THERMODYNAMICS OF SODIUM SULFATE IN MIXED BINARY SOLVENTS

D. SAHU AND A. K. PATNAIK*

Utkal University, Vani-Vihar, Bhubaneswar, India

ABSTRACT:

The conductivities data of Na_2SO_4 $.10H_2O$ in Isopropyl alcohol,1,4-dioxane, ethylene glycol andglycerol +water mixtures at different concentrations at 30-40^{0}C have been studied and ion solvent interaction have been inferred. The several properties like conductance (Λ_0), Walden product($\Lambda_0\eta_o$),dissociation constant(K),change in free energy($\Delta G^0{}_t$),change in entropy($\Delta S^0{}_t$) of electrolyte solutions in aquo-organic solvents have been studied with a view to understand the nature of the ion-ion and ion–solvent interactions.

1.INTRODUCTION:

The physical propertiesviz., dielectric constant, dipole moments of the mixed solvents likeIsopropyl alcohol + water , 1,4-Dioxane + water , glycol + water , glycerol + water are very much different from those of water. The organic solvents are more or less aprotic but water is an amphiprotic. Studies of ion solvent interactions [1, 2] have been a subject of interest among the physical chemists. In the present communication, conductivities of Na_2SO_4 in Iso-propyl alcohol, 1,4-dioxane, glycol and glycerol +water mixtures (10, 20 and 30%w/w) at 30-40 ^{0}C have been studied and attempt has been made to deal with the ion-solvent interaction and hydrogen bonding.

2.METHODS AND MATERIAL:

The salts (Anal R grade)used wereprocured from E. Merck (India) Ltd.They were used after drying over P_2O_5in a desiccator for few hours. Freshly distilled conductivity water was used for preparing the mixed aquo-organic solvents. The conductance of sodium sulphate solutions in Iso-propyl alcohol, 1,4-dioxane, glycol and glycerol +water mixtures (10, 20 and 30%w/w) at 30-40 ^{0}C is measured by conductometer. The conductance measurements were performed within accuracy of 0.002 and in the concentration from 0.01 to 0.001 equiv. dm^{-3}

3.RESULTS AND DISCUSSION:

The Onsagar equation for the completely dissociated electrolytes is

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

Where A and B are independent of concentration of the electrolytes. It satisfactorily accounts from the change in equivalent conductivities with concentration. The correct evaluation of Λ_0 can be made by exapolating to zero concentration of the line obtained by plotting Λ and $C^{1/2}$. 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. The extended Onsager's equation has been devised and tabulated the dissociation constants of a variety of salts, especially higher valency type. Electrolytic conductivities have been used to study ion solvent interaction and solvents of various cations and anions in aqueous and non-aqueous solution.

The equivalent conductivity of Na_2SO_4 investigatedby weight % of Iso-propyl alcohol, 1,4-dioxane, glycol and glycerol +water mixtures (10, 20, 30%) at 30-40^{0}C and found to be almost linear with $C^{1/2}$. The theoretical slope (S_t) 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.The S_t and S values are almost in fair agreement and differ by2 to 3%, Λ_0 values are given in Table-1.

The Walden product $\Lambda_0\eta_o$ (Table-2) has been actually employed to study ion solvent interaction in solution from conductivity data. The plot of $\Lambda_0\eta_o$ and 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 $\Lambda_0\eta_o$ the greater is the ion solvent interaction. Also electrostatic charge densities of the ion play an important role in inducing ion solvent interaction and salvation. It also appears that during this migration of ions covered with a sheath of solvent molecules resulting in a larger size of the solvodynamic unit and a decrease in $\Lambda_0\eta_o$ (Table-2), so that the size of the solvated ion-solvent interaction is of the order: Isopropyl alcohol + water >1,4-Dioxane + water > glycol + water > glycerol+ water is an agreement with the viscosity and apparent molar volume data.

Table-1:Λ_0 ($\Omega^{-1}cm^2$)

Mixed solvent	Temperature(^{0}C)	10%	20%	30%
Iso-propyl alcohol+water	30 35 40	187.5 192.0 200.1	161.2 162.5 174.0	144.6 148.1 152.0
1,4-dioxane+water	30 35 40	164.8 167.0 176.0	140.0 144.1 150.9	123.5 123.8 128.2
Glycol+water	30 35 40	164.0 167.9 176.5	138.5 143.5 150.1	115.8 118.1 129.7
Glycerol+water	30 35 40	164.2 160.0 172.1	141.5 142.1 149.8	119.1 122.0 127.2

Table-2:$\Lambda_0\eta_o$ ($\Omega^{-1}cm^2$)

Mixed solvent	Temperature(°C)	10%	20%	30%
Isopropyl alcohol+water	30	1.35	1.36	1.37
	35	1.34	1.35	1.37
	40	1.35	1.36	1.38
1,4-dioxane+water	30	1.41	1.41	1.42
	35	1.42	1.41	1.41
	40	1.41	1.42	1.41
Glycol+water	30	1.43	1.42	1.44
	35	1.42	1.43	1.44
	40	1.43	1.43	1.43
Glycerol+water	30	1.54	1.54	1.54
	35	1.53	1.53	1.52
	40	1.53	1.53	1.52

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 utilised to calculate the dissociation constant and $\Lambda_c$simultaneously values calculated by both the methods are good in agreement and are recorded in Table-3. The K values decreases with the decrease in dielectric constant.

Table- 3: K X10^2

Mixed solvent	Temperature(°C)	10%	20%	30%
Isopropyl alcohol+water	30	12.62	9.80	9.36
	35	12.21	9.18	8.54
	40	11.64	8.28	7.80
1,4-dioxane+ water	30	11.52	9.20	9.12
	35	11.50	9.10	9.00
	40	11.40	9.10	8.90
Glycol+ water	30	11.41	9.40	8.10
	35	11.20	9.10	8.20
	40	11.10	9.20	8.20
Glycerol+ water	30	10.62	8.80	7.65
	35	10.30	8.71	7.58
	40	10.20	8.65	7.51

The standard thermodynamic parameter ΔG^o and ΔS^o have been calculated in the usual manner. The plot of ΔG^o and ΔS^o vs. Solvent composition are found to be linear. The extrapolated values give the thermodynamic parameter for water. The standard thermodynamic quantities ($\Delta G^o_t$and ΔS^o_t)for transfer process from water to 10,20and 30%of organic solvent + water have been calculated by using Feakin's and Tuner's method[5]. ΔG^o_tvalues are tabulated in Table 4,5and 6. The ΔG^o_tvalues are all negative, which indicates that the ion pairs are in a 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 theΔG^o_t values into two parts suggested by Roy et al;[7] i e, chemical contribution ($\Delta G^o_{t(ch)}$) andelectrostatic contribution($\Delta G^o_{t(el)}$) which

$$\Delta G^o_{t(el)} = -\frac{Ne^2}{2}\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right)(2)$$

Where r_+ and r_- are the crystallographic radii or the cation and anion andϵ_s and ϵ_w are the dielectric constants of the mixed solvents and water respectively.

Where $\frac{d\ln\epsilon_s}{dT}$ and $\frac{d\ln\epsilon_w}{dT}$ can be evaluated from the simple empirical equation:

$$\frac{d\ln\ \epsilon w}{dT} = -\frac{1}{\varphi}\ (3)$$

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

$$\Delta S^o_{t(el)} = \frac{Ne2}{2}\left(\frac{1}{\epsilon_s\varphi_s} - \frac{1}{\epsilon_w\varphi_w}\right)\left(\frac{1}{r+} + \frac{1}{r-}\right) \qquad (4)$$

From the knowledge of $\Delta G^o_{t(el)}$ *and* $\Delta S^o_{t(el)}$,the chemical contribution[8,9,10,11,12] of the free energy transfer and entropy transfer could be calculated by subtracting the respective electrostatic contribution values from the molar quantities and are tabulated in table 7&8. 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:Iso-propyl alcohol + water >1,4-Dioxane +water > Glycol+ Water> Glycerol +water. This is due to decrease of change in free energy of the sodium sulfate in mixed binary solvents at the given temperature.

Table -4: ΔG^0_t (J mole $^{-1}$)

Mixed solvent	Temperature(^oC)	10%	20%	30%
Propan-2-ol+water	30	825	1225	2170
	35	870	1295	2140
	40	925	1340	2310
1,4-dioxane+ water	30	845	1391	2235
	35	855	1395	2295
	40	865	1465	2565
Glycol+ water	30	875	1605	2505
	35	905	1645	2635
	40	925	1655	2670
Glycerol+ water	30	954	1885	2655
	35	1105	1955	2735
	40	1215	2055	2795

The$\Delta S^o_{t(el)}$ is also negative in all cases including chemical interaction and is of the order:Iso-propyl alcohol + water > Dioxane + water > Glycol + Water >Glycerol + water.Iso-propyl alcohol contains 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 organic solvent to water may give rise to two effects.If the organic solvent is accommodated in the solvent structure, it may strengthen the water structure. But it cannot be accommodated because of its bulky size then it may cause a breakdown in the three dimensional water structures. It is observed that ΔE and ΔG increase with increase in the organic solvent content and hence, the three-dimensional water structure is broken down.Na^+ ions are more solvated due to its smaller size in sodium sulphate solution than K^+ in potassium sulfate. That is why the conductance of Na_2SO_4in mixed solvents is less. Using this conductivity data, the dissociation constant of the salt is calculated and also other thermodynamic parameters determined.

$$\Delta G^0_t = \Delta G^0_{t(el)} + \Delta G^0_{t(ch)} \quad (5)$$

$\Delta G^0_{t(el)}$ is the electrostatic part corresponding to a change in dielectric constant in the medium and $\Delta G^0_{t(ch)}$ is the non-electrostatic part corresponding to chemical contribution arising due interaction between ion pair and the solvents.

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

Mixed solvent	Temperature(°C)	10%	20%	30%
Propan-2-ol+water	30	345	795	1280
	35	345	885	1323
	40	395	895	1329
1,4-dioxane+ water	30	380	815	1320
	35	408	918	1365
	40	435	935	1398
Ethylene glycol+ water	30	415	865	1350
	35	427	950	1385
	40	455	991	1405
Glycerol+ water	30	462	895	1365
	35	485	965	1408
	40	498	1050	1427

Table- 6: $\Delta G^0_{t(ch)}$ (J mole $^{-1}$)

Mixed solvent	Temperature(°C)	10%	20%	30%
Propan-2-ol+water	30	1160	2005	3380
	35	1205	2095	3463
	40	1315	2180	3640
1,4-dioxane+ water	30	1225	2210	3555
	35	1265	2335	3760
	40	1320	2398	3898
Ethylene glycol+ water	30	1285	2470	3855
	35	1332	2585	3985
	40	1375	2620	4075
Glycerol+ water	30	1405	2720	3995
	35	1590	2950	4105
	40	1705	3150	4205

Table -7:ΔS^0_t (J K^{-1}mole $^{-1}$)

Mixed solvent	Temperature(°C)	10%	20%	30%
Propan-2-ol+water	30	15.30	16.80	24.60
	35	15.70	17.00	25.80
	40	16.20	17.20	26.30
1,4-dioxane+ water	30	17.20	17.65	25.65
	35	18.35	18.85	26.30
	40	19.50	20.05	26.85
Ethylene glycol+ water	30	19.35	20.15	27.15
	35	20.25	21.35	28.35
	40	21.45	22.50	29.05
Glycerol+ water	30	24.35	27.10	29.85
	35	25.85	28.25	31.15
	40	27.15	29.15	32.65

Table -8: $\Delta S^0_{t(el)}$ ($J\ K^{-1} mole^{-1}$)

Mixed solvent	Temperature(°C)	10%	20%	30%
Propan-2-ol+water	30	7.33	12.08	20.18
	35	7.49	12.15	21.15
	40	8.37	13.20	21.28
1,4-dioxane+ water	30	7.85	12.65	21.35
	35	8.15	13.15	21.98
	40	9.25	13.75	22.26
Ethylene glycol+ water	30	8.17	14.17	24.40
	35	8.85	14.85	25.12
	40	9.45	15.32	25.98
Glycerol+ water	30	8.75	15.65	26.23
	35	9.12	16.25	27.05
	40	10.25	17.15	27.85

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

4. ACKNOWLEDGEMENT: Authors are thankful to H.O.D of Chemistry, Ravenshaw University for the permission to carry out the research work and the support received from all the fellow colleagues for assistance in various ways.

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