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THE THERMODYNAMICS OF K_2SO_4 IN MIXED SOLVENTS

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The conductivities data of K_2SO_4 in Methanol, Ethanol Isopropanol, Dioxane, Glycol and Glycerol + water mixtures at different concentration at 30-40°C have been studied and ion solvent interaction have been inferred.

INTRODUCTION

Conductance of electrolyte solutions in aquo-organic solvents have been studied with a view to understand the nature of the ion-ion and ion-solvent interaction [1, 2]. In the present communication conductance of K_2SO_4 in Methanol, Ethanol, Isopropanol, dioxane, glycol and glycerol + water mixtures (10, 20 and 30% w/w) at 30-40°C have been studied and attempt has been made to deal with the ion-solvent interaction and hydrogen bonding.

EXPERIMENTAL

The salts are of E. Merck "Extra pure varieties. Purification of solvents, preparation of solutions and method of measurements is the same that of before [1, 2]. The temperature of investigation was 30-40°C. The conductance measurements were of an accuracy of $\pm$ 2 in 1000°.

DISCUSSION

The Onsagar equation for a completely dissociated electrolyte is

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\, C^{1/2} \qquad \ldots(1)$$

where A and B are independent of concentration of the electrolytes. It satisfactorily accounts from the change in equivalent conductivities with concentration. Correct evaluation of Λ_0 can be made by extrapolating to zero concentration of the line obtained by plotting Λ vs $C^{1/2}$. However the above method of extrapolation has been reported to be unreliable in case of a number of electrolytes involving incomplete dissociation or ion association. Devise has extended the Onsagar's equation and has tabulated the dissociation constants of a variety of salts, specially of higher valency type. Electrolytic conductivities have been used to study ion solvent interaction and salvation of various cations and anions in aqueous and non-aqueous solution.

The equivalent conductivity of K_2SO_4 investigated by weight % of ethanol, methanol, isopropanol, dioxane, glycol, glycerol (10, 20 and 30%) water mixture at 30 to 40°C and found to be almost linear with $C^{1/2}$. The theoretical slope (S_1) calculated from the determined Λ_0 values for different electrolytes at different solvent composition have been obtained and compared with the experimental slope (S). Dielectric constants were calculated from the data of Akenlof and Short, viscosities were determined experimentally [1, 2]. The S_1 and S values are almost in fair agreement and differ by 2 to 3%. Λ_0 values are given in Table 1.

Table 1 : Λ_0/Ω^{-1} cm^2

	10%	20%	30%
Methanol+water	185	170	150
	195	190	162
	201	194	174
Ethanol+water	140	135	115
	175	172	164
	198	192	190
Isopropanol + water	145	120	105
	160	148	154
	175	184	175
Dioxane+water	156	128	110
	157	132	114
	165	134	117
Glycol+water	100	92	85
	105	96	90
	107	99	90
Glycerol+water	101	88	81
	105	91	85
	109	88	90

The Walden product $\Lambda_0\eta_0$ (Table 2) has been actually employed to study ion-solvent interaction in solution from conductivity data. The plot of $\Lambda_0\eta_0$ vs. *t* are found to be linear and is almost independent of temperature. Further the mere constancy of the Walden product at different temperature is most presumably due to compensating conductivity by the negative temperature coefficient of the viscosity of the solvent. The lesser the value of $\Lambda_0\eta_0$ the greater is the ion solvent interaction. Also electrostatic charge densities of the ion plays an important role in inducing ion-solvent interaction and salvation. It also appears that during these migration ions are covered with a sheath of solvent molecules resulting in a larger size of the solvodynamic unit, and a decrease in $\Lambda_0\eta_0$ (Table 2, so that the size of the solvated ions-solvent interaction is of the order; ethanol + water > methanol + water > isopropanol + water > dioxane + water > glycol + water > glycerol + water is in agreement with the viscosity and apparent molar volume data. (To be published later).

Because of the use of aquo-organic solvents, the dielectric constant of the medium is lowered and there is more probability of ion-pair formation. Hence the method of Fuoss and Krauss [3] and that of Shedlovsky [4] have been utilized to calculated the dissociation constant and Λ_c simultaneously, *K* values calculated by both the methods are in good agreement and are recorded in Table 3. The *K* values decreases with the decreases in dielectric constant, *i.e.*, with increase in non-aqueous solvent.

Table 2 : $\Lambda_0\eta_0/\Omega^{-1}$ cm^2

	10%	20%	30%
Methanol + water	1.30	1.29	1.29
	1.28	1.28	1.30
	1.29	1.31	1.31
Ethanol + water	1.24	1.23	1.24
	1.23	1.24	1.24
	1.23	1.24	1.25
Isopropanol + water	1.29	1.30	1.30
	1.30	1.28	1.30
	1.31	1.29	1.39
Dioxane + water	1.35	1.36	1.36
	1.34	1.35	1.35
	1.34	1.36	1.36
Glycol + water	1.38	1.37	1.36
	1.39	1.39	1.38
	1.38	1.39	1.39
Glycerol + water	1.47	1.40	1.41
	1.48	1.42	1.40
	1.48	1.41	1.41

Table 3 : $K \times 10^2$

	10%	20%	30%
Methanol + water	11.64	9.10	8.32
	11.92	9.06	8.05
	11.42	9.27	8.42
Ethanol + water	0.72	8.62	7.52
	0.91	8.98	7.38
	0.82	8.72	7.48
Isopropanol + water	11.61	9.63	9.8
	11.51	9.70	9.2
	11.40	9.80	9.3
Dioxane + water	12.71	9.67	8.56
	12.68	9.56	8.66
	12.54	9.42	8.64
Glycol + water	11.80	9.20	8.20
	11.20	9.40	8.50
	11.20	9.60	8.70
Glycerol + water	10.20	9.90	8.42
	10.31	10.10	8.50
	10.50	10.20	8.60

The standard thermodynamic parameter ΔG^0 and ΔS^0 have been calculated in the usual manner. The plots of ΔG^0 and ΔS^0 vs. solvent composition are found to be linear. The extrapolated values give the thermodynamic parameter for water. The standard thermodynamic quantities (ΔG_t^0 and ΔS_t^0) for transfer process from water to 10, 20, and 30% of organic solvent + water have been calculated by using Feakin's and Tuner's method [5]. ΔG_t^0 values are tabulated in Tables 7 and 8. The ΔG_t^0 values are all negative, which indicates that the ion pairs are in the lower free energy state in aquo-organic solvent than in water and hence the ion pair formation is favoured by decreasing the dielectric constant of the medium.

Since single ion values of free energies are not available presently for the solvent mixtures studied the method adopted by Khoo [6] is followed to study ion solvent interaction. The Born equation may be expected to fit increasingly better as the organic solvent content is increased. It is possible to split the ΔG_t^0 values into two parts suggested by Roy, *et al*., [7] *i.e*., chemical contribution denoted in terminology by $\Delta G^0_{t(ch)}$ and an electrostatic contribution $\Delta G^0_{t(el)}$, which

$$\Delta G^0_{t(el)} = \left(\frac{Ne^2}{2}\right)\left[\left(\frac{1}{\Sigma S}\right)-\left(\frac{1}{\Sigma W}\right)\right]\left[\left(\frac{1}{r_+}\right)-\left(\frac{1}{r_-}\right)\right] \qquad \ldots(2)$$

where, r_+ and r_- are the crystallographic radii or the cation and anion and *ts* and *Tw* are the dielectric constants of the mixed solvent and water respectively.

$$\frac{d\ln \Sigma w}{dT} \text{ and } \frac{d\ln \Sigma s}{dT}$$

can be evaluated from the simple empirical equation :

$$\frac{d\ln \Sigma^c}{dT} = \frac{1}{\phi} \qquad \ldots(3)$$

In which ϕ is a constant characteristic of the medium, so equation may be written as :

$$\Delta S^0_{t(el)} = \frac{Ne^2}{2}\left[\left(\frac{1}{\Sigma S\phi S}\right)-\left(\frac{1}{\Sigma w\phi W}\right)\right]\left[\frac{1}{r_+}+\frac{1}{r_-}\right] \qquad \ldots(4)$$

From the knowledge of $\Delta S^0_{t(el)}$ and $\Delta S^0_{t(el)}$ the chemical contribution of the free energy transfer, $\Delta S^0_{t(ch)}$ and entropy transfer, $\Delta S^0_{t(ch)}$ could be calculated by subtracting the respective electrostatic contribution values from the molar quantities and are tabulated in Tables 4 to 6. It is evident that the chemical contribution of the free energy of transfer is negative in all cases and hence is thermodynamically favourable as far as the chemical interactions are concerned, and is of the order :

Ethanol + water > methanol + water > isopropanol + water > dioxane
+ water > glycol + water > glycerol + water.

The $\Delta S^0_{t(el)}$ is also negative in all cases indicating chemical interaction and is of the order.

Table 4 : ΔG_t^0/J mole^{-1}

	Temp.	10%	20%	30%
Methanol + water	30	950	1620	2470
	35	915	1515	2440
	40	948	1598	2080
Ethanol + water	30	1040	1719	2568
	35	1000	1615	2508
	40	1050	1715	2520
Isopropanol + water	30	851	1800	2470
	35	862	1850	2390
	40	885	1780	2450
Dioxane + water	30	714	1418	2203
	35	815	1415	2340
	40	815	1414	2345
Glycol + water	30	664	1114	1825
	35	715	1214	2050
	40	744	1312	2092
Glycerol + water	30	694	1280	1845
	35	700	1215	1850
	40	710	1275	1820

Table 5 : $\Delta G^0_{t(ch)}$/J mole^{-1}

	10%	20%	30%
Methanol + water	620	780	1407
	670	840	1515
	602	774	1404
Ethanol + water	640	960	1204
	560	940	1508
	610	950	1300
Isopropanol + water	518	815	1500
	500	805	1510
	516	820	1530
Dioxane + water	416	713	1682
	360	740	1452
	387	708	1443
Glycol + water	372	658	1220
	300	600	1214
	250	575	1109
Glycerol + water	304	590	1380
	300	550	1370
	315	540	1365

Ethanol + water > methanol + water > isopropanol + water > dioxane + water > glycol + water > glycerol + water.

Table 6 : $\Delta S^0_{t(ch)}$ /JK^{-1} mole^{-1}

	10%	20%	30%
Methanol + water	3.61 3.21 3.51	7.10 6.42 7.02	9.45 9.72 9.42
Ethanol + water	4.28 3.82 4.25	7.22 6.91 7.10	10.55 9.91 9.98
Isopropanol + water	2.69 2.73 2.76	6.15 6.30 6.40	9.30 9.10 9.50
Dioxane + water	2.52 2.62 2.81	5.12 5.42 4.62	8.20 8.72 7.41
Glycol + water	2.40 2.62 2.81	4.80 4.90 5.30	7.40 7.60 8.10
Glycerol + water	2.40 3.40 3.50	4.90 4.80 4.90	7.60 7.50 7.30

The reasons for the behaviour is as follows :

Ethanol, methanol and isopropanol 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. If it cannot be accommodated because of its bulky size then it may cause a breakdown in three dimensional water structures. Several authors have observed that dioxane + 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 though the quanta is less than that of ethanol and methanol + water mixtures.

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. This is probably due to the low ion-solvent dipole interaction energy which is unable to break the strong intermolecular hydrogen bond.

REFERENCES

1. Das, N.C., Misra, P.K. and Das, P.B., *Acta Ciencia Indica*, **3**, 136 (1979).
2. Das, P.B., Ion-Solvent Interaction, *D.Sc. Thesis*, Sambalpur University (1984).
3. Fuoss, R.M. and Knauss, A.J., *J. Am. Chem. Soc.,* **45**, 476 (1933).
4. Schedlovsky, T.J., *Franklin Inst*., **225**, 439 (1939).
5. Feakin, D. and Tumer, D.J., *J. Chem. Soc.,* 4984 (1973).
6. Khoo, K. and Chan, C.C., *Aust. J. Chem.,* **28**, 721 (1973).
7. Roy, R.N., Verson, W. and Bothwell, A.L.M., *Electrochimica Acta*, **15**, 826 (1977).

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