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VISCOSITY OF POTASSIUM SULPHATE 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 potassium in ethanol, methanol, isopropanol, sulphate dioxane, glycol and glycerol + water mixture at 10, 20 and 30% (w/w) within the temperature range 30-40°C.

KEYWORDS : Viscosity, Mixed solvents, Potassium Sulphate, 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 potassium in ethanol, methanol, isopropanol, sulphate 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 performed as described previously [3]. The temperature ranged from 30 to 313 $\pm$ 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 Jone-Dole equation.

$$\eta_r = 1 + A\sqrt{C} + BC$$

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 Falkenhagan 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 $\eta_r - 1/C^{1/2}$ is $C^{1/2}$. In the present investigation, the viscosities of potassium sulphate 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 × 10^3/$L^{1/2}$ $mol^{1/2}$

	Temperature (°C)	Composition (%)		
		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
	35	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	5.2
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

‘*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 al 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. 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 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.

Table 2. B/L mol^{-1}

	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	0.26
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, ΔE (which does not differ very much from ΔH), ΔG and ΔS for the solvents and salts at 10, 20 and 30% ethanol and methanol + water mixtures at 35°C along the data of dioxane + water mixture have been calculated and tabulated in Tables 3-5.

It is observed that ΔE, ΔG and ΔS values are less than those of the solvents, indicating a structure breaking effect. Further, the thermodynamic parameter ΔG 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 ΔE ideal behaviour. Also, slight positive deviation in ΔE and ΔS 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 is 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 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 :

Table – 3. ΔE kJ mol^{-1}

	Composition (%)		
	10	20	30
Methanol + water	14.19	15.31	16.12
Potassium sulphate	13.66	14.80	15.40
Ethanol + water	14.07	15.02	15.78
Potassium sulphate	13.10	14.20	14.40
Isopropanol + water	10.52	28.28	20.21
Potassium sulphate	14.80	15.40	14.30
Dioxane + water	17.01	17.38	16.81
Potassium sulphate	16.70	17.19	16.56
Glycol + water	17.10	18.40	18.30
Potassium sulphate	17.00	18.00	18.10
Glycerol + water	17.27	17.57	16.81
Potassium sulphate	14.60	14.30	14.50

Table 4. ΔG kJ mol^{-1}

	Composition (%)		
	10	20	30
Methanol + water	15.78	16.51	17.20
Potassium sulphate	14.10	16.51	17.20
Ethanol + water	15.48	16.31	16.40
Potassium sulphate	14.40	15.40	15.80
Isopropanol + water	10.30	10.67	11.04
Potassium sulphate	8.90	7.60	7.80
Dioxane + water	9.57	10.41	10.78
Potassium sulphate	9.10	9.40	9.80
Glycol + water	–	–	–
Potassium sulphate	–	–	–
Glycerol + water	9.67	10.45	10.78
Potassium sulphate	8.70	8.80	8.90

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 ΔE and ΔG increase with increase in dioxane content and hence the three-dimensional water structure is broken down through the quanta is less than that of ethanol and methanol + water mixture.

Table 5. ΔS JK^{-1} mol^{-1}

	Composition (%)		
	10	20	30
Methanol + water	16.12	16.71	17.74
Potassium sulphate	15.40	15.70	16.20
Ethanol + water	15.98	16.51	17.12
Potassium sulphate	14.41	15.24	16.20
Isopropanol + water	24.45	24.84	25.32
Potassium sulphate	20.80	20.60	20.90
Dioxane + water	24.33	22.61	19.56
Potassium sulphate	13.40	21.20	17.40
Glycol + water	25.40	24.90	23.20
Potassium sulphate	23.50	21.20	18.10
Glycerol + water	24.52	23.84	21.52
Potassium sulphate	23.80	26.40	21.60

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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