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THE THERMODYNAMICS OF MGSO$_4$, MNSO$_4$, AND CDSO$_4$ IN METHANOL+WATER AND ETHANOL + WATER MIXTURE AT 30°, 35°, AND 40°C

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The conductivity date of $MgSO_4$, $MnSO_4$ and $CdSO_4$ in methanol and ethanol + water mixtures at temperature 30-40°C along with the data of dioxane have been computed and ion solvent interaction have been inferred.

INTRODUCTION

In the present investigation the conductivity of $MgSO_4$, $MnSO_4$ and $CdSO_4$ methanol + water and ethanol + water mixtures at 30°C, 35°C and 40°C have been studied.

From data thus obtained along with the data of Das [1] the inference regarding Ion Solvent interaction have been inferred.

Material and Methods

The salts are of E merck "extra pure" varieties. Purification of solvents, preparation of solutions and methods of measurements is same that of before [1]. The temperature of investigation was 30°C to 40°C. The conductances measurement were of an accuracy of $\pm$ 2 in 1000.

DISCUSSION

The Onsager equation [2] for completely dissociated electrolyte,

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

satisfactorily accounts for the change of equivalent conductance with concentration. Correct evaluation of Λ_o can be made by extrapolating the plot of Λ vs $C^{1/2}$ to zero concentration. This method of extrapolation has been reported to be unreliable in case of a number of electrolytes involving incomplete dissociation or ion association. In the present case there is more probability of ion association since the dielectric constant of the medium is low. Hence the methods of Fuoss and Krauss [3] and Shedlovsky [4] have been utilised to calculate simultaneously the value of limiting equivalent conductance Λ_o and the dissociation constant K. The values of Λ_o and K obtained by application of the two methods are in good agreement. These values along with that of dioxane are recorded in table 1 and 2. The K values are found the decrease with increase in temperature for all solvent compositions as well as for the electrolytes, $MgSO_4$, $MnSO_4$, $CdSO_4$.

Table 1. $\Lambda^0 / \Omega^{-1}\ cm^2$

		Methyl alcohol			Ethyl alcohol			Dioxane		
		10%	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
$MgSO_4$	30	125	140	68.5	130	112	69.5	131	116	72
	35	140	123	80	142	126	84	144	129	89
	40	155	135	92	158	140	95	160	145	99
$MnSO_4$	30	112	80	57.5	114	84	62	116	87	65
	35	134	944	73	136	87	77	138	90	89
	40	148	112	91	151	118	95	154	121	99
$CdSO_4$	30	110	72	65	75	78	68	78	82	72
	35	121	94	77	130	99	80	133	104	84
	40	134	111	88	142	116	94	145	118	98

Table 2. $K \times 10^2$

		CH_2aOH			C_2H_5OH			Dioxane		
		10%	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
$MgSO_4$	30	6.4	5.4	4.7	5.7	4.8	4.3	5.8	5.0	4.7
	35	6.4	5.1	4.6	5.9	4.9	4.4	5.6	4.8	4.3
	40	6.5	5.5	4.8	5.7	4.7	4.3	5.9	5.2	4.8
$MnSO_4$	30	7.1	5.9	5.9	5.9	5.1	4.7	6.1	5.3	5.1
	35	7.2	5.8	5.0	6.1	5.3	4.5	5.9	5.1	4.9
	40	7.4	6.0	5.3	6.4	5.2	4.8	6.0	5.4	5.4
$CdSO_4$	30	8.2	6.0	5.0	6.3	6.2	5.2	6.3	5.6	5.0
	35	8.4	6.2	5.4	6.7	6.0	4.9	6.4	5.7	5.1
	40	8.3	6.0	5.1	6.9	6.4	5.4	6.7	6.0	4.3

The K values also decreases with decrease in dielectric constant, *i.e.,* with increase in percentage of organic solvent in the aquo-organic mixture. This is attributed to the incomplete dissociation or ion-association.

The Walden product [5] (table 3) has been actually exployed ion-solvent interaction in solution from conductivity data. The plot of $\Lambda^\circ\Omega_o$ vs *t* is almost linear and is independent of temperature. Further the mere constancy of the walden product at different temperatures is almost presumably due to compensating contribution of temperature coefficient of conductivity by negative temperature coefficient of viscosity of the solvent. The lesser the value of $\Lambda^\circ\Omega_o$, the greater is the ion-solvent interaction. From table 3 it is observed to be of order

$$Mg^{++} > Mn^{++} > Cd^{++}$$

and $$M + W > E + W > \text{dioxane} + \text{water}.$$

The standard thermodynamic parameters ΔG° and ΔS° vs solvent composition are found to be linear. The extrapolated values give the thermodynamic parameters for water. The standard thermodynamic quantities ΔG°_t and ΔS_t° for the transfer process from water to 10, 20 and 30% of organic solvent + water mixtures have been calculated by using the Feakins and Turners method [7]. These are given in table 4 and 6. Probable uncertainty in ΔG°_t is ± 15 J mole^{-1} and that in ΔS°_t is $\pm$ 0.5 J k^{-1} mole^{-1} in all solvent compositions. The ΔG°_t values are all negative which indicates that the ion pairs are in a lower free energy state in the mixed solvent than in water and hence the ion pair formation is favoured by decrease of dielectric constant of the medium.

Table 3. $\Lambda^{\circ\eta^{\circ}}$ / Ω^{-1} cm^2

	t	CH_2OH			C_2H_5OH			Dioxane		
		10%	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
$MgSO_4$	30	1.50	1.51	1.52	1.52	1.53	1.54	1.60	1.61	1.62
	35	1.51	1.52	1.52	1.53	1.54	1.55	1.59	1.60	1.61
	40	1.50	1.51	1.53	1.53	1.53	1.54	1.58	1.61	-
$MnSO_4$	30	1.55	1.56	1.57	1.56	1.57	1.59	1.64	1.63	1.63
	35	1.54	1.55	1.56	1.57	1.57	1.62	1.62	1.62	1.62
	40	1.55	1.56	1.57	1.57	1.58	1.59	1.64	1.64	1.64
$CdSO_4$	30	1.59	1.69	1.60	1.63	1.63	1.65	1.65	1.67	1.66
	35	1.58	1.59	1.59	1.62	1.62	1.63	1.60	1.64	1.65
	40	1.60	1.61	1.62	1.63	1.64	1.65	1.65	1.67	1.66

Table 4. – ΔG^{o}_t / KJ mol^{-1}

	°C	Methyl alcohol			Ethyl alcohol			Dioxane		
		10%	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
$MgSO_4$	30	4.8	7.1	9.3	3.4	7.2	8.6	3.1	6.2	8.7
	35	4.9	7.2	9.4	3.34	7.02	8.8	2.9	6.02	8.68
	40	5.0	7.3	9.5	3.6	7.4	8.5	3.2	6.4	8.9
$MnSO_4$	30	4.0	6.6	8.3	2.9	6.3	7.4	2.0	5.5	6.9
	35	3.9	6.5	8.4	2.8	6.4	7.4	1.85	5.41	6.8
	40	4.1	6.4	8.3	3.0	6.5	7.3	2.9	5.8	7.0
$CdSO_4$	30	3.3	6.0	7.3	2.4	5.5	6.3	1.61	4.4	5.9
	35	3.34	6.1	7.2	2.2	5.4	6.4	1.51	4.1	5.89
	40	3.2	6.1	7.4	2.3	3.6	6.5	1.64	4.5	6.1

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

	Tem.	Methyl alcohol			Ethyl alcohol			Dioxane		
		10%	**20%**	**30%**	**10%**	**20%**	**30%**	**10%**	**20%**	**30%**
$MgSO_4$	30	4.5	5.3	6.7	4.0	5.1	5.5	3.2	4.2	4.8
	35	4.4	5.4	6.5	3.8	4.8	5.4	2.9	3.9	4.4
	40	4.7	5.6	6.8	4.1	5.3	5.8	3.1	4.7	5.1
$MnSO_4$	30	3.7	4.8	5.3	2.8	4.4	4.8	2.4	4.1	4.4
	35	3.8	4.6	5.5	2.9	4.0	4.7	2.2	3.7	4.0
	40	3.9	4.9	5.4	2.7	4.3	5.0	2.6	4.2	4.2
$CdSO_4$	30	3.2	4.1	5.0	2.0	3.1	4.4	1.4	3.0	3.8
	35	3.0	3.9	4.8	2.2	3.2	4.1	4.8	2.9	3.5
	40	3.3	4.2	5.1	2.2	3.0	4.7	1.5	3.2	3.7

Table 6. – ΔS^{o}_t/J.K^{-1} mol^{-1}

	Tem.	Methyl alcohol			Ethyl alcohol			Dioxane		
		10%	20%	30%	10%	20%	30%	10%	20%	30%
$MgSO_4$	30	2.0	2.9	3.4	2.0	2.6	3.2	1.8	2.4	2.6
	35	2.2	2.7	3.2	1.9	2.4	2.9	1.6	2.0	2.2
	40	2.4	3.0	3.6	1.9	2.7	3.4	1.9	2.0	2.7
$MnSO_4$	30	2.0	2.4	3.0	1.8	2.2	2.8	1.3	1.8	2.1
	35	1.9	2.2	2.8	1.7	2.0	2.5	1.4	1.86	2.0
	40	1.6	2.3	2.9	1.6	2.3	3.2	1.4	1.9	2.2
$CdSO_4$	30	1.4	2.1	2.6	1.2	1.8	2.4	1.4	1.4	1.8
	35	1.5	1.9	2.4	1.4	1.6	2.0	1.2	1.3	1.7
	40	1.3	2.0	2.5	1.3	1.9	2.4	1.2	1.2	1.8

Since single ion values of free energies are not available presently for the solvent mixtures studies, the method adopted by Khoo and Chan [8] is applied to study ion solvent interaction. Since the ion pairs remain in lower free energy state with decrease in dielectric constant of the medium the Born equation is expected to conform to the data for increasing organic solvent content. Same observation has been made elsewhere by Feakins and Turner.

It is possible to split the ΔG^o_t values into two parts $\Delta G^o_{t(el)}$ and $\Delta G^o_{t(ch)}$ as Roy *al et.* [9, 10] have done $\Delta G^o_{t(el)}$ denoting the electrostatic contribution and $\Delta G^o_{t(ch)}$, the 'non-electro- static or chemical contribution'. $\Delta G^o_{t(el)}$ 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 crystallographic radii or the cation and anion, and ε_s and ε_w are the dielectric constants of the mixed solvent and water respectively.

From the knowledge of $\Delta G^o_{t(el)}$ the chemical contribution of free energy of transfer $\Delta G^o_{t(ch)}$ has been obtained by subtracting respective electrostatic contribution from molar quantities. These values have been recorded in table 5. It is evident from table 5 that the chemical contribution of the free energy of transfer is negative in all cases predicting the condition thermodynamically favourable as far as chemical interactions are concerned. Similarly ΔS^o_t calculated are recorded in table 6. The following conclusion have been observed from both table 5 and 6, that the ion solvent interaction order is Methanol + water > Ethanol + water > dioxane + water. The ΔS^o_t is negative in all cases and becomes more negative with increase in organic solvent content, indicating disorder in solvent content, indicating disorder in solvent structure. The order is Mg > Mn > Cd and

Methanol + water > Ethanol + water > Dioxane + water and is in agreement with result obtained from viscosity and apparent molar volume measurement. Methanol + water and Ethanol + water have got one OH group where as water is an electron donor or acceptor. Hence the organic solvents could accept a proton from water and the three dimensional water structure is broken down easily and is of the order M+W > E+W. Methanol has no $-CH_2$ group whereas ethanol has one $-CH_2$ group attached to CH and hence the difference is noticed.

Addition of small amount of dioxane to water may give rise to two effects. (A) If dioxane is accommodated in the solvent structure, it may strengthen the water structure because dioxane is a better proton acceptor (B). If it is can not be accommodated because of its bulky size then it may cause a breakdown in the three dimensional water structure. In the present context ion-solvent interaction occurs which indicates that due to the bulkyness, the dioxane is not accommodated in the water structure and hence it breaks down the three dimensional water structure.

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