ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

THE THERMODYNAMICS OF K_2SO_4 IN MIXED BINARY SOLVENTS

D. SAHU AND A. K. PATNAIK

Department of chemistry, Visiting professor, Utkal University,Vani-Vihar, Bhubaneswar, Odisha, India

Manuscript Info

Manuscript History:

Received: 18 March 2015
Final Accepted: 22 April 2015
Published Online: May 2015

Key words:

Potassium sulfate, equivalent conductance, free energy, entropy

***Corresponding Author**

D. SAHU

Abstract

The conductivities data of K_2SO_4 in Methanol, Ethanol, Propan-2-ol, 1,4-Dioxane, Glycol and Glycerol + Water mixtures at different concentrations at 30-40^{0}C have been studied and ion solvent interactions have been inferred.

INTRODUCTION

Conductances 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, 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^{0}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^{0}C. The conductance measurements were of an accuracy of ±2 in 1000^o.

RESULTS AND DISCUSSION:

The Onsagar equation for the completely dissociated electrolytes is

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

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 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. Devise the extended the Onsager's equation and has 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 conductance of K_2SO_4 investigated by weight % of Methanol, Ethanol, Propan-2-ol, 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 [1, 2].The St and S values are almost in fair agreement and differ by 2 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: Ethanol + water > Methanol + water > propan-2-ol + water > 1,4-Dioxane + water > glycol + water > glycerol+ water is an agreement with the viscosity and apparent molar volume data.

Table-1: $\Lambda_0(\Omega^{-1}cm^2\ g\ eq.^{-1})$

	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	143	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

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

	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

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 (K) and Λ 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

	10%	20%	30%
Methanol+water	11.64 11.92 11.42	9.10 9.06 9.27	8.32 8.05 8.42
Ethanol+water	10.72 10.91 10.82	8.62 8.98 8.72	7.52 7.38 7,48
Isopropanol+water	11.61 11.51 11.40	9.63 9.70 9.80	9.80 9.20 9.30
Dioxane+ water	12.71 12.68 12.54	9.67 9.56 9.42	8.56 8.66 8.64
Glycol+ water	11.80 11.20 11.20	9.20 9.40 9.60	8.20 8.50 8.70
Glycerol+ water	10.20 10.31 10.50	9.90 10.10 10.20	8.42 8.50 8.60

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 (ΔG^o_t and ΔS^o_t)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^o_t values are tabulated in Table- 4 and 5. The ΔG^o_t values 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 the ΔG^o_t values into two parts suggested by Roy et al;[7] i e, chemical contribution ($\Delta G^o_{t(ch)}$) and electrostatic contribution($\Delta G^o_{t(el)}$) which

$$\Delta G^o_{t(el)} = \frac{Ne2}{2}\left(\frac{1}{\epsilon s} - \frac{1}{\epsilon w}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \text{ ------------------------------------- } (2)$$

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

Where $\frac{d \ln \in s}{dT}$ and $\frac{d \ln \in w}{dT}$ can be evaluated from the simple empirical equation:

$$\frac{d \ln \in w}{dT} = -\frac{1}{\emptyset} \text{ ------------------------------------- } (3)$$

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

$$\Delta S^o_{t(el)} = \frac{Ne2}{2}\left(\frac{1}{\epsilon \phi s\ \emptyset S} - \frac{1}{\epsilon \phi w \emptyset W}\right)\left(\frac{1}{r+} + \frac{1}{r-}\right) \text{ -------------------------- } (4)$$

From the knowledge of $\Delta G^o_{t(el)}$ and $\Delta S^o_{t(el)}$, the chemical contribution[8-12] 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- 5 & 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 > 1,4-Dioxane + water > Glycol + Water > Glycerol + water.

Table -4: ΔG^{0}_{t} (J mol $^{-1}$)

	Temp.	10%	20%	30%
Methanol+water	30	950	1620	2470
	35	915	1515	2440
	40	948	1598	2480
Ethanol+water	30	1040	1719	2568
	35	1000	1615	2508
	40	1050	1715	2520
Propan-2-ol+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

The $\Delta S^{o}_{t(el)}$ is also negative in all cases including chemical interaction and is of the order: Ethanol + water > Methanol + water > Isopropanol + water > Dioxane + water > Glycol + Water > Glycerol + water.

The reasons for the behaviour is 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[13-18] 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 because organic solvent 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 organic solvent + 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 that of ethanol and methanol + water mixtures.

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

	10%	20%	30%
Methanol + water	620	780	1407
	670	840	1515
	602	770	1404
Ethanol + water	640	960	1204
	560	940	1508
	610	950	1300
Propan-2-ol+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	595	1380
	300	555	1370
	315	540	1365

Table -6: $\Delta S^0_{t(ch)}$ (J K^{-1}mol $^{-1}$)

	10%	20%	30%
Methanol + water	3.61	7.10	9.45
	3.21	6.42	9.72
	3.51	7.02	9.42
Ethanol +water	4.28	7.22	10.55
	3.82	6.91	9.91
	4.25	7.10	9.98
Propan-2-ol+water	2.71	6.20	9.30
	2.73	6.30	9.10
	2.76	6.40	9.40
Dioxane+ water	2.52	5.12	8.20
	2.62	5.42	8.32
	2.81	4.62	7.41
Glycol+ water	2.40	4.80	7.40
	2.62	4.90	7.60
	2.81	5.30	8.10
Glycerol+ water	2.40	4.90	7.60
	3.40	4.80	7.50
	3.50	4.90	7.30

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.

ACKNOWLEDGEMENT: Authors are thankful to the H.O.D. of chemistry,Utkal University for the permission to carry out the research workand support receieved from all the fellow colleagues for assistance in various ways.

REFERENCES:

1. Das, N.C., Mishra, P.K. and P.B. Das, Acta Ciencia Indica ,**3**,136 (1979)
2. Das, P.B., Ion solvent interaction, D.Sc. Thesis, Sambalpur University(1984)
3. Fuoss, R.M and A J Knauss, J. Am. Chem. Soc., **45**, 476 (1933)
4. Shedlovsky, T.J. ,Franklin Ins., **225**, 439, (1939)
5. Feakin, D. and D.J Tuner, J. Chem Soc. 4984 (1973)
6. Khoo, K. And C.C Chan, Aust J. Chem., **28**, 721 (1973)
7. Roy, R. N., Version, W. And A.L.M. Bothwell, Electrochimica acta, **15**, 826 (1977)
8. Das U.N et al; J.Phy &Chem of liquids Vol 49,Issue-4,(2011)
9. Pal P.C. et al; Acta Ciencia Indica Vol XXXIC, No-**2**,087(2005)
10. Mishra S. Et al; Acta Ciencia Indica Vol XLC, No-**3**,117(2014)
11. Laxmidhar et al; Acta Ciencia Indica Vol XLC, No-**3**,127(2014)
12. Mohanty P.C. et al; Asian J. Chem. Vol-17,No-**2**,895-901(2005)
13. Robert J. LeSuer , Catherine Buttolph and William E. Geiger, Anal. Chem.,**76 (21)**, 6395–6401 (2004).
14. Cinzia Chiappe and Daniela Pieraccini, J. Phy. Org. Chem., **18**, 275–297(2005).
15. U.N. Dash, G.S. Roy, D. Moharatha & M. Talukdar, Int. J. Phy. & Chem. of Liq., **49(4)**, 421-429 **(**2011**).**
16. Veerati Radhika, Der Chemica Sinica, **2 (2)**, 136-143(2011).
17. Abdul Ahad, Mohd. Shafique, Vidya Pradhan and Mazahar Farooqui, Sci. Revs.Chem.Commun., **2(4)**, 602-605, (2012).
18. Milan Chandra Roy, Mahendra Nath Roy, J. Mol. Liq.,**195**, 87–91, (2014).