Acta Ciencia Indica, Vol. XLI C, No. 1, 55 (2015)

THERMODYNAMICS OF CHLORIDE, BROMIDE AND NITRATE OF MAGNESIUM IN DIOXANE + WATER AND GLYCOL + WATER MIXTURES AT DIFFERENT TEMPERATURES FROM CONDUCTANCE DATA

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RECEIVED : 29 January, 2014

Ion solvent interaction of $MgCl_2$, $MgBr_2$ and $Mg(NO_3)_2$ at 10, 20 and 30% (w/w) of dioxane + water and glycol + water mixtures have been inferred from conductance data. It is of the order

$NO_3^- > Br^- > Cl^-$ and D + W > G + W

In the present study the ion-solvent interaction of $MgCl_2$, $MgBr_2$, $Mg(NO_3)$ have been studied from conductance data at wt. 10, 20 and 30% (w/w) of dioxane + water and glycol + water mixtures at 30, 35 and 40°C.

MATERIALS AND METHODS

The salts used were of E. Merck Extra pure varieties. The methods of the preparation of solvent, solutions and measurements were same as that of Das. Conductance measurements were of an accuracy of, solutions and measurements were same as that of Das. Conductance measurements were of an accuracy of ±2 in 1000. The concentration range was from 0.02 to 0.002 equiv./lit.

DISCUSSION

Righellato and Davies [2] have pointed out that in case of biunivalent electrolytes, equilibrium of the type.

$$MA_2 \qquad M^{++} + 2A^- \qquad \ldots(1)$$

$$M^{++} + A^- \quad MA^+ \qquad \ldots(2)$$

exist. The dissociation constant of MA^+ is given by

$$K = \frac{[M^{++}][A^-]f_{M^{++}}}{[MA^+]} \times \frac{f_{A^-}}{f_{MA^+}}$$

where '*f*' represent the activity coefficient of the corresponding ions and the square bracket indicate the molar concentration.

Following the method of calculation adopted by Jenkin and Monk [3], the first stage of dissociation is assumed to be complete and we have only to deal with the second equilibrium.

$$MA^{+} \qquad M^{++} + A^{-}$$

Let '*m*' represent the molar concentration of the salts and '*a*' is the fraction that does not take part in the ion association, that,

$$[MA^{+}] = (1 - \alpha)\, m$$

$$[MA^{++}] = \alpha\, m$$

$$K^{+}_{I-P} = \frac{\alpha(1+\alpha)\, m\, f_{M^{++}}}{(1-\alpha)} \times \frac{f_{A^{-}}}{F_{I-P}} \qquad \ldots (4)$$

Table 1 : $\Lambda^0/\Omega\ cm^2$

		D + W			***G + W***		
		10%	**20%**	**30%**	**10%**	**20%**	**30%**
$MgCl_2$	30	136.5	131.2	101.4	137.2	122.4	102.2
	35	146.60	135.80	113.00	148.4	134.9	115.4
	40	157.70	147.5	125.2	159.2	144.2	129.5
$MgBr_2$	30	134.2	121.2	104.3	130.2	114.2	102.4
	35	144.0	132.0	117.50	141.4	128.50	116.50
	40	156.5	144.4	129.4	155.2	140.3	128.2
$Mg(NO_3)_2$	30	131.3	112.5	95.3	130.8	112.4	96.2
	35	144.60	123.5	105.2	142.45	124.42	107.52
	40	158.4	136.5	118.4	156.5	138.4	120.4

Table 2 : $K \times 10^2$

		D + W			***G + W***		
		10%	**20%**	**30%**	**10%**	**20%**	**30%**
$MgCl_2$	30	11.02	4.31	3.21	12.12	5.72	3.74
	35	10.94	4.36	3.02	11.94	4.22	3.64
	40	10.74	5.1	2.93	12.25	5.94	3.56
$MgBr_2$	30	10.72	6.20	3.52	11.65	6.64	4.08
	35	10.41	5.93	3.42	11.45	6.22	3.94
	40	10.52	6.04	3.58	11.55	6.34	4.01
$Mg(NO_3)_2$	30	9.65	5.25	3.12	10.41	6.85	3.75
	35	9.45	5.15	3.01	10.32	6.75	3.55
	40	9.55	5.35	3.11	10.45	6.80	3.65

The solution as a whole can be regarded as two types of salts, (i) biunivalent yielding M^{++} and A^{-} and (ii) univalent MA^{+} and A^{-}. For 2-1 type electrolyte the equivalent conductance is given by the expression :

$$\Delta_{2-1} = \Delta^0_{2-1} - (A_{2-1} + B_{2-1} A^0_{2-1}) \sqrt{I} \qquad \ldots(5)$$

and for the 1-1 electrolyte

$$\Delta_{1-1} = \Delta^0_{1-1} (A_{1-1} + B_{1-1}) \sqrt{I} \qquad \ldots(6)$$

where A and B are Onsager constants, Δ^0 is the equivalent conductance at zero concentration and Δ, that of the actual ionic strength 1.

$$\mathrm{I} = \frac{1}{2}[(A^-) + (MA^+) + 4(M^{++})] = m\,(1 + 2\alpha) \qquad \ldots(7)$$

Table 3 : $\lambda^0\eta_0/\Omega^{-1}$ cm^2

		D + W			***G + W***		
		10%	**20%**	**30%**	**10%**	**20%**	**30%**
$MgCl_2$	30	1.50	1.51	1.53	1.59	1.60	1.58
	35	1.51	1.51	1.52	1.58	1.59	
	40	1.52	1.53	1.52	1.59	1.58	
$MgBr_2$	30	1.43	1.46	1.44	1.51	1.48	1.51
	35	1.44	1.45	1.43	1.48	1.49	
	40	1.42	1.45	1.44	1.50	1.50	
$Mg(NO_3)_2$	30	1.43	1.42	1.40	1.40	1.39	1.40
	35	1.42	1.44	1.43	1.39	1.40	1.41
	40	1.41	1.42	1.40	1.41	1.40	1.41

Table 4 : $-\Delta G^0$ / KJ mole^{-1}

		D + W			***G + W***		
		10%	**20%**	**30%**	**10%**	**20%**	**30%**
$MgCl_2$	30	3.5	4.1	4.4	3.1	3.1	4.0
	35	3.2	3.8	4.2	3.0	3.3	3.8
	40	3.6	4.2	4.5	3.2	3.5	4.2
$MgBr_2$	30	4.8	5.2	6.1	4.2	4.2	5.1
	35	4.4	4.8	5.7	4.1	4.4	5.2
	40	4.7	5.4	6.4	4.2	4.9	5.3
$Mg(NO_3)_2$	30	5.1	5.5	7.1	4.4	5.1	6.0
	35	4.9	5.4	6.4	4.2	4.9	5.8
	40	5.4	5.6	7.4	4.5	5.2	6.3

K_{2-1} and K_{1-1} be the specific conductance of 2-1 and 1-1 types of salts respectively are given by :

$$K_{2-1} = (1\alpha m \times A_{2-1}) \times 1000 \text{ and } K_{1-1} = [(1-\alpha)\, m\, \Delta_{1-1}] \times 1000$$

If K be specific conductance containing a mixture of the two types, may therefore be expressed as :

$$K = K_{2-1} + K_{1-1} = [(2\alpha\, m\, \Delta_{2-1)} + (1-\alpha)\, m\, \Delta_{1-1}]\, 10^{-3}$$

or, $$(10^3 K/2m) = \alpha\Delta_{2-1} + \frac{1}{2}(1-\alpha)\Delta_{1-1} \qquad \ldots(8)$$

where 'Δ' is the measured equivalent conductance.

The Onsagar constants A and B are calculated theoretically for 2-1 and 1-1 type salts $\Delta^0_{2\text{-}1}$ has been determined from plot of Δ vs. $C^{1/2}$ (table-1). The value of $\Delta^0_{1\text{-}1}$ has been calculated by taking the mobility of MA^+ as two third of the bivalent M^{++} and making use of mobility determined by Das [1]. The two unknown quantities are 'a' and 'I'. For the determination of 'a' the method of successive approximation is used as follows. Let '∂' be equal to unity when an approximate value of I is calculated according to equation (7). This value of I is used for calculating a true value of 'α' is obtained. By using this constant value 'α' and the activity coefficient from the usual Debye-Huckel expression, the dissociation constants at various concentrations been determined according to equation (4). The same procedure was followed for the ion-pair. The average 'K' values decreases with the decreases in dielectric constant with increase of organic solvent. This is attributed to incomplete dissociation or ion association. The 'K' value is of the Glycol + water > Dioxane + water.

The structural thermodynamic change ΔG^0, ΔH^0 and ΔS^0 have been calculated by the usual methods. The plot of ΔG^0 vs. solvent compositions were found to be linear. The standard thermodynamic quantity (ΔG^0_t) for the transfer process from water to dioxane and glycol could be calculated and recorded in table-3 by using Feakins and Turner's method [5]. The ΔG^0_t recorded in Table-3 are all negative. This indicates that the ion pairs are in a lower free energy state in aquoorganic solvent than that of water, suggesting that the ion-pair formation is favoured by decreasing the dielectric constant of the medium.

Knowing the ΔG^0_t values and the ionic radii of the ion pairs. ΔG^0 has been split up into two parts by Roy *et. al.* $\Delta G^0_{t\,(el)}$, the electrostatic part corresponding to a change in dielectric constant in the medium and a non-electrostatic part $\Delta G^0_{t\,(ch)}$ corresponding to chemical contributions arising from the specific chemical interaction between the ion pairs and the solvents $\Delta G^0_{t\,(ch)}$ were computed from :

$$\Delta G^0_t = \Delta G^0_{t\,(el)} + \Delta G^0_{t\,(ch)}$$

These are tabulated in Tables-4 and 5 respectively. It is evident that $\Delta G^0_{t\,(ch)}$ values are negative in both the cases. This indicates that the transfer of ion-pairs from water to aquo-organic solvent is favoured as far as chemical interaction is concerned and is of the order.

Dioxane + water > glycol + water.

Table 5 : $\Delta G^0_{t\,(ch)}$/K cals mol^{-1}

		D + W			***G + W***		
		10%	**20%**	**30%**	**10%**	**20%**	**30%**
$MgCl_2$	30	5.7	6.1	7.1	5.0	6.1	6.4
	35	5.5	5.8	6.2	5.4	5.6	6.0
	40	5.6	6.4	6.0	5.8	6.4	7.0
$MgBr_2$	30	7.2	6.8	7.4	5.4	6.7	7.5
	35	6.2	6.9	7.6	6.0	6.2	7.1
	40	6.8	7.2	7.8	6.8	7.1	7.4
$Mg(NO_3)_2$	30	7.4	8.6	9.4	7.0	8.1	8.0

	35	7.2	8.1	8.8	6.8	7.7	8.2
	40	7.8	8.7	9.3	7.4	8.2	8.9

The $\Delta S°_t$ has been compared in Table-6 and minima is noticed in both the solvent mixtures indicating the structure breaking effect and is of the order.

Dioxane + water ? glycol + water

This can be explained as follows : dioxane being a protein acceptor could have strengthen the water structure provided is accommodated in the solvent structure. But because of its bulky size it could not be accommodated and hence causes a breakdown in the three dimensional water structure. Glycol though contain two –OH groups is not able to break the hydrogen bond of water to such an extent as it is expected and is due to low dipole interaction energy.

Table 6 : ΔS^0_t/J.K. mol^{-1}

		D + W			***G + W***		
		10%	**20%**	**30%**	**10%**	**20%**	**30%**
$MgCl_2$	30	2.9	3.3	4.0	2.0	2.5	3.0
	35	2.4	2.9	3.4	2.1	2.6	3.2
	40	2.5	3.4	3.9	2.8	2.9	3.8
$MgBr_2$	30	3.4	3.0	4.1	2.2	2.9	3.3
	35	3.7	3.4	3.9	2.4	3.0	3.5
	40	3.2	3.7	4.2	2.8	3.4	3.8
$Mg(NO_3)_2$	30	3.9	4.1	5.0	3.0	3.5	4.2
	35	3.4	3.7	4.7	2.9	3.2	4.0
	40	3.8	4.0	5.0	3.2	3.6	4.4

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