Acta Ciencia Indica, Vol. XLII C, No. 3, 175 (2016)

THERMODYNAMICS OF KF IN MIXED SOLVENT AT 30°-40°C

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RECEIVED : 23 August, 2016

INTRODUCTION

The ion solvent interaction of Flouride in ethanol+water, CH_3OH + water, Isopropanol + water, Glycol + water, Glycerol + water obtained from conductance have been compared at 10, 20 and 30% (w/w) solvent composition with temp. range 30°-40°C have been studied from conductance measurement. The K, $\Delta G°$, $\Delta G°_{(t)}$, $\Delta G°_{t(el)}$ and $\Delta G°_{t(ch)}$ have been calculated and ion-solvent interactions are inferred.

The physical properties of the mixed solvents like ethanol + water, methanol + water, isopropanol + water, dioxane + water, Glycol + water and Glycerol + water viz. dielectric constant, dipole moments are very much different from that of waster. These organic solvents are more or less aprotic water is both an electron donor and electron acceptor. These and several other properties make a study of their aqueous mixture an interesting thing to explore particularly of the ionic processes accompanying the solution of strong electrolytes.

In the present communication conductivities of potassium fluoride in Ethanol + water, Methanol + water, Isopropanol + water, Dioxane + water, Glycol + water and Glycerol + water mixture at 30° to 40° have been measured to investigate the ion solvent interaction.

EXPERIMENTAL

The salt used was of E Merck 'extrapure' variety. The purification of solvent, preparation of solvent and solution and measurement of the conductance have been described previously [3]. The conductance measurements were within accuracy of 0.002 and within the concentration range from 0.01 to 0.001 equivalent litre^{-1}. The temperature of investigation was from 303 to 313 $\pm$ 0.01K.

DISCUSSION

The Onsagar equation [1] for a completely dissociated electrolyte is

$$\Lambda = \Lambda° - (A + B\Lambda°)\sqrt{C} \qquad \ldots(1)$$

where A and B are independent of concentration of the electrolytes. It satisfactorily accounts from the change in the equivalent conductivities with concentration. Correct evaluation of Λ° 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. Davies 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 KF investigated by weight % of ethanol, methanol, isopropanol, dioxane, glycol, glycerol (10, 20 and 30%) water mixture at 30°-40°C and found to be almost linear with $C^{1/2}$. The theoretical Slope (S_T) calculated from the determined Λ° values for different electrolytes at different solvent composition have been obtained and compared with the experiment 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 by 2 to 3%. Λ° values are given in Table-1.

Table 1. $\Lambda°\Omega^{-1}$ cm^2

	Temp. °C	**10%**	**20%**	**30%**
Methanol	30	136	91	80
+	35	150	108	82
Water	40	156	122	92
Ethanol	30	111	185	95
+	35	122	95	88
Water	40	131	116	96
Isopropanol	30	131	102	98
+	35	155	118	110
Water	40	170	130	130
Dioxane	30	158	88	76
+	35	132	90	80
Water	40	138	95	81
Glycol	30	135	100	90
+	35	140	104	95
Water	40	145	107	99
Glycerol	30	136	102	100
+	35	145	114	118
Water	40	150	126	134

The walden product [2] $\Lambda°\eta_0$ (table 2) has been actually employed to study ion-solvent interaction in solution from conductivity data. The plot of $\Lambda°\eta_0$ 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 contribution of the temperature coefficient of the viscosity of the solvent. The lesser the value of $\Lambda°\eta_0$, 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 $\Lambda°\eta_0$ (Table-2), so that the size of the solvated ions and the ion-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).

Table 2. $\Lambda°\eta_o$ / Ω^{-1} cm^2

	Temp. °C	**10%**	**20%**	**30%**
Methanol	30	1.17	1.19	1.19
+	35	1.18	1.20	1.20
Water	40	1.19	1.21	1.21
Ethanol	30	1.12	1.12	1.13
+	35	1.12	1.12	1.12
Water	40	1.13	1.12	1.12
Isopropanol	30	1.16	1.18	1.20
+	35	1.15	1.18	1.20
Water	40	1.16	1.17	1.21
Dioxane	30	1.25	1.26	1.26
+	35	1.24	1.25	1.25
Water	40	1.24	1.26	1.26
Glycol	30	1.28	1.27	1.26
+	35	1.29	1.29	1.28
Water	40	1.31	1.30	1.29
Glycerol	30	1.27	1.30	1.21
+	35	1.28	1.32	1.20
Water	40	1.28	1.31	1.21

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 Λ° simultaneously. K values calculated by both the methods are in good agreement and are recorded in Table-3. The K values decreases with the decrease in dielectric constant, i.e. with increase in non-aqueous solvent.

The standard thermodynamic parameter ΔG° and ΔS° have been calculated in the usual manner. The plots of ΔG° and ΔS° vs. solvent composition are found to be linear. The extrapolated values give the thermodynamic parameter for water. The standard thermodynamic quantities ($\Delta G°_t$ and $\Delta S°_t$) for transfer process from water to 10, 20 and 30% of organic solvent + water have been calculated by using Feakin's and Tuner's [5] method. $\Delta G°_t$ values are tabulated in table-7 and 8. The $\Delta G°_t$ 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 $\Delta G°_t$ values into two parts as suggested by Roy *et al.* [7]

i.e. chemical contribution denoted in their terminology by $\Delta G^\circ_{t(ch)}$ and an electrostatic contribution $\Delta G^\circ_{t(el)}$, which has been calculated from the Born equation :

$$\Delta G^{o}_{t(el)} = (Ne^2/2) - [(1/\varepsilon_s) - (1/\varepsilon_w)] - [(1/r_+) - (1/r_-)] \qquad \ldots (2)$$

where, r_+ and r_- are the crystallorgraphic radii of the

Where,

$$d\ln\varepsilon_w / dT \quad \& \quad d\ln\varepsilon_s / dT$$

can be evaluated from the simple empirical equation :

$$d\ln\varepsilon^{o} / dT \; = \; -1/\theta \qquad \ldots (3)$$

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

$$\Delta S^{o}_{t(el)} = (Ne^2/2) - [(1/\varepsilon_s\theta_s) - (1/\varepsilon_w\theta_w)] - [(1/r_+) - (1/r_-)] \qquad \ldots (4)$$

Table 3. K × 10^2

	Temp. °C	**10%**	**20%**	**30%**
Methanol	30	11.14	9.10	8.15
+	35	11.22	9.16	8.45
Water	40	11.12	9.12	8.25
Ethanol	30	10.72	8.62	8.52
+	35	10.91	8.98	8.38
Water	40	10.82	8.72	8.48
Isopropanol	30	11.61	9.63	9.80
+	35	11.50	9.70	8.66
Water	40	11.40	9.80	8.64
Dioxane	30	11.71	9.67	8.56
+	35	11.68	9.56	8.66
Water	40	11.54	9.42	8.64
Glycol	30	9.80	9.20	8.20
+	35	10.20	9.40	8.50
Water	40	10.20	9.60	8.70
Glycerol	30	10.20	9.90	8.42
+	35	10.31	10.10	8.50
Water	40	10.50	10.20	8.60

From the knowledge of $\Delta G^{o}_{t(el)}$ and $\Delta S^{o}_{t(el)}$, the chemical contribution of the free energy transfer, $\Delta G^{o}_{t(ch)}$ and entropy transfer, $\Delta S^{o}_{t(ch)}$ could be calculated by subtracting the respective electrostatic contribution values from the molar quantities and are tabulated in table 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 $\Delta S^{o}_{t(ch)}$ is also negative in all cases indicating chemical interaction and is of the order :

Table 4. – ΔG°_{t} /J mol^{-1}

	Temp. °C	10%	20%	30%
Methanol	30	690	1302	1909
+	35	671	1214	1815
Water	40	702	1290	1905
Ethanol	30	756	1350	2002
+	35	751	1290	1910
Water	40	770	1309	1998
Isopropanol	30	794	1400	1849
+	35	800	1380	1805
Water	40	780	1370	1830
Dioxane	30	554	1471	1545
+	35	562	1614	1717
Water	40	722	1698	1840
Glycol	30	415	1301	1502
+	35	465	1314	1515
Water	40	522	1411	1585
Glycerol	30	500	1370	1475
+	35	520	1350	1480
Water	40	505	1290	1500

Ethanol + water > Methanol + water > Isopropanol + water > Dioxane + water > Glycol + water > Glycerol + water.

The reasons for this 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 dimentional 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 accommodataed 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 structure. Several authors have observed that dioxane+water is less ordered than pure water. It is 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 & 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.

Table 5. – $\Delta G^\circ_{t(ch)}$/J mol^{-1}

	Temp. °C	10%	20%	30%
Methanol	30	520	780	1407
+	35	470	840	1515
Water	40	502	774	1404
Ethanol	30	640	960	1204
+	35	560	940	1508
Water	40	610	950	1300
Isopropanol	30	518	815	1500
+	35	500	805	1510
Water	40	516	820	1530
Dioxane	30	416	713	1682
+	35	360	740	1452
Water	40	387	708	1443
Glycol	30	372	608	1212
+	35	300	600	1214
Water	40	250	575	1109
Glycerol	30	304	590	1380
+	35	300	560	1370
Water	40	315	540	1365

Table 6. – $\Delta S^\circ_{t(ch)}$/JK^{-1} mol^{-1}

	Temp. °C	10%	20%	30%
Methanol	30	3.61	7.10	9.45
+	35	3.21	6.42	9.72
Water	40	3.51	7.02	9.42
Ethanol	30	4.28	7.22	10.55
+	35	3.82	6.91	9.91
Water	40	4.25	7.10	9.98
Isopropanol	30	2.69	6.15	9.3
+	35	2.73	6.30	9.1
Water	40	2.76	6.40	9.5
Dioxane	30	2.52	5.12	8.2
+	35	2.62	5.42	8.72
Water	40	2.81	4.62	7.41
Glycol	30	2.4	4.8	7.4
+	35	2.62	4.9	7.6
Water	40	2.81	5.3	8.1
Glycerol	30	2.4	4.9	7.6
+	35	3.4	4.8	7.5
Water	40	3.5	4.9	7.3

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