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Research Article

THERMODYNAMICS OF SOME POTASSIUM SALTS IN METHANOL + WATER MIXTURE AT 30⁰ TO 40⁰ C

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ABSTRACT

The ion-solvent interaction of five potassium salts in methanol + water along with the data of ethanol + water and dioxane + water obtained from conductance have been compared at 10, 20 and 30% (w/w) solvent composition within the temperature range 30-40⁰ . The K (dissociation constant) ΔG⁸ 1(el) (change in free energy transfer due to electrical contribution) and ΔG⁸ 1(el) (change in free energy transfer due to electrical contribution) ΔG⁸ (oh) (change in free energy transfer due to electrical contribution) have been calculated and ion-solvent interactions are inferred.

Keywords: Methanol, Electrolyte, Free energy, Dissociation constant

INTRODUCTION

Organic solvent like methanol + water is more or less aprotic. Water is both an electron donor and acceptor. This and several other prop2erties 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 potassium salts in methanol + water have been determined and compared with the data of ethanol + water[1] and dioxane + water [2] mixtures between 30 and 40⁰C.

EXPERIMENTAL

The salts used were of E. Merks 'Extrpure' varieties. The purification of solvent and solutions and measurement of conductance have been described previously.[3] The conductance measurements were within the accuracy of ± 1 Ω^{-1} cm^2 and within the concentration range from 0-01 to 0-001 equiv.$Litre^{-1}$. The temperature of investigation was from 303 K to 313 ± 0.01K.

RESULTS AND DISCUSSION

The Onsager equation4 for completely dissociated electrolytes is $=\Lambda^0$ - (A+B Λ^0) $\sqrt{C}$, where A and B are Onsager's constants. It satisfactorily accounts for 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^0 and K values obtained by both the methods are in good agreement and are given in tables-1 and 2 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_1^* at 35°C have been calculated in the usual manner[7] and are recorded in table-3 . ΔG_1^* is the thermodynamic quantity for transfer process from water to 10.20 and 30% organic solvent water.

This is obtained by Feakin's method8 , ΔG_1^* values are all negative which indicate that the ion-pairs are in a lower free energy state in aquo-organic solvents than in water. Hence, the ion-pair formation is favoured by decreasing the dielectric constant of the medium.

Single ion free energy is not available presently for the solvent mixture studied. Hence, the method adopted by Khoo and Chan[9] was followed to study ion-solvent is increased. It was possible to split ΔG_1^* into two pairs according to Roy et al[10], i.e. the Chemical contribution denoted by their terminology by ΔG^* and an electrical contribution ΔG^* t (el) which could be calculated from Born equation.

Table 1: $(\Lambda^*\Omega)^{*-1}$ at 35° C

	M + W			E + W			D + W		
	10%	20%	30%	10%	20%	30%	10%	20%	30%
KF	150	82	132	122	95	90	132	90	80.0
KCI	195	162	175	162	175	172	157	132	80.0
KBr	187	164	152	176	160	145	150	127	110.0
KI	187	164	160	192	146	118	154	174	170.0
KNO3	172	162	145	122	135	148	144	122	106.0

Table 2: $K^* \times 10^2$ at 35° C

	M + W			E + W			D + W		
	10%	20%	30%	10%	20%	30%	10%	20%	30%
KF	11.22	9.16	8.45	10.92	8.98	8.38	11.68	9.56	8.66
KCI	11.28	9.01	8.05	9.72	8.78	7.95	12.21	9.17	8.54
KBr	9.96	8.82	7.52	9.52	8.42	7.32	10.30	8.94	7.78
KI	9.96	9.94	8.56	9.72	9.42	8.82	10.42	10.1	9.1
KNO3	8.01	6.52	5.98	7.98	6.43	5.78	8.34	6.62	6.18

*Dissociation constant.

Table 3: $(-\Delta G_t^* / J.\ mole^{-1})$ **at 35° C**

	M + W			E + W			D + W		
	10%	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
KF	671	1214	1815	751	1290	1910	562	1614	1714
KCI	651	1114	1715	708	1214	1815	513	1014	1614
KBr	681	1314	1915	790	1340	2050	504	1123	1505
KI	424	628	828	478	750	980	510	718	1078
KNO3	751	1450	2040	850	1580	2250	608	1160	1673

*Free energy transfer from water to mixed solvent.

Table 4: $(-\Delta G^o_{t(ch)} J.\ mole^{-1})$ **at 35° C**

	M + W			E + W			D + W		
	10%	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
KF	470	840	1414	560	940	1580	360	740	1452
KCI	401	698	1204	501	780	1365	374	628	1196
KBr	508	780	1415	650	1100	2505	559	470	1220
KI	250	305	805	305	505	905	220	380	808
KNO3	646	1004	1615	750	1280	1415	505	306	1291

*Free energy transfer due to chemical contribution.

From the knowledge $\Delta G^*_{t\,(el)}$, the electrical contribution, the free energy transfer could be calculated by the equation :

$$\Delta G^*_{t\,(Ch)} = \Delta G^*_{t\,(el)}$$

and are recorded in table-4. The $\Delta G^*_{t\,(Ch)}$ 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 chemical interaction are concerned and the lower the value, the greater is he interaction, the order being E+W>M+W>D+W.

CONCLUSION

Ethanol and methanol have got – OH group and water is both an electron donor and acceptor. So, the three dimensional water structure is easily broken down in potassium salts. Dioxane is more basic and less acidic than that of pure water, because of electron releasing tendency of the methylene group in the molecule. A waster 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. An anion will interact less strongly with the hydrogen atom. Hence, the quanta of ion-solvent interaction is less than that of ethanol and methanol.

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