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THERMODYNAMICS OF $Sr(NO_3)_2$ AND $Cd(NO_3)_2$ IN AQUO-ORGANIC SOLVENTS FROM CONDUCTANCE DATA

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ABSTRACT

The ion–solvent interaction of $Sr(NO_3)_2$ and $Cd(NO_3)_2$ in 10, 20 and 30 wt.% organic solvent (dioxane, glycol, methyl alcohol)–water mixtures at different temperatures has been studied using electrolytic conductivity data. The dissociation constant of the ion-pair $Sr(NO_3)^+$ and $Cd(NO_3)^+$ 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 and the interaction is of 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 the left or right. Frank and Wen [1] gave a picture in which an ion is surrounded by concentric regions of water molecules polarized, immobilized and electrostricted by the ion, analogous to a kind of freezing; this they called region A. The water molecules in region C have the normal three-dimensional network as stated above. The centrosymmetric structure imposed by the ion in region A is compatible with the normal structure in region C and the tendency to resist such order and balance between the two competing forces gives rise to 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 an opposite behaviour and are net structure makers.

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Dioxane, glycol and 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 acceptor. The dielectric constants are also different. These and several other properties make studies of their aqueous mixtures an interesting field of exploration, particularly the ionic processes accompanying the solutions of strong electrolytes. It becomes relevant to enquire whether a given mixed solvent like dioxane + water, glycol + water and methyl alcohol + water mixtures will resist the centrosymmetric ordering of the ion more or less than pure water.

In the present case, therefore, the conductivity of $Sr(NO_3)_2$ and $Cd(NO_3)_2$ in dioxane + water and glycol + water mixtures at 30–45°C and methyl alcohol + water mixtures at 30–40°C have been studied as mass fractions of 10, 20 and 30% of the organic solvent to study the ion–solvent interaction.

MATERIALS AND METHODS

The salts $Sr(NO_3)_2$ and $Cd(NO_3)_2$ were of Merck extra pure grade. Purification of the dioxane, glycol and methyl alcohol, preparation of the solvents and solutions, and conductance measurements have been described previously [2]. The conductance measurements were of an accuracy of ±2 in 1000 and the concentration ranges were from 0.02 to 0.002 mole l^{-1}. The temperature of investigation was 30–45 ± 0.01°C for dioxane + water and glycol + water, and 30–40 ± 0.01°C for methyl alcohol + water mixtures.

RESULTS AND DISCUSSION

Righellaty and Davies [3] have pointed out that in the case of bi-univalent electrolytes, equilibria of the type

$$MA_2 \rightleftharpoons M^{2+} + 2\,A^- \tag{1}$$

$$M^{2+} + A^- \rightleftharpoons MA^+ \tag{2}$$

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

$$K = \frac{[M^{2+}][A^-]}{[MA^+]} \times \frac{f_{M^{2+}} \times F_{A^-}}{f_{MA^+}} \tag{3}$$

where f is the activity coefficient of the corresponding 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

$$Sr(NO_3)^+ \rightleftharpoons Sr^{2+} + NO_3^-$$

Let M be the molar concentration of $Sr(NO_3)^+$ and α is the fraction that does not take part in the ion association, then

$$[Sr(NO_3)^+] = (1-\alpha)M$$

$$[Sr^{2+}] = \alpha M$$

$$[NO_3^-] = M(1+\alpha)$$

so that

$$K_{Sr(NO_3)^+} = \frac{\alpha(1+\alpha)M}{(1-\alpha)} \times \frac{f_{Sr^{2+}} \times f_{NO_3^-}}{f_{Sr(NO_3)^+}} \tag{4}$$

The solution as a whole can be regarded as two types of salts. (i) bi-univalent $Sr(NO_3)_2$ yielding Sr^{2+} and NO_3^-, and (ii) uni-univalent $Sr(NO_3)^+$ and NO_3^-. For the 2–1 type electrolyte the equivalent conductance is given by the expression

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

and for the 1–1 electrolyte

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

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

$$I = \tfrac{1}{2}\{[NO_3^-] + [Sr(NO_3)^+] + 4[Sr^{2+}]\} = M(1+2\alpha) \tag{7}$$

k_{2-1} and k_{1-1} are the specific conductances of 2–1 and 1–1 types of salts, respectively, and are given by

$$k_{2-1} = \frac{2\alpha M \times \Lambda_{2-1}}{1000} \text{ and } k_{1-1} = \frac{(1-\alpha)M\Lambda_{1-1}}{1000}$$

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

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

or

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

where Λ is the measured equivalent conductance.

The Onsager constants A and B are calculated theoretically for 2–1 and 1–1 type salts. Λ^0_{2-1} has been determined from the plot of A vs. $C^{1/2}$. The value of Λ^0_{1-1} has been calculated by taking the mobility of $Sr(NO_3)^+$ as two-thirds of the bivalent Sr^{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 following approximation method is used. Let α be equal to unity when an approximate value of I is 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–Huckel expression, the dissociation constants at various concentrations have been determined according to eqn. (4). The same procedure was followed for the ion-pair $Cd(NO_3)^+$. The average K values of the ion-pairs are tabulated in Table 1. The K values decrease with decrease in dielectric constant, i.e. with increase in organic solvent. This is attributed to incomplete dissociation or ion association. The K values follow the order: MeOH + water > glycol + water > dioxane + water.

The standard thermodynamic changes calculated from the equation

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

are found to be positive and are recorded in Table 2. They increase with increase in temperature but decrease with increase in organic solvent. ΔS^0 was calculated from

TABLE 1

Dissociation constants

Ion-pair	Temp. (°C)	10%	20%	30%
$Sr(NO_3)^+$	*Dioxane + water*			
	30	0.0660	0.0586	0.0470
	35	0.0734	0.0675	0.0607
	40	0.0833	0.0763	0.0693
	45	0.0906	0.0765	0.0720
	Glycol + water			
	30	0.0771	0.0686	0.0552
	35	0.0850	0.0699	0.0612
	40	0.0961	0.0806	0.0706
	MeOH + water			
	30	0.0833	0.0681	0.0566
	35	0.0878	0.0760	0.0668
	40	0.1000	0.0871	0.0770
$Cd(NO_3)^+$	*Dioxane + water*			
	30	0.00070	0.00582	0.00521
	35	0.00838	0.00739	0.00610
	40	0.00913	0.00857	0.00685
	45	0.01063	0.00862	0.00731
	Glycol + water			
	30	0.00844	0.00702	0.00702
	35	0.00922	0.00828	0.00681
	40	0.01023	0.00910	0.00891
	45	0.01160	0.01003	0.00888
	MeOH + water			
	30	0.00939	0.00767	0.00645
	35	0.00873	0.00839	0.00723
	40	0.01162	0.01000	0.00880

TABLE 2

ΔG^0 (J mole^{-1})

Temp. (°C)	$Sr(NO_3)^+$			$Cd(NO_3)^+$		
	10%	20%	30%	10%	20%	30%
	Dioxane + water					
30	382.52	339.63	272.40	40.98	33.73	30.19
35	432.43	397.67	357.61	49.37	43.54	35.94
40	498.72	456.81	414.90	54.66	51.31	41.01
45	551.09	465.33	437.95	64.66	52.43	44.46
	Glycol + water					
30	446.85	397.59	319.93	48.92	40.67	30.05
35	500.77	411.81	360.55	54.32	48.78	40.12
40	575.35	482.56	422.69	61.25	54.48	53.34
45	663.62	572.38	515.30	70.56	61.01	54.01
	MeOH + water					
30	482.79	394.69	328.04	54.42	44.45	37.38
35	517.27	447.75	393.55	51.43	49.43	42.59
45	598.70	521.47	461.00	69.57	59.87	52.69

the temperature coefficient of the free energy, then the ΔH^0 values were calculated using the equation

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

These values are given in Tables 3 and 4. 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 ion-pairs. The ΔS^0 values are found to be negative at all temperatures and for all solvent compositions for both the ion-pairs.

Plots of ΔG^0 vs. solvent composition were found to be linear. The extrapolated values gave the thermodynamic parameter for water. The standard thermodynamic quantities (ΔG_t^0) for the transfer process from water to 10, 20 and 30% organic solvent + water mixtures were calculated and recorded in Table 5 by using the method of Feakins and Turner [6]. The ΔG_t^0 values are positive in all cases but are high in the case of $Sr(NO_3)^+$ and low for $Cd(NO_3)^+$. This indicates that the ion-pairs are in a higher 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 $Cd(NO_3)^+$ is more than that of $Sr(NO_3)^+$.

Knowing the ΔG_t^0 values and the ionic radii of the ion-pairs, Roy et al. [7] have split ΔG_t^0 into two parts: an electrostatic part, $\Delta G_{t(el)}^0$, corresponding to a change in the dielectric constant of the medium, and non-electrostatic part, $\Delta G_{t(ch)}^0$, corresponding to chemical contributions arising from the specific chemical interaction

TABLE 3

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

Temp. (°C)	$Sr(NO_3)^+$			$Cd(NO_3)^+$		
	10%	20%	30%	10%	20%	30%
	Dioxane + water					
35	2641.94	3179.47	4891.16	467.70	560.52	317.77
40	3651.14	3245.45	3171.69	276.60	435.19	276.60
45	2779.66	76.15	1028.09	571.16	19.04	175.16
	Glycol + water					
35	2820.45	464.12	2142.11	278.47	449.84	210.78
40	4093.70	3946.19	3466.74	372.49	302.42	774.48
45	4950.09	5140.47	5368.94	521.66	354.12	11.42
	MeOH + water					
35	1606.58	2820.45	3641.59	232.64	257.05	278.47
40	4499.38	4093.70	3761.78	1065.84	593.77	579.02

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 6 and 7. It is evident that $\Delta G^0_{t(ch)}$ values are negative in all cases 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 of the order: dioxane + water > methyl alcohol + water > glycol + water, and it is

TABLE 4

$-\Delta S^0$ (J K^{-1} mole^{-1})

Temp. (°C)	$Sr(NO_3)^+$			$Cd(NO_3)^+$		
	10%	20%	30%	10%	20%	30%
	Dioxane + water					
35	9.98	11.61	17.04	1.69	1.96	1.75
40	13.26	11.83	11.46	1.06	1.55	1.01
45	10.47	1.70	4.61	1.99	0.22	0.69
	Glycol + water					
35	10.78	2.84	8.13	1.08	1.62	0.81
40	14.92	14.15	12.43	1.39	1.14	2.64
45	17.65	17.96	18.50	1.86	1.31	0.13
	MeOH + water					
35	6.90	10.61	13.10	0.60	1.00	1.04
40	10.29	14.74	13.49	3.63	2.09	2.02

TABLE 5

ΔG_t^0 (J mole^{-1})

Temp. (°C)	$Sr(NO_3)^+$			$Cd(NO_3)^+$		
	10%		30%	10%	20%	30%
	Dioxane + w					
30	73.5	[illegible]	183.4	6.0	12.7	15.2
35	33.4	68.7	108.6	7.4	13.5	21.9
40	42.7	84.8	126.9	7.7	10.3	20.0
45	54.1	140.3	168.9	9.7	21.4	29.5
	Glycol + water					
30	69.8	118.6	196.9	6.9	14.7	18.0
35	75.7	164.8	215.5	7.3	13.8	21.1
40	55.3	148.5	208.7	4.2	11.5	12.3
45	67.6	158.4	215.2	8.6	17.0	24.0
	MeOH + water					
30	63.8	151.7	217.0	7.4	17.4	24.4
35	48.3	118.7	172.5	6.4	8.4	15.6
40	62.7	139.5	199.0	7.6	17.8	24.7

TABLE 6

$\Delta G^0_{t(el)}$ and $\Delta G^0_{t(ch)}$ values for $Sr(NO_3)^+$

Temp. (°C)	$\Delta G^0_{t(el)}$ (J mole^{-1})			$\Delta G^0_{t(ch)}$ (J mole^{-1})		
	10%	20%	30%	10%	20%	30%
	Dioxane + water					
30	754.0	1641.0	2927.1	748.0	1628.3	2911.3
35	798.3	1774.0	3104.5	790.9	1761.3	3089.1
40	842.7	1862.7	3237.6	835.0	1760.5	3215.7
45	842.7	1907.0	3282.0	833.0	1885.6	3252.5
	Glycol + water					
30	310.8	532.2	798.3	303.9	517.5	780.3
35	310.8	532.2	842.7	303.5	518.4	821.6
40	399.2	532.2	842.7	395.0	520.7	830.4
45	354.8	576.6	842.7	390.6	559.6	818.7
	MeOH + water					
30	354.8	798.3	1286.2	374.4	780.9	1261.8
35	354.8	887.0	1330.5	348.4	878.6	1314.9
40	399.2	887.0	1330.5	391.6	869.1	1305.8

TABLE 7

$\Delta G^0_{t(el)}$ (J mole^{-1}) and $-\Delta G^0_{t(ch)}$ (J mole^{-1}) values for $Cd(NO_3)^+$

Temp. (°C)	$\Delta G^0_{t(el)}$ (J mole^{-1})			$-\Delta G^0_{t(ch)}$ (J mole^{-1})		
	10%	20%	30%	10%	20%	30%
	Dioxane + water					
30	679.3	1478.5	2637.4	605.8	1361.9	2454.0
35	719.3	1598.4	2797.2	685.9	1529.7	2688.6
40	759.2	1678.3	2917.1	716.5	1593.5	2790.2
45	759.2	1717.3	2957.0	705.1	1578.0	2788.1
	Glycol + water					
30	280.0	480.0	719.3	210.2	361.4	522.4
35	280.0	480.0	759.2	204.3	315.2	543.7
40	359.6	480.0	759.2	304.3	331.5	550.5
45	319.7	519.5	759.2	252.1	361.1	544.0
	MeOH + water					
30	319.7	719.3	1158.8	255.9	567.6	941.8
35	319.7	799.2	1198.8	271.4	680.5	1026.3
40	359.6	799.2	1198.8	269.9	659.7	999.8

more in the case of $Cd(NO_3)^+$ than $Sr(NO_3)^+$.

This can be explained as follows. Dioxane, being a proton acceptor, could have strengthened 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 break down in the three-dimensional water structure. Methyl alcohol is also a proton acceptor and hence breaks the hydrogen bond of water. Although glycol contains two –OH groups, it is not able to break the hydrogen bond of water to the extent expected.

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