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THERMODYNAMICS OF $CdCl_2$ AND $CdBr_2$ IN AQUO-ORGANIC SOLVENTS FROM CONDUCTANCE DATA

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ABSTRACT

The ion–solvent interaction of $CdCl_2$ and $CdBr_2$ with organic solvent (10, 20 and 30 wt.% dioxane, glycol or methyl alcohol) + water mixtures at different temperatures has been studied using electrolytic conductivity data. The dissociation constant of the ion pair $CdCl^+$ and $Cd(Br)^+$ has been calculated along with ΔG_t^0, $\Delta G_{t(el)}^0$ and $\Delta G_{t(Ch)}^0$. The ion pairs interact with the solvents in the order dioxane + water > methyl alcohol + water > glycol + water.

INTRODUCTION

Water at ordinary temperatures has a quasi-crystalline structure [1]. A dynamic equilibrium seems to exist between the three-dimensional hydrogen bonded clusters and the denser monomers [1]

$$(H_2O)_c \rightleftharpoons (H_2O)_d$$

Electrolytes which dissolve in water have been classified as structure makers or structure breakers, depending on whether the above equilibrium is shifted to left or right. Frank and Wen [1] gave a picture in which an ion is surrounded by concentric regions of water molecules polarised, immobilised and electrostricted by the ion, analogous to a freezing fluid. This they called region A. The water molecules in region C has the normal three-dimensional network as stated above. The centrosymmetric structure imposed by the ion in region A is incompatible with the normal structure in region C and there is a tendency to resist such order and balance between the two competing forces giving rise to a region B. Ions with a low charge density have a smaller width of region A and larger width of region B and are net structure breakers. On the other hand, ions with a high charge density show the

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opposite behaviour and are net structure makers.

Dioxane, glycol, methyl alcohol are miscible with water at all solvent compositions. Dioxane is an aprotic solvent, glycol has two –OH groups and methyl alcohol has one –OH group, whereas water is both an electron donor and an acceptor. The dielectric constants are also different. These and several other properties make their aqueous mixtures an interesting field to explore, particularly the ionic processes accompanying the solutions of strong electrolytes. It becomes relevant to enquire whether a given mixed solvent such as dioxane + water, glycol + water and methyl alcohol + water mixtures will resist the centrosymmetric ordering of the ion more or less than pure water.

So, in the present case, the conductivities of $CdCl_2$ and $CdBr_2$ in dioxane + water, and glycol + water mixtures at 30–45°C and methyl alcohol + water mixtures at 30–40°C have been studied at 10, 20 and 30 wt.% of the organic solvent to investigate the ion–solvent interaction.

MATERIALS AND METHODS

The salts $CdCl_2$ and $CdBr_2$ used were of Merck extra pure grade. The purification of the dioxane, glycol and methyl alcohol, the preparation of the solvents and solutions and the measurement of conductance have been described previously [2]. The conductance measurements were of an accuracy of ±2 in 1000 and the concentration range was from 0.02 to 0.002 mole l^{-1}. The temperature of the investigation was $30–45 \pm 0.01$°C for dioxane + water and glycol + water and $30–40 \pm 0.01$°C for methyl alcogol + water mixtures.

RESULTS AND DISCUSSION

Righellato and Davies [3] have pointed out that in the case of biunivalent electrolytes, equilibria of the type

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

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

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

$$K = \frac{[M^{2+}][A^-]}{[MA^+]} \times \frac{f_{M^{2+}} \times f_{A^-}}{f_{MA^+}} \qquad (3)$$

where f represents the activity coefficient of the respective ion and the square brackets indicate molar concentration.

Following the method of calculation adopted by Jenkin and Monk [4]. The first stage of dissociation is assumed to be complete and we have only to deal with the second equilibrium

$$CdCl_2^+ \rightleftharpoons Cd^{2+} + 2\,Cl^-$$

Let m represent the molar concentration of $CdCl_2$ and α the fraction that does not take part in the ion association. Then

$$[CdCl^+] = (1-\alpha)\,m$$

$$[Cd^{2+}] = \alpha m$$

$$[Cd^-] = m(1+\alpha)$$

$$K_{CdCl^+} = \frac{(1+\alpha)\,m}{(1-\alpha)} \times \frac{f_{Cd^{2+}} \times f_{Cl^-}}{f_{Cd(Cl)^+}} \tag{4}$$

The solution as a whole can be regarded as two types of salt, (i) biunivalent $CdCl_2$ yielding Cd^{2+} and Cl^- and (ii) uniunivalent $Cd(Cl)^+$ and Cl^-. For the 2-1 type electrolyte, the equivalent conductance is given by

$$\Lambda_{2\text{-}1} = \Lambda^0_{2\text{-}1} - \left(A_{2\text{-}1} + B_{2\text{-}1}\Lambda^0_{2\text{-}1}\right)\sqrt{I} \tag{5}$$

and for the 1-1 electrolyte

$$\Lambda_{1\text{-}1} = \Lambda^0_{1\text{-}1} - \left(A_{1\text{-}1} + B_{1\text{-}1}\Lambda^0_{1\text{-}1}\right)\sqrt{I} \tag{6}$$

where A and B are Onsager constants, Λ^0 is the equivalent conductance at zero concentration and Λ is the equivalent conductance at ionic strength I.

$$I = \tfrac{1}{2}\{[Cl^-] + [CdCl^+] + 4[Cd^{2+}]\} = m(1+2\alpha) \tag{7}$$

$k_{2\text{-}1}$ and $k_{1\text{-}1}$, the specific conductances of 2-1 and 1-1 type of salts, respectively, are given by

$$k_{2\text{-}1} = \frac{2\alpha m \Lambda_{2\text{-}1}}{1000}$$

and

$$k_{1\text{-}1} = \frac{(1-\alpha)\,m\Lambda_{1\text{-}1}}{1000}$$

If k is the specific conductance containing a mixture of the two types, it may therefore be expressed as

$$k = k_{2\text{-}1} + k_{1\text{-}1} = \{2\alpha m\Lambda_{2\text{-}1} + (1-\alpha)\,m\Lambda_{1\text{-}1}\}\ 10^{-3}$$

or

$$\frac{10^3 k}{2m} = \alpha\Lambda_{2\text{-}1} + \tfrac{1}{2}(1-\alpha)\,\Lambda_{1\text{-}1} \tag{8}$$

where Λ is the measured equivalent conductance.

The Onsager constants A and B are calculated theoretically for 2-1 and 1-1 type salts. $\Lambda^0_{2\text{-}1}$ has been determined from the plot of Λ vs. $C^{1/2}$ (Table 1). The value of $\Lambda^0_{1\text{-}1}$ has been calculated by taking the mobility of $CdCl^+$ as

TABLE 1

Λ^0 (Ω^{-1} cm^2)

Temp. (°C)	$CdCl_2$			$CdBr_2$		
	wt. % organic solvent			wt. % organic solvent		
	10	20	30	10	20	30
Dioxane + water						
30	136.4	126.5	103.5	138.4	119.2	99.3
35	141.4	127.6	106.4	145.4	125.6	103.5
40	147.2	136.5	112.5	151.5	132.4	109.6
45	157.7	142.3	119.7	157.5	138.4	115.7
Glycol + water						
30	138.4	123.3	105.6	139.8	121.4	101.2
35	143.3	129.4	108.4	145.8	126.8	104.7
40	149.2	138.5	113.8	153.3	134.4	110.7
45	158.9	143.8	120.2	158.4	140.1	117.4
Methyl alcohol + water						
30	138.1	122.8	106.2	139.6	120.8	101.4
35	143.4	128.5	109.2	146.2	127.7	105.6
40	149.1	140.2	114.7	154.2	135.5	111.7

two-thirds of the bivalent Cd^{2+} [3] and making use of the mobility determined by us [5]. The two unknown quantities are α and I. For the determination of α, the method of approximation is used as follows. Let α be equal to unity. An approximate value of I is then calculated according to eqn. (7). This value of I is used for calculating a truer value of α and this process is repeated till a constant value of α is obtained. By using this constant value of α and the activity coefficient from the usual Debye–Hückel expression, the dissociation constants at various concentrations have been determined according to eqn. (4). The same procedure was followed for the ion pair $Cd(Br)^+$. The average K values of the ion pairs are tabulated in Table 2. The K values decrease with decrease in dielectric constant, i.e. with increase with organic solvent. This is attributed to incomplete dissociation on ion association. The K values are in the order MeOH + water > glycol + water > dioxane + water.

The standard thermodynamic change calculated from the equation

$$\Delta G^0 = -RT \ln K \tag{9}$$

is found to be negative and values are recorded in Table 3. It increases with increase in temperature but decreases with increase in organic solvent. ΔS^0 was calculated from the temperature coefficient of the free energy. The ΔH^0

TABLE 2

$K \times 10^3$

Temp. (°C)	$CdCl^+$			$CdBr^+$		
	wt.% organic solvent			wt.% organic solvent		
	10	20	30	10	20	30
Dioxane + water						
30	9.8	8.7	6.8	8.5	7.8	6.2
35	10.1	8.8	7.5	9.5	8.1	5.8
40	10.3	9.1	7.7	9.9	8.8	7.2
45	11.4	10.5	9.0	11.2	10.4	9.4
Glycol + water						
30	9.8	8.5	7.5	10.2	8.4	7.8
35	11.8	9.5	8.2	11.2	9.8	8.1
40	12.3	11.3	9.7	11.4	10.5	7.8
45	12.9	11.8	10.5	11.5	9.7	8.8
Methyl alcohol + water						
30	10.2	8.4	7.9	9.8	9.0	7.1
35	11.2	9.3	8.5	10.5	8.5	6.8
40	13.0	11.4	9.6	11.8	10.4	8.2

TABLE 3

ΔG^0(kJ mole^{-1})

Temp. (°C)	$CdCl^+$			$CdBr^+$		
	wt. % organic solvent			wt. % organic solvent		
	10	20	30	10	20	30
Dioxane + water						
30	11.65	11.95	12.57	12.01	12.23	12.81
35	11.77	12.12	12.53	11.92	12.33	13.19
40	11.91	12.23	12.66	12.01	12.32	12.84
45	11.83	12.05	12.23	11.88	12.07	12.34
Glycol + water						
30	11.65	12.01	12.33	11.55	12.04	12.23
35	11.37	11.92	12.30	11.50	11.84	12.33
40	11.45	11.67	12.06	11.64	11.86	12.63
45	11.50	11.74	12.05	11.81	12.26	12.51
Methyl alcohol + water						
30	11.55	12.04	12.19	11.65	11.87	12.46
35	11.50	11.98	12.21	11.67	12.21	12.78
40	11.30	11.64	12.09	11.55	11.88	12.50

values were then calculated by utilising the equation

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \tag{10}$$

These values are given in Tables 4 and 5. The ΔH^0 values are negative, showing that the reaction is exothermic, and are of the order MeOH + water > glycol + water > dioxane + water for both the ion pairs. The ΔS^0 values are found to be negative at all temperatures and for all solvent compositions for both the ion pairs.

The plots of ΔG^0 vs. solvent compositions were found to be linear. The extrapolated values gave the thermodynamic parameter for water. The standard thermodynamic quantity (ΔG_t^0) for the transfer process from water to 10, 20 and 30 wt.% organic solvent + water mixtures could be calculated, and are recorded in Table 6, by using the Feakins and Turner method [6]. The ΔG_t^0 values are negative in all cases. This indicates that the ion pairs are in a lower free energy state in aquo-organic solvent than water, suggesting that the ion pair formation is favoured by decreasing the dielectric constant of the medium. From the result, it is also seen that the formation of $CdBr^+$ is more than that of $CdCl^+$.

ΔS_t^0 has been calculated from the temperature coefficient of ΔG_t^0 and is tabulated in Table 7. Minima are noticed in the cases of dioxane + water and CH_3OH + water but not in the case of glycol + water. This indicates that the structure breaking order is dioxane + water > Ch_3OH + water > glycol + water.

TABLE 4

ΔS° (J K^{-1} $mole^{-1}$)

Temp. (°C)	$CdCl^+$			$CdBr^+$		
	wt. % organic solvent			wt. % organic solvent		
	10	20	30	10	20	30
Dioxane + water						
30	23.01	33.59	−8.69	−17.33	21.03	76.42
35	27.99	21.90	26.98	17.25	−3.10	−69.72
40	−15.61	−36.59	−87.06	−26.87	−48.98	−99.65
Glycol + water						
30	−56.65	−17.33	−5.02	−9.78	−39.21	21.02
35	15.31	−51.59	−47.49	28.13	2.55	59.68
40	11.38	14.38	−3.36	32.58	70.78	−23.43
Methyl alcohol + water						
30	−9.78	−12.39	2.76	3.12	68.43	63.24
35	−40.22	−67.07	−23.70	−22.86	−65.36	−55.94

TABLE 5

$-\Delta H^0$ (kJ mole^{-1})

Temp. (°C)	$CdCl^+$			$CdBr^+$		
	wt. % organic solvent			wt. % organic solvent		
	10	20	30	10	20	30
Dioxane + water						
30	4.68	1.77	15.20	17.26	5.86	-10.34
35	3.14	5.37	4.22	6.61	13.29	34.66
40	16.79	23.68	39.91	20.42	27.65	44.12
Glycol + water						
30	28.82	17.26	13.85	14.51	23.92	5.86
35	6.65	27.81	26.93	2.84	11.06	6.05
40	7.88	7.16	13.12	1.44	13.12	19.96
Methyl alcohol + water						
30	14.51	15.79	11.36	10.71	8.87	6.70
35	23.89	32.64	19.51	18.71	32.34	30.01

TABLE 6

$-\Delta G_t^0$ (kJ mole^{-1})

Temp. (°C)	$CdCl^+$			$CdBr^+$		
	wt. % organic solvent			wt. % organic solvent		
	10	20	30	10	20	30
Dioxane + water						
30	0.39	0.69	1.31	0.24	0.46	1.03
35	0.30	0.65	1.06	0.41	0.82	1.68
40	0.36	0.68	1.11	0.43	0.74	1.26
45	0.25	0.47	0.65	0.19	0.39	0.66
Glycol + water						
30	0.34	0.70	1.01	0.32	0.82(81)	0.99
35	0.45	1.00	1.38	0.42	0.76	1.05
40	0.32	0.54	0.94	0.51	0.73	1.50
45	0.31	0.55	0.85	0.57	0.92	1.18
Methyl alcohol + water						
30	0.34	0.83	0.98	0.48	0.70	1.29
35	0.27	0.75	0.97	0.55	1.09	1.66
40	0.35	0.69	1.14	0.37	0.70	1.32

TABLE 7

ΔS_t^0 (J K^{-1} $mole^{-1}$)

Temp. (°C)	$CdCl^+$			$CdBr^+$		
	wt. % organic solvent			wt. % organic solvent		
	10	20	30	20	20	30
Dioxane + water						
30	−18.1	−8.12	−50.01	34.2	72.3	130.3
35	12.2	6.07	10.08	4.03	−16.1	−84.2
40	−22.1	−42.3	−92.4	−48.4	−70.5	−120.4
Glycol + water						
30	22.2	60.3	74.4	20.1	−10.06	12.05
35	−26.1	−92.2	−88.3	18.1	−6.02	90.30
40	−2.02	2.04	−18.2	12.2	38.3	−64.4
Methyl alcohol + water						
30	−14.1	−16.2	−2.02	14.2	78.4	74.2
35	−16.2	−12.4	−34.2	−36.2	−78.2	−68.4

TABLE 8

$\Delta G_{t(el)}$ and $\Delta G_{t(ch)}$ values for $CdCl^+$

Temp. (°C)	$\Delta G^0_{t(el)}$ kJ $mole^{-1}$)			$\Delta G^0_{t(ch)}$ (kJ $mole^{-1}$)		
	wt. % organic solvent			wt. % organic solvent		
	10	20	30	10	20	30
Dioxane + water						
30	0.75	1.64	2.93	−0.36	−0.95	−1.62
35	0.80	1.77	3.10	−0.50	−1.12	−2.04
40	0.84	1.86	3.24	−0.48	−1.18	−2.13
45	0.84	1.91	3.28	−0.59	−1.44	−2.63
Glycol + water						
30	0.31	0.53	0.80	0.03	0.17	0.21
35	0.31	0.53	0.84	0.14	0.47	0.55
40	0.40	0.53	0.84	−0.08	0.01	0.10
45	0.35	0.58	0.84	−0.04	−0.03	0.01
Methyl alcohol + water						
30	0.35	0.80	1.29	−0.01	0.03	−0.31
35	0.35	0.89	1.33	−0.08	−0.14	−0.36
40	0.40	0.89	1.33	−0.05	−0.20	−0.17

TABLE 9

$\Delta G_{t(el)}$ and $\Delta G_{t(ch)}$ values for $CdBr^+$

Temp. (°C)	$\Delta G^0_{t(el)}$ (kJ mole^{-1})			$\Delta G^0_{t(ch)}$ (kJ mole^{-1})		
	wt. % organic solvent			wt. % organic solvent		
	10	20	30	10	20	30
Dioxane + water						
30	0.68	1.48	2.64	−0.44	−1.02	−1.61
35	0.72	1.60	2.80	−0.31	−0.78	−1.12
40	0.76	1.68	2.92	−0.33	−0.94	−1.66
45	0.76	1.72	2.96	−0.57	−1.33	−2.30
Glycol + water						
30	0.28	0.48	0.72	0.04	0.33	0.27
35	0.28	0.48	0.76	0.14	0.28	0.35
40	0.36	0.48	0.76	0.15	0.25	0.74
45	0.32	0.52	0.76	0.25	0.40	0.94
Methyl alcohol + water						
30	0.32	0.72	1.16	0.16	−0.02	0.13
35	0.32	0.80	1.20	0.23	0.29	0.46
40	0.36	0.80	1.20	0.01	−0.10	0.12

Knowing the ΔG^0_t values and the ionic radii of the ion pairs, ΔG^0_t has been split into two parts by Roy et al. [7], an electrostatic part, $\Delta G^0_{t(el)}$ corresponding to a change in the dielectric constant of 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. $\Delta G^0_{t(el)}$ has been calculated from the Born equation [8] and $\Delta G^0_{t(ch)}$ was then determined. These are tabulated in Tables 8 and 9. It is evident that $\Delta G^0_{t(ch)}$ values are negative in the cases of dioxane and CH_3OH and increase with increase in organic solvent content. This indicates that the transfer for ion pairs from water to aquo-organic mixtures is favoured as far as chemical interaction is concerned and is generally of the order dioxane + water > methyl alcohol + water > glycol + water. It is greater in case of $CdBr^+$ than $CdCl^+$.

This can be explained as follows. Dioxane, being a proton acceptor, could strengthen the water structure provided it 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. Methyl alcohol is also a proton acceptor and hence breaks the hydrogen bond of water. Glycol, although it contains two –OH groups, is not able to break the hydrogen bond of water to the extent that would be expected.

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