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RESEARCH ARTICLE

VISCOSITY OF POTASSIUM SULFATE IN MIXED SOLVENTS AT DIFFERENT TEMPERATURES

D. SAHU AND A. K. PATNAIK
Department of chemistry, Visiting Professor, Utkal University,Vani-Vihar,Bhubaneswar, Odisha, India

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***Corresponding Author**

D. SAHU

Abstract

Ion-solvent interaction has been inferred from the B coefficient of Jones-dole equation for potassium sulfate in ethanol, methanol, propan-2-ol, 1,4-dioxane, glycol and glycerol + water at 10%, 20% and 30% (w/w) within the temperature range 30^o-40^oC.

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INTRODUCTION

Ion-solvent interaction has been a subject of interest among the physical chemists for the last two decades. The inference regarding the ion solvent interactions[1-5] is derived either from viscosity or molar volume and conductance measurements. In the present study, the viscosity of potassium sulphate in Methanol, Ethanol, Propan-2-ol, 1,4-Dioxane, Ethylene Glycol, Glycerol + water mixture at 10%, 20% , 30% (w/w) at 30^o, 35^o, 40^o C has been measured. Ion- solvent interaction has been inferred from B coefficient of Jones-Dole equation.

EXPERIMENTAL:

The solvents and chemicals were purchased from E. Merck, India. The purification of solvents, preparation of solutions and measurements of viscosity performed as described previously. The temperature ranged from 303-313 ± 0.01 K during the study.

RESULTS AND DISCUSSION:

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

$$\eta_r = 1 + A\,C^{1/2} + B\,C$$

$$\text{Or} \qquad \eta_r - 1 = A\,C^{1/2} + B\,C$$

$$\text{Or} \qquad \frac{\eta_r - 1}{C^{1/2}} = A + B\,C^{1/2}$$

Where η_r is relative co-efficient viscosity and A and B are constants. The constant A is long-range inter-ionic attraction coefficient and can be calculated theoretically by Falkenhagen and Vernon's expression; B is the measure of solute-solvent interaction and C is the concentration in moles per dm^3. 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 sulfate in 10%, 20% , 30% (w/w) of ethanol, methanol, propan-2-ol, 1,4-dioxane, glycol, glycerol + water have been studied at 30^o, 35^o, 40^o C and in all three 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 2.

Table-1 A x 10^3 ($dm^{3/2}\,mol^{-1/2}$)

	Temperature (^oC)	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

Table-2 B (dm^3mol^{-1})

	Temperature (^oC)	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	0.026
Propan-2-ol+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

A values :

The different A values (Table-1) indicate the ion-ion interactions in the electrolyte. It is also seen that the A values increase with the increase in organic solvents of the solution. This may be attributed to the change in mobility of the ions with a change in the dielectric constant of the medium. Positive A values suggest ion-ion interactions is due to the 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 the 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. Thus, the net structure breaking or ion-solvent interaction (lesser B values) is found to be ethyl alcohol + water > methyl alcohol + water > propan-2-ol + water > 1,4-dioxane + water > ethylene 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 to the large size of the molecules and strong association through hydrogen bonding. For larger solvated ions would lead to larger value 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:

Eyring [6] et al. applied the theory of absolute reaction 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_a (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 1,4-dioxane + water mixture have been calculated and tabulated[9-10] in Tables 3-5.

TABLE – 3 ΔE_a (kJ mol^{-1})

	Composition (%)		
	10	20	30
Methanol+water	14.19 13.66	15.31 14.80	16.12 15.40
Ethanol+water	14.07 13.10	15.02 14.20	15.78 14.40
Propan-2-ol+water	10.52 14.80	28.28 15.40	20.21 14.30
Dioxane+ water	17.01 16.70	17.38 17.19	16.81 16.56
Glycol+ water	17.10 17.00	18.40 18.00	18.30 18.10
Glycerol+ water	17.27 14.60	17.57 14.30	16.81 14.50

TABLE – 4 ΔG^* (kJ mol^{-1})

	Composition		
	10%	20%	30%
Methanol+water	15.78 14.10	16.51 16.51	17.20 17.20
Ethanol+water	15.48	16.31	16.40

	14.40	15.40	15.80
Propan-2-ol+water	10.30 8.90	10.67 7.60	11.04 7.80
Dioxane+ water	9.57 9.10	10.41 9.40	10.78 9.80
Glycol+ water	9.43 8.65	10.25 8.92	10.71 9.12
Glycerol+ water	9.67 8.70	10.47 8.80	10.78 8.90

Table- 5 ΔS^* (J K^{-1} mol^{-1})

	Composition		
	10%	20%	30%
Methanol + water	16.12 15.40	16.71 15.70	17.74 16.20
Ethanol + water	15.98 14.41	16.51 15.24	17.12 16.20
Propan-2-ol+water	24.45 20.80	24.84 20.60	25.32 20.90
Dioxane+ water	24.33 13.40	22.61 21.20	19.56 17.40
Glycol+ water	25.40 23.50	24.90 21.20	23.20 18.10
Glycerol+ water	24.52 23.80	23.84 26.40	21.52 21.60

It is observed that ΔE_a, ΔG^*, ΔS^* values are less than those of the solvents indicating a structure[11] breaking effect. Further the thermodynamic parameter ΔG for the above mixtures shows continuous increase with the increase in non-aqueous solvents. The curves, i. e., plot of salt-solvent mixture vs. composition % solvent are slightly concave downward showing thereby slight positive deviation from the ideal behaviour and hence the slight positive deviation in ΔE ideal behaviour. Also, slight positive deviation in ΔE_a and ΔS^* is observed and might be the consequence of structure breaking effect of one component on the other[12-15]. The interaction due to non-aqueous solvents and water is such that the basic geometric structure of both the components will be distorted and the individual methanol, ethanol, isopropanol, dioxane, glycol and glycerol water molecules will be loosely associated through the hydrogen-bonding. This loose association of the molecules would give rise to apparent slight positive deviation in ΔE_a and ΔS^* values as observed. It is of the order Ethanol + water > Methanol + water > Propan-2-ol + water > 1,4-Dioxane + water > Glycol + Water > Glycerol + water. This can be explained as follows:

Ethanol, methanol and iso-propanol have got one –OH and 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. It cannot be accommodated because of its bulky size then it may cause a breakdown in the three dimensional water structures. Several authors have also observed that dioxane + water is less ordered than pure water. It is observed that ΔEa and ΔG^* increase with increase in dioxane content and hence, the three-dimensional water structure is broken down though the quanta is less that of ethanol and methanol + water mixtures[16-20].

Glycol has got two –OH groups and glycerol has got three –OH groups. So it should have more tendencies to break hydrogen bonds more readily than ethanol and methanol. But the reverse is seen to be true. This is probably due to low ion-solvent dipole interaction energy which is unable to break the strong inter-molecular hydrogen bond.

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