8.7
	35	7.2	7.6	8.8
	40	7.2	7.7	8.9
Dioxane + water	30	7.2	7.6	8.7
	35	7.2	7.6	8.8
	40	7.2	7.7	8.9
Glycol + water	30	6.5	7.4	8.2
	35	6.5	7.5	8.2
	40	6.6	7.3	8.4
Glycerol + water	30	6.5	7.2	8.5
	35	6.6	7.1	8.6
	40	6.5	7.2	8.6

A-VALUES : The difference '*A*' values (Table 1) indicate ionic interactions. It is also seen that the '*A*' values also increase with the increase in organic solvent 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, possibily due to cation-catio 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 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 interation (lesser *B* values) is found to be of the order: ethyl + water > methyl alcohol + water > isopropanol + water >dioxane + water > glycol + water > glycerol + water. It is also seen that it is differing slightly with temperature.

Table 2 : B/1 mole^{-1}

	Temp.^{0}C	10%	20%	30%
Methanol + water	30	.081	.081	.086
	35	.080	.083	.086
	40	.079	.083	.084
Ethanol + water	30	.057	.065	.070
	35	.055	.064	.069
	40	.055	.063	.068
Isopropanol + water	30	.060	.088	.099
	35	.062	.100	.110
	40	.060	.090	.120
Dioxane + water	30	.081	.100	.155
	35	.090	.110	.165
	40	.101	.112	.200
Glycol + water	30	.082	.120	.170
	35	.1080	.110	.170
	40	.1090	.120	.190
Glycerol + water	30	.095	.140	.190
	35	.099	.143	.195
	40	.108	.145	.200

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 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 non-aqueous solvent in the mixture.

Activation Parameter : Erying *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 ΔE (which does not differ very much from ΔH), ΔG and ΔS for the solvent and salts at 10, 20 and 30% ethanol and methanol + water mixtures at 35^0C along the data of dioxane + water mixtures have been calculated and tabulated in Tables-3 to 5. It is observed that ΔE, ΔG and ΔS values are less than that of the solvents, indicating a structure breaking effect. Further, the thermodynamic parameter ΔG for the above mixtures shows continuous increase with the increase in non-aqueous 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 ΔE 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 non-aqueous solvents and water is such that the basic geometric structure of both the components with 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 ΔE and ΔS 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.

Table 3 : $\Delta E/KJ$ mole^{-1}

	10%	20%	30%
Methanol + water Na_2CO_3	14.19 13.2	15.31 14.3	16.12 15.3
Ethanol + water Na_2CO_3	14.07 12.8	15.02 14.3	15.78 14.4
Isopropanol + water Na_2CO_3	19.52 14.9	20.28 14.8	20.31 14.9
Dioxane + water Na_2CO_3	17.01 17.07	17.38 17.18	16.81 16.49
Glycol + water Na_2CO_3	17.1 16.9	18.4 16.9	18.3 17.1
Glycerol + water Na_2CO_3	17.27 14.9	17.57 14.7	16.81 14.1

Table 4 : $\Delta G/KJ$ mole^{-1}

	10%	20%	30%
Methanol + water Na$_2$CO$_3$	15.78 14.10	16.51 15.2	17.20 16.1
Ethanol + water Na$_2$CO$_3$	15.48 13.3	16.31 14.2	16.91 15.3
Isopropanol + water Na$_2$CO$_3$	10.30 8.8	10.67 7.8	11.04 8.1
Dioxane + water Na$_2$CO$_3$	9.57 9.45	10.41 10.25	10.78 10.13
Glycol + water Na$_2$CO$_3$	9.7 9.4	11.5 10.3	12.4 10.2
Glycerol + water Na$_2$CO$_3$	9.67 8.7	10.45 9.1	10.78 9.4

Table 5 : $\Delta S/KJ$ mole^{-1}

	10%	20%	30%
Methanol + water Na$_2$CO$_3$	16.12 15.0	16.71 14.98	17.74 15.84
Ethanol + water Na$_2$CO$_3$	15.98 14.03	16.31 14.82	17.12 15.78
Isopropanol + water Na$_2$CO$_3$	24.45 20.4	24.84 20.7	25.32 20.9
Dioxane + water Na$_2$CO$_3$	24.33 24.56	22.61 22.24	19.56 20.9
Glycol + water Na$_2$CO$_3$	25.4 24.0	24.9 22.0	23.2 19.0
Glycerol + water Na$_2$CO$_3$	24.52 23.0	23.84 23.6	21.52 21.4

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 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 ΔE and ΔG increase with 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.

$\mathcal{R}$EFERENCES

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