Association and Hydration Equilibria in Concentrated Aqueous Solutions containing Magnesium Nitrate. Part 1. Cadmium(II) Chloride Complexes in Aqueous Solutions of Magnesium Nitrate and Its Mixtures with Ammonium Nitrate

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Association constants K_1 and K_2 for the formation of $CdCl^+$ and $CdCl_2$ respectively have been evaluated from electromotive force measurements of a concentration cell with Ag–AgCl electrodes. Solutions of $Mg(NO_3)_2$ containing water (8.5—12.96 mol) and NH_4NO_3–$Mg(NO_3)_2$ (7:3) containing water (2.12—4.86 mol) are used as solvents. The dependence of the formation constant, K_1, on water concentration in the solvents is predictable from calculations based on the quasi-lattice concept of aqueous melts.

THE physico-chemical properties of highly concentrated aqueous solutions of polyvalent ions [1,2] have been studied by investigating the chemical equilibria in hydrate melts and in concentrated aqueous solutions of some nitrate salts.[3-6] It was shown that melts containing water in concentrations which are insufficient for complete hydration of the ions can be considered as molten salts with weak field cations. Association and hydration equilibria in these media have been interpreted using several models which enable prediction of the chemical equilibria in the corresponding anhydrous melts.[3,7-9] In concentrated aqueous solutions containing bivalent metal cations it is assumed that nearly all the water molecules are retained in the co-ordination sphere of the more polarizing bivalent metal cation.[1,2,9-11]

Cadmium halide complex formation has been investigated in highly concentrated solutions of $Ca(NO_3)_2$ [8,9] and mixed solvents containing $Ca(NO_3)_2$.[7,9-11] The solvent effect on the association constants and Helmholtz free energy of association has been correlated with the sizes and charges of the solvent and solute ions on the basis of a reciprocal Coulomb effect. However, the association constants in some mixed solvents containing $Ca(NO_3)_2$ are not consistent with this treatment.[10,11]

In the present study, complex formation between cadmium ions and chloride ligands is investigated in $Mg(NO_3)_2$ solutions containing water (8.5—12.96 mol per mol of salt) at 343 K and in NH_4NO_3–$Mg(NO_3)_2$ (7 : 3) containing water (2.12—4.86 mol per mol of salt mixture) at 328 and 343 K. The salt mixture $NH_4NO_3 + Mg(NO_3)_2 + H_2O$ (7 : 3 : 25) was also studied at 358 K.

Stability constants for $CdCl^+$ and $CdCl_2$ in both types of solvent were calculated from electromotive force (e.m.f.) measurements of a concentration cell. The results obtained here are compared with published data for the corresponding equilibria in concentrated solutions (aqueous melts) of NH_4NO_3,[5] $Ca(NO_3)_2$,[9,12] and NH_4NO_3–$Ca(NO_3)_2$ (7 : 3).[10]

EXPERIMENTAL

The stability constants of $CdCl^+$ and $CdCl_2$ were evaluated from e.m.f. measurements of the cell shown below where Ag,AgCl are silver–silver chloride electrodes and x is the number of moles of water per mol of $Mg(NO_3)_2$ or per mol of the salt mixture. The total concentration of the chloride ligand (n_{Cl}) was equal in both half-cells, while the concentration of cadmium (n_{Cd}) in the indicator half-cell varied with ligand concentrations. Both concentrations are expressed as Temkin's [13] ionic fractions. The cell and the measurement technique have been described previously.[5,9] The temperature of the cell was maintained to within ±0.05 K while the e.m.f. values remained stable to within ±0.1 mV over 15—30 min. In preliminary experiments the validity of the Nernst equation was tested. The theoretical Nernst slope (when $n_{Cd} = 0$ and n_{Cl} differ in the two half-cells) was obtained within ±2%.

Reagent grade $Mg(NO_3)_2{\cdot}6H_2O$ was used without further purification while reagent grade NH_4NO_3 was carefully dried and stored in a dry atmosphere. Solutions of the desired composition were prepared from known weights of the salts and distilled water.

Ag, AgCl	$Mg(NO_3)_2$ or NH_4NO_3–$Mg(NO_3)_2$ (7 : 3) x H_2O $MgCl_2$ or NH_4Cl (n_{Cl}) $Cd(NO_3)_2$ (n_{Cd})	$Mg(NO_3)_2$ or NH_4NO_3–$Mg(NO_3)_2$ (7 : 3) x H_2O $MgCl_2$ or NH_4Cl (n_{Cl})	AgCl, Ag

RESULTS

A complete listing of the changes in e.m.f. (ΔE) on addition of $Cd(NO_3)_2$ into the cell containing a fixed concentration of chloride ions in both half-cells is deposited in Supplementary Publication No. SUP 23281 (14 pp.).† Only the measurements in NH_4NO_3–$Mg(NO_3)_2$–H_2O (7 : 3 : 25) at 343 K are shown in Table 1 as an example. Equilibrium constants K_1 and K_2 were calculated from e.m.f. measurements. The

$$K_1 = [CdCl^+]/[Cd^{2+}][Cl^-] \quad (1)$$

$$K_2 = [CdCl_2]/[CdCl^+][Cl^-] \quad (2)$$

method of calculation in solvents containing ions with different charges has been described elsewhere.[7,8,10] Table 2 lists the values of the equilibrium constants K_1 and K_2 for all the systems investigated. The estimated uncertainties are ±5% for K_1 and ±10% for K_2.

DISCUSSION

The dependence of the equilibrium constants K_1 and K_2 on water concentration and temperature shows the

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† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 1

E.m.f. measurements in NH_4NO_3–$Mg(NO_3)_2$–H_2O (7 : 3 : 25) at 343 K

$n_{Cl} = 1.57 \times 10^{-4}$		$n_{Cl} = 2.36 \times 10^{-4}$		$n_{Cl} = 3.65 \times 10^{-4}$	
$10^4\ n_{Cd}$	ΔE/mV	$10^4\ n_{Cd}$	ΔE/mV	$10^4\ n_{Cd}$	ΔE/mV
1.28	1.4	1.23	1.3	1.29	1.4
2.55	2.7	2.64	2.8	2.62	2.7
3.76	3.9	4.03	4.2	3.92	4.0
5.06	5.2	5.30	5.4	5.23	5.2
6.34	6.4	6.64	6.6	6.45	6.4
7.70	7.6	8.12	8.0	7.73	7.5
9.05	8.8	9.22	9.1	9.24	8.8

$n_{Cl} = 5.10 \times 10^{-4}$		$n_{Cl} = 7.10 \times 10^{-4}$	
$10^4\ n_{Cd}$	ΔE/mV	$10^4\ n_{Cd}$	ΔE/mV
1.40	1.1	1.35	1.3
2.94	3.0	2.71	2.3
4.25	4.0	3.90	3.5
5.58	5.2	5.22	4.7
6.96	6.5	6.59	6.3
8.32	7.7	7.89	7.4
9.57	8.7	9.19	8.5

trend usually obtained for metal–halide complexes in aqueous and anhydrous melts.[3-12] The value of K_1/K_2 lies in the range 2—3, which corresponds to the statistical value for non-directional ligand co-ordination in molten salts with a quasi-lattice co-ordination number $Z = 6$.[14] Similar values of K_1/K_2 are obtained in aqueous melts.[5-11]

TABLE 2

Equilibrium constants K_1 and K_2 for $CdCl^+$ and $CdCl_2$ formation respectively (ion fraction scale)

Solvent	T/K	K_1	K_2
$Mg(NO_3)_2 + H_2O$ (1 : 8.5)	343	264	102
(1 : 9.0)	343	240	76
(1 : 10.0)	343	180	67
(1 : 12.96)	343	130	55
$NH_4NO_3 + Mg(NO_3)_2 + H_2O$ (7 : 3 : 21.2)	343	637	303
(7 : 3 : 25)	328	578	228
	343	500	217
	358	416	256
(7 : 3 : 27)	343	446	165
(7 : 3 : 30)	328	497	219
(7 : 3 : 38.9)	328	286	140
	343	260	130
(7 : 3 : 40)	343	252	96
(7 : 3 : 48.5)	328	226	105
	343	200	85

The K_1 values were used to calculate specific Helmholtz free energies of association from the known models derived for ionic association equilibria in aqueous melts.[3,9] One of the models, developed by Braunstein,[3] yields a linear relationship between Z/K_1 and the water–nitrate salt concentration in the solvent, equation (3). Here Z

$$Z/K_1 = \exp(\Delta E_1/RT) + r\ \exp[(\Delta E_1 - \Delta h)/RT] \quad (3)$$

is the quasi-lattice co-ordination number, K_1 is the first complex-formation constant in the solvent with r mol of water per mol of nitrate, ΔE_1 denotes the increase in the Helmholtz free energy of the metal–ligand bond relative to the metal–nitrate bond, and Δh the increase in the Helmholtz free energy of the metal–water bond relative to the solvent cation–water bond. It has been shown that in many charge-symmetric molten salts, and salt mixtures with low water concentrations, this model successfully predicts values of K_1 at different temperatures and water contents.[3-6,15] Extrapolation to zero water concentration allows the calculation of K_1 in anhydrous melts. However, in some aqueous melts, mostly with charge-unsymmetric salts, the linear relationship of Braunstein's model only holds if the water concentrations in the melt are very low.

Equation (3) applied to the K_1 values of Table 2 did not produce straight lines with positive intercepts, therefore a model derived by Gal *et al.*,[9] which enables prediction of association equilibria in aqueous melts with higher water concentrations, was used in the present case. According to this model, K_1 is calculated from equation (4) where $\Delta G^{\ominus}$'is the standard Gibbs free-energy change,

$$\Delta G^{\ominus} = -RT\ln K_1 = \Delta E_1 + \frac{\Delta E_2 - \Delta E_1}{(Z-y)\exp[(\Delta E_2 - \Delta E_1)/RT] + y} - RT\left\{\frac{(Z-y)\ln(Z-y)}{(Z-y) + \exp[(\Delta E_1 - \Delta E_2)/RT]} + \frac{y\ln y}{(Z-y)\exp[(\Delta E_2 - \Delta E_1)/RT] + y}\right\} \quad (4)$$

ΔE_1 has the same meaning as in equation (3), ΔE_2 is the increase in the Helmholtz free energy when a ligand replaces a water molecule from the co-ordination sphere of the metal ion, $\Delta E_1 - \Delta E_2$ corresponds to the parameter Δh in Braunstein's model, Z is the co-ordination number, and y is the average hydration number of the metal ion.

When $y = 0$, equation (4) is identical to the relation given by Blander's model for ionic association in anhydrous molten salts, equation (5).[16] When total

$$\Delta E_1 = -RT\ln K_{1(y=0)} + RT\ln Z \quad (5)$$

hydration of a metal ion is attained ($y = Z$), ΔE_2 can be calculated from equation (6).

$$\Delta E_2 = -RT\ln K_{1(y=Z)} + RT\ln Z \quad (6)$$

In order to apply this model to our experimental results three parameters have to be known: the quasi-lattice co-ordination number Z and the bond-energy parameters ΔE_1 and ΔE_2. The hydration number of the metal ion, y, which varies with water concentration, must also be evaluated. The hydration numbers of the cadmium ion in both solutions at different water concentrations were calculated approximately by assuming that the hydration number is proportional to the charge on the solvent cations and inversely proportional to the corresponding Pauling radii.[9,17] Thus, for co-ordination number $Z = 6$, total hydration of the cadmium ions in the inner co-ordination sphere was attained in $Mg(NO_3)_2$ solutions containing 12.96 mol of water and in NH_4NO_3–$Mg(NO_3)_2$ (7 : 3) solutions containing 4.85 mol of water per mol of the salt mixture. The K_1 values, determined for these two solutions, were used to calculate ΔE_2 from equation (6).

Equilibrium constants K_1 for the corresponding anhydrous melts could not be determined experimentally due to thermal decomposition of the salts above their melting points. Therefore, ΔE_1 could not be calculated from equation (5). Hence the values of ΔE_1 were obtained from the best fit of equation (4) to our experimental data and the calculated values of ΔE_2 and y. From equation (4), standard Gibbs free-energy changes, $\Delta G^{\ominus}$, were calculated for the association reaction in the solvents with variable water concentrations. A comparison between experimental and calculated $\Delta G^{\ominus}$ values for all the systems investigated is given in Table 3.

TABLE 3

Comparison of experimental and calculated values of $\Delta G^{\ominus}$ (kJ mol^{-1})

			$-\Delta G^{\ominus} = RT \ln K_1$		Bond-energy parameters from equation (4)/ kJ mol^{-1}
x	y	T/K	Expt.	Calc.	
(a) $Mg(NO_3)_2$ + x H_2O					
8.50	3.94	343	3.80	3.81	$-\Delta E_1 = 14.63$ $-\Delta E_2 = 8.78$
9.00	4.17	343	3.73	3.72	
10.00	4.63	343	3.57	3.55	
12.96	6.00	343	3.32	(3.32)	
(b) 0.7 NH_4NO_3 + 0.3 $Mg(NO_3)_2$ + x H_2O					
2.50	3.09	328	4.15	4.24	$-\Delta E_1 = 15.47$ $-\Delta E_2 = 9.86$
3.00	3.70	328	4.05	4.06	
3.89	4.80	328	3.69	3.63	
4.86	6.00	328	3.53	(3.53)	
2.12	2.62	343	4.40	4.38	$-\Delta E_1 = 15.47$ $-\Delta E_2 = 10.03$
2.50	3.09	343	4.24	4.25	
2.70	3.33	343	4.16	4.19	
3.89	4.80	343	3.79	3.66	
4.00	5.31	343	3.77	3.64	
4.86	6.00	343	3.61	(3.61)	

The data of Table 3 show that the model derived by Gal *et al.*[9] can be used successfully for the interpretation of $CdCl^+$ complex formation in the two solvents. There is good agreement between experimental and calculated $\Delta G^{\ominus}$ values. In the solvent NH_4NO_3–$Mg(NO_3)_2$ (7 : 3) with variable concentrations of water the same value for ΔE_1 was obtained at 328 and 343 K while ΔE_2 changed only slightly with temperature. According to the model, the standard enthalpy change, $\Delta H^{\ominus}$, also changes slightly with temperature [9] and can be calculated from equation (7). The value of $\Delta H^{\ominus}$ for NH_4NO_3–$Mg(NO_3)_2$–H_2O

$$\Delta H^{\ominus} = \Delta E_1 + (y/Z)(\Delta E_2 - \Delta E_1)\exp[(\Delta E_1 - \Delta E_2)/RT] \quad (7)$$

(7 : 3 : 25) at 343 K calculated from the above equation is 15.05 kJ mol^{-1}. Using the values of K_1 for the same solvent at 328, 343, and 358 K, $\Delta H^{\ominus}$ was also calculated from the plot of ln K_1 against $1/T$. The value of 12 ± 3.5 kJ mol^{-1} obtained in this way can be considered only as an approximate value due to the uncertainties of ±5% in K_1 and the errors in graphical evaluation of $\Delta H^{\ominus}$ at the three temperatures.

A more negative value of ΔE_1 in NH_4NO_3–$Mg(NO_3)_2$–H_2O (7 : 3 : x) relative to that in $Mg(NO_3)_2$–H_2O (1 : x) accords with prediction by the reciprocal Coulomb effect.[18] However, the opposite solvent effect on ΔE_1 was found in the case of NH_4NO_3–$Ca(NO_3)_2$–H_2O (7 : 3 : x).[10] The effect of the solvent on the bond-energy parameter ΔE_1 for $CdCl^+$ formation is shown in Table 4. In addition to the results from this work, Table 4 lists the ΔE_1 values calculated from published data in highly concentrated solutions of NH_4NO_3,[5] $Ca(NO_3)_2$, $Ca(NO_3)_2$–KNO_3 (1 : 1),[9] NH_4NO_3–$Ca(NO_3)_2$ (7 : 3),[10] and in anhydrous KNO_3.[19] In the same Table are listed the formation constants, K_1, for $CdCl^+$ in the corresponding supercooled anhydrous melts at 343 K, obtained by extrapolation from equation (5). A co-ordination number $Z = 6$ for cadmium was assumed for the calculation of ΔE_1 and K_1.

TABLE 4

Values of ΔE_1 and extrapolated values of K_1 ($x = 0$) for $CdCl^+$ formation in various solvents at 343 K

Solvent	x (mol H_2O)	$-\Delta E_1$/ kJ mol^{-1}	K_1 ($x = 0$)	Ref.
NH_4NO_3	1.5—3.0	15.47	1 370	5
$Ca(NO_3)_2$	3.5—6.0	18.83	4 420	9
$Mg(NO_3)_2$	8.5—12.96	14.63	1 020	This work
KNO_3	0	20.00	6 860	19
$Ca(NO_3)_2$–KNO_3 (1 : 1)	3.5—6.0	19.25	5 120	9
NH_4NO_3–$Ca(NO_3)_2$ (7 : 3)	2.0—5.2	18.56	3 820	10
NH_4NO_3–$Mg(NO_3)_2$ (7 : 3)	2.5—4.86	15.47	1 370	This work

The stability of $CdCl^+$ complexes can be seen to decrease in the following order: $KNO_3 > KNO_3$–$Ca(NO_3)_2$ (1 : 1) $> Ca(NO_3)_2 > NH_4NO_3$–$Ca(NO_3)_2$ (7 : 3) $> NH_4NO_3 \geqslant NH_4NO_3$–$Mg(NO_3)_2$ (7 : 3) $> Mg(NO_3)_2$. If the solvent effect is attributed to a reciprocal Coulomb effect, assuming only a change in Coulombic energy on exchange of nearest-neighbour ions,[18] then greater stability should be observed in solvents with larger cations and the following order of $CdCl^+$ stability would be expected: $NH_4NO_3 > KNO_3 > NH_4NO_3$–$Ca(NO_3)_2$ (7 : 3) $> NH_4NO_3$–$Mg(NO_3)_2$ (7 : 3) $> Ca(NO_3)_2$–KNO_3 (1 : 1) $> Ca(NO_3)_2 > Mg(NO_3)_2$. Hence, it can be concluded that the observed order of stability of $CdCl^+$ is not in accordance with the reciprocal Coulomb effect. There is a large difference in $CdCl^+$ stability between $Ca(NO_3)_2$ and $Mg(NO_3)_2$ and their mixtures with NH_4NO_3. Greater complex stability is observed in $Ca(NO_3)_2$ than in $Mg(NO_3)_2$ or in NH_4NO_3, while $CdCl^+$ is less stable in $Mg(NO_3)_2$ than in NH_4NO_3. Moreover, in the $Ca(NO_3)_2$–KNO_3 (1 : 1) and NH_4NO_3–$Mg(NO_3)_2$ (7 : 3) mixtures the solvent effect accords with the reciprocal Coulomb effect, although the opposite is found in NH_4NO_3–$Ca(NO_3)_2$ (7 : 3).

Disagreement between the solvent effect and the reciprocal Coulomb effect was found for other complexes in charge-symmetric melts containing $LiNO_3$ and the phenomenon was attributed to different sizes of nitrate ions in different nitrate melts.[20] It is difficult to accept the same explanation for the observed order of stability of $CdCl^+$ in the solvents listed in Table 4. Although a single value of effective ionic radius cannot be assigned to the nitrate ion, it is unlikely to explain the pronounced discrepancy in solvent effect between $Ca(NO_3)_2$ and $Mg(NO_3)_2$ and between their mixtures with NH_4NO_3 when only the charges and size of the corresponding ions are considered. It appears necessary to incorporate other factors which may influence metal-complex formation with halide ligands. There is experimental evidence for certain types of interactions of bivalent metal ions with nitrate ions in anhydrous nitrate melts [21] and in concentrated aqueous solutions of some nitrate salts.[22] Different metal ions differ significantly in their relative affinities for chloride and nitrate ions.

In order to obtain further information on $CdCl^+$ complex stability in binary salt mixtures containing bivalent metal cations, the investigation of ionic equilibria has been extended to concentrated solutions of $Ca(NO_3)_2$–$Mg(NO_3)_2$. The results of this study will appear in a subsequent paper.

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