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THERMODYNAMICS OF SOME SODIUM SALTS IN ETHANOL+WATER MIXTURES AT 30°-40°C

J.R. MOHANTY

S.B. Women's College, Cuttack

P.C. MOHANTY

Kendriya Vidyalaya, Charbatia, Cuttack

ABANI SAHU

Stewart Science College, Cuttack

Mrs. S. PATNAIK

B.J.B. College, Bhubanewar

AND

P.K. MISRA

Ex-P.G. Department of Chemistry, Ravenshaw College, Cuttack 753003 (India)

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The ion-solvent interaction of five sodium salts in Ethanol+water along with the data of methanol+water and dioxane + at 10, 20 and 30% (W/W) within the temperature range of 30°-40°C, have been compared from conductance data. The dissociation constants K, $\Delta G°$, $\Delta G_t°$, $\Delta G_t°_{(el)}$, $\Delta G_t°_{(Ch)}$ have been computed and the ion-solvent interactions have been inferred.

INTRODUCTION

The physical properties of the mixed solvents like ethanol + water, methanol + water and dioxane + water, viz. di-electric constants, dipolemoments are very much different from that of water. These organic solvents are more or less aprotic, water is both an electron donor and acceptor. These and several other properties make a study of their aqueous mixtures an interesting thing to explore particularly of the ionic processes accompanying the solution of strong electrolytes.

In the present communication, the conductivities of five sodium salts in ethanol + water along with the data of methanol + water [1] and dioxane + water [2] mixtures at 30 to 40°C, have been compared to investigate the ion-solvent interaction.

EXPERIMENTAL

The salts used were of E. Merck extrapure varieties. The purification of solvents, preparation of solvent and solutions and measurement of conductance have been described previously [3]. The conductance measurements were within the accuracy of 0.002 and within the concentration range from 0.01 to 0.001 equiv. litre^{-1}. The temperature of investigation was from 303 to 313 ± 0.01K.

RESULTS AND DISCUSSION

The Onsager equation [3] for completely dissociated electrolytes is :

$$\Lambda = \Lambda^\circ - (A+B\Lambda^\circ)\sqrt{C}$$

where, A and B are Onsager's constants. It satisfactorily accounts for the change of equivalent conductance with concentration, since the plot of Λ Vs. $C^{1/2}$ is linear and the theoretical slope (S_T) is almost the same as that of the experimental slope (S). However, the above methods are unreliable in the cases of number of electrolytes involving incomplete dissociation or ion-association. Hence the method of Fuoss and Krauss [5] and that of Shedlovsky [6] have been utilized to calculate the Λ° and K simultaneously. The Λ° and K values obtained by both the methods are in good agreement and are given in table-1 and table-2 (only data at 35°C). The K values are found to decrease with the decrease in dielectric constant caused by the increase in organic solvents. This is attributed due to incomplete dissociation or ion-association.

The standard thermodynamic parameter ΔG_t° have been calculated in the usual manner [7] and are recorded in table-3 (data at 35°C only). This ΔG_t° is the thermodynamic quantity for transfer process from water to 10, 20 and 30% organic solvent-water were being obtained by Feakin's method [8]. The ΔG_t° values are all negative which indicates that the ion-pairs are in a lower free energy state in aquo-organic solvents than in water and hence the ion-pair formation is favoured by decreasing the dielectric constant of the medium.

Single ion free energy are not available presently for the solvent mixtures studied. Hence, the method adopted by Khoo and Chan [9] was followed to study ion-solvent interaction. The Born equation was expected to fit increasingly better as the organic solvent is increased. It was possible to split the ΔG_t° into two parts as Roy *et al.* [10] had sone, *i.e.* the 'Chemical Contribution' denoted by their terminology by $\Delta G_t^\circ{}_{(Ch)}$) and an electrical contribution $\Delta G_t^\circ{}_{(el)}$ could be calculated from the Born equation. From a knowledge of $\Delta G_t^\circ{}_{(el)}$, the electrical contribution, the free energy transfer could be calculated by the equation,

$$\Delta G_t^\circ{}_{(Ch)} = \Delta G_t^\circ - \Delta G_t^\circ{}_{(el)}$$

and are tabulated in table-4 (data of 35°C only). The $\Delta G_t^\circ{}_{(Ch)}$, *i.e.* the chemical contribution to the energy of transfer is negative in all cases and hence the process is thermodynamically favourable as far as the chemical interactions are concerned and the lower the value the greater is the interaction and the order is E + W > M + W > D + W.

The reason can be explained as follows :

Ethanol and methanol has got – OH group and water is both an electron donor and acceptor. So the three dimensional water structure is easily broken down in sodium salts. Dioxane is more basic and less acidic in nature than that of pure water, because of the electron releasing tendency of the methylene groups on the molecules. A water molecule, which is hydrogen bonded with oxygen atom of a dioxane molecule also becomes more basic and less acidic than that of pure water. A cation will interact more strongly with the oxygen atom of D+W and an anion will interact less strongly with the hydrogen atom. Hence, the quanta of ion-solvent interaction is less than that of ethanol and the methanol.

Table 1. $\Delta^\circ / \Omega^{-1}\ cm^2$ at 35°C only

	E + W			**M + W**			**D + W**		
	10%	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
NaF	142	105	102	130	106	100	120	99	90
NaCl	196	172	109	197	155	140	144	121	105
NaBr	199	148	120	122	188	110	138	116	101
NaI	135	115	87	132	122	114	109	100	90
$NaNO_3$	136	121	111	170	165	130	132	113	94

Table 2. K × 10^2 at 35°C only

	E + W			**M + W**			**D + W**		
	10%	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
NaF	17.42	14.53	10.44	18.52	15.61	11.71	20.5	16.4	12.5
NaCl	18.91	11.91	10.11	19.81	12.81	10.51	20.89	13.52	10.72
NaBr	15.82	13.52	10.52	16.58	14.78	11.95	17.38	16.22	12.88
NaI	9.05	7.98	6.04	9.98	8.12	6.12	10.3	8.3	6.2
$NaNO_3$	11.82	10.42	9.04	12.45	11.56	9.58	13.80	12.30	10.23

Table 3. – $\Delta G_t°$ / J. mol^{-1} at 35°C only

	E + W			**M + W**			**D + W**		
	10%	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
NaF	1000	1615	25.05	915	1515	2440	815	1415	2340
NaCl	900	1605	2415	843	1504	2340	743	1521	2373
NaBr	1020	1715	2515	9515	1615	2500	552	871	1681
NaI	705	1014	1115	605	914	1014	505	814	1012
$NaNO_3$	1178	1750	2570	1004	1615	2550	804	952	1573

Table 4. – $\Delta G_t°_{(Ch)}$/J.mol^{-1} at 35°C only

	E + W			**M + W**			**D + W**		
	10%	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
NaF	915	1100	1780	815	1015	1750	690	912	1614
NaCl	660	855	1104	560	789	1005	227	291	1083
NaBr	998	1248	1890	801	1114	1705	973	1101	1690
NaI	660	950	1280	500	880	1170	450	750	1073
$NaNO_3$	1004	1355	2044	988	1099	1855	438	993	1755

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