# Formation Constants of Chlorocadmium(II) and Cadmium Dichloride in Aqueous Melts of Calcium Dinitrate and Calcium Dinitrate–Potassium Nitrate

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Formation constants of $[CdCl]^+$ and $CdCl_2$ in aqueous melts of $Ca[NO_3]_2\cdot xOH_2$ and $Ca[NO_3]_2\cdot K[NO_3]\cdot xOH_2$ ($x$ = 3.5—7) have been determined at 50, 65, and 80 °C from e.m.f. measurements in suitable concentration cells. The results are discussed in terms of a quasi-lattice structure of aqueous melts, and a model is proposed which predicts the dependence of thermodynamic data for $[CdCl]^+$ formation on the temperature and water content of the molten salt.

IN previous papers [1-4] it has been shown that quasi-lattice models of anhydrous [5] and aqueous [6] molten salts predict thermodynamic data for the formation of halide complexes of $Ag^{I}$, $Cd^{II}$, $Pb^{II}$, and $Hg^{II}$. However, disagreement with the aqueous quasi-lattice model [6] has been noted in the case of $[ZnCl]^+$ in aqueous ammonium nitrate [4] and in the case of $[CdBr]^+$ in aqueous calcium nitrate and calcium nitrate–potassium nitrate.[7,8a] Braunstein and his co-workers [7,8a] recently proposed a model which enabled the formation constant of $[CdBr]^+$ to be related to the temperature and water activity of the melt. Their model does not assume a quasi-lattice structure or any particular structure of the melt, but it incorporates an ' average hydration number ' of the central metal ion which is constant and independent of the water content of the melt. It seems that this number is actually an adjustable parameter of questionable physical significance.

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[1] I. J. Gal, *Inorg. Chem.*, 1968, **7**, 1611.

[2] R. M. Nikolić and I. J. Gal, *J.C.S. Dalton*, 1972, 162.

[3] I. J. Gal, G. Djurić, and L. Melovski, *J.C.S. Dalton*, 1973, 2066.

[4] R. M. Nikolić and I. J. Gal, *J.C.S. Dalton*, 1974, 985.

[5] M. Blander, *J. Chem. Phys.*, 1961, **34**, 432.

[6] J. Braunstein, *J. Phys. Chem.*, 1967, **71**, 3402.

[7] H. Braunstein, J. Braunstein, A. S. Minano, and R. E. Hagman, *Inorg. Chem.*, 1973, **12**, 1407.

[8] (*a*) H. Braunstein, J. Braunstein, and P. Hardesty, *J. Phys. Chem.*, 1973, **77**, 1907: (*b*) M. Temkin, *Acta Physicochim. U.R.S.S.*, 1945, **20**, 411.

In the present work the formation of $[\mathrm{CdCl}]^+$ and $\mathrm{CdCl_2}$ has been studied in aqueous $\mathrm{Ca[NO_3]_2}$ and $\mathrm{Ca[NO_3]_2}$–$\mathrm{KNO_3}$ melts of variable water content ($\mathrm{H_2O}$ : Ca ratio from 3.5 to 7 : 1) and at three temperatures, 50, 65, and 80 °C. The purpose of the work is two-fold: first, to provide some missing thermodynamic data for halide complexes of cadmium in charge-unsymmetrical aqueous melts; and, secondly, to analyse the data in terms of a quasi-lattice concept of the melt. Our interpretation of the results led us to suggest a simple model of ionic association in aqueous melts.

## EXPERIMENTAL

The electromotive force (e.m.f.) of the following concentration cell has been measured:

$$\text{Ag, AgCl}\left|\begin{array}{l}\mathrm{Ca[NO_3]_2{\cdot}}x\mathrm{OH_2}\\ \text{(or }\mathrm{Ca[NO_3]_2{\cdot}K[NO_3]{\cdot}}x\mathrm{OH_2})\\ \mathrm{KCl}\ (n_{\mathrm{Cl}})\\ \mathrm{Cd[NO_3]_2}\ (n_{\mathrm{Cd}})\end{array}\right\|\left.\begin{array}{l}\mathrm{Ca[NO_3]_2{\cdot}}x\mathrm{OH_2}\\ \text{(or }\mathrm{Ca[NO_3]_2{\cdot}K[NO_3]{\cdot}}x\mathrm{OH_2})\\ \mathrm{KCl}\ (n_{\mathrm{Cl}})\\ \\ \end{array}\right|\text{AgCl, Ag}$$

Here (Ag, AgCl) is the silver–silver(I) chloride electrode and $x$ is the number of moles of water per mole of solvent salt, $\mathrm{Ca[NO_3]_2}$ or $\mathrm{Ca[NO_3]_2{\cdot}K[NO_3]}$. The total concentration of $\mathrm{Cl^-}$ ligand is $n_{\mathrm{Cl}}$ and the total cadmium concentration is $n_{\mathrm{Cd}}$, both expressed in ionic fractions (*e.g.*, cationic and anionic fractions according to Temkin).[8b] The chloride concentration is equal in both half-cells. The accuracy of e.m.f. measurements was ±0.1 mV, and the temperature was constant to ±0.05 °C. In both solvent salt systems and at each temperature and water content, the theoretical Nernst gradient (when $n_{\mathrm{Cd}} = 0$ and $n_{\mathrm{Cl}}$ differs in the two half-cells) was obtained within ±2%, which indicates that KCl behaves ideally in the concentration range investigated and justifies the neglect of the liquid-junction potential. The e.m.f. cell and the instruments have been described in a previous paper.[2]

Aqueous melts of desired composition were prepared from known amounts of carefully dried salts and distilled water. Reagent-grade KCl and $\mathrm{K[NO_3]}$ were dried at 120 °C, whereas dry $\mathrm{Ca[NO_3]_2}$ was obtained by prolonged heating at 220 °C in a dry atmosphere.

## RESULTS

As e.m.f. measurements have been extended in both salt systems, $\mathrm{Ca[NO_3]_2{\cdot}}x\mathrm{OH_2}$ and $\mathrm{Ca[NO_3]_2{\cdot}K[NO_3]{\cdot}}x\mathrm{OH_2}$, at three temperatures (50, 65, and 80 °C), varying the water content from $x = 3.5$ to 7, they are too extensive to be tabulated in this paper. Therefore, they have been deposited in Supplementary Publication No. SUP 21598 (25 pp).[*] Only measurements in the solvent $\mathrm{Ca[NO_3]_2{\cdot}3.5OH_2}$ at 80 °C are presented in Table 1 as an example of data obtained. From these data the stability constants $K_1 = [\mathrm{CdCl^+}]/[\mathrm{Cd^{2+}}][\mathrm{Cl^-}]$ and $K_2 = [\mathrm{CdCl_2}]/[\mathrm{CdCl^+}][\mathrm{Cl^-}]$ were obtained using a graphical method [9] modified for melts of unsymmetrical charge distribution.[7,8a] The method is similar to that used in our earlier papers.[2,4] The stability constants obtained are listed in Table 2 for $\mathrm{Ca[NO_3]_2{\cdot}K[NO_3]{\cdot}}x\mathrm{OH_2}$ and in Table 3 for $\mathrm{Ca[NO_3]_2{\cdot}}x\mathrm{OH_2}$. The estimated accuracy of these data is *ca.* ±5% for $K_1$ and ±10% for $K_2$. Tables 2 and 3 show that the stability constants decrease with temperature, which is the usual behaviour in anhydrous and aqueous melts.[4] Further, $[\mathrm{CdCl}]^+$ is more stable in $\mathrm{Ca[NO_3]_2{\cdot}K[NO_3]{\cdot}}x\mathrm{OH_2}$ than in $\mathrm{Ca[NO_3]_2{\cdot}}x\mathrm{OH_2}$, for the same value of $x$. This phenomenon is due to the reciprocal Coulomb effect in mixtures of 1 : 1 and 2 : 1 salts, as discussed in one of our earlier papers.[3] The decrease of the stability constants with the water content $x$ is also a well established trend predicted by Braunstein's quasi-lattice model of aqueous melts.[6]

## DISCUSSION

The values of the first consecutive stability constants $K_1$ of Tables 2 and 3 were used first to test the statistical-mechanical model of Braunstein [6] based on the quasi-lattice structure of aqueous melts. The result of the test was disappointing, because in most cases it appeared that the $K_1$ value at $x = 0$ (*i.e.*, in an anhydrous nitrate melt) should have a negative value. This, of course, has no physical meaning and is in contradiction with experiment. Our preliminary measurements [10] in anhydrous $\mathrm{Ca[NO_3]_2{\cdot}K[NO_2]}$ at 320 °C gave for $[\mathrm{CdCl}]^+$ a $K_1$ value of 292, which corresponds to Blander's [5] ' free energy of bonding ' parameter of $-19.25$ kJ $\mathrm{mol^{-1}}$ for a co-ordination number $Z = 6$. This parameter is, according to the generalized quasi-lattice theory,[5] practically independent of temperature.

TABLE 1

E.m.f. measurement in the system $\mathrm{Cd[NO_3]_2}$–KCl–$\mathrm{Ca[NO_3]_2{\cdot}3.5OH_2}$ at 80 °C

| $n_{\mathrm{Cl}} = 2.02 \times 10^{-4}$ | | $n_{\mathrm{Cl}} = 4.11 \times 10^{-4}$ | | $n_{\mathrm{Cl}} = 6.34 \times 10^{-4}$ | |
|---|---|---|---|---|---|
| $10^4 n_{\mathrm{Cd}}$ | $\Delta E$/mV | $10^4 n_{\mathrm{Cd}}$ | $\Delta E$/mV | $10 n_{\mathrm{Cd}}$ | $\Delta E$/mV |
| 1.61 | 2.7 | 3.69 | 6.8 | 1.50 | 1.7 |
| 3.36 | 5.2 | 5.78 | 9.6 | 3.14 | 4.1 |
| 5.26 | 7.7 | 8.03 | 11.7 | 4.85 | 6.8 |
| 7.31 | 10.2 | 10.51 | 14.2 | 6.70 | 9.1 |
| 9.50 | 12.7 | 13.24 | 16.9 | 8.77 | 11.6 |
| 11.91 | 15.0 | 16.05 | 19.5 | 11.05 | 14.4 |
| 14.47 | 17.6 | | | 13.48 | 16.8 |

| $n_{\mathrm{Cl}} = 7.95 \times 10^{-4}$ | | $n_{\mathrm{Cl}} = 9.01 \times 10^{-4}$ | |
|---|---|---|---|
| $10^4 n_{\mathrm{Cd}}$ | $\Delta E$/mV | $10^4 n_{\mathrm{Cd}}$ | $\Delta E$/mV |
| 1.58 | 2.4 | 3.00 | 3.9 |
| 3.29 | 5.3 | 6.58 | 9.1 |
| 4.73 | 7.2 | 8.65 | 11.2 |
| 8.02 | 11.8 | 10.80 | 13.4 |
| 10.03 | 14.4 | 13.23 | 15.6 |

A second test was made using the latest ionic-association model for aqueous melts.[7,8a] This model should be suitable for higher water concentrations and, as mentioned earlier, it does not depend on any particular structure of the melt. Our $K_1$ values in Tables 1 and 2

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[*] For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

[9] J. Braunstein, M. Blander, and R. M. Lindgren, *J. Amer. Chem. Soc.*, 1962, **84**, 1529.

[10] D. Antić, R. M. Nikolić, and I. J. Gal, unpublished work.

fit the model if an ' average hydration number ' of 2 is assumed for $Cd^{2+}$ ions. This number, however, is not reasonable, because our melts have 3.5—7 molecules of water per $Ca^{2+}$ ion, and according to Angell,[11] in fused hydrated salts such as $Ca[NO_3]_2{\cdot}xOH_2$ the water is almost entirely bound to the small bivalent cations.

TABLE 2

Stability constants * for $[CdCl]^+$ and $CdCl_2$ in $Ca[NO_3]_2{\cdot}K[NO_3]{\cdot}xOH_2$

| $T$/K | $x$ | $K_1$ | $K_2$ |
|---|---|---|---|
| 323 | 4.0 | 1 410 | 710 |
| | 5.0 | 1 090 | 540 |
| | 6.0 | 875 | 365 |
| | 7.0 | 750 | 230 |
| 338 | 4.0 | 1 185 | 570 |
| | 5.0 | 920 | 460 |
| | 6.0 | 760 | 360 |
| | 7.0 | 645 | 230 |
| 353 | 3.5 | 1 080 | 555 |
| | 4.0 | 975 | 515 |
| | 5.0 | 810 | 390 |
| | 6.0 | 675 | 275 |

* On the mole fraction scale.

Cadmium(II) ion has a slightly smaller Pauling radius than $Ca^{2+}$, and therefore it is not reasonable to assume that $Cd^{2+}$ is less hydrated than $Ca^{2+}$. Consequently, it is concluded that neither of Braunstein's models describes satisfactorily the formation of $[CdCl]^+$ in $Ca[NO_3]_2{\cdot}xOH_2$ or $Ca[NO_3]_2{\cdot}K[NO_3]{\cdot}xOH_2$. However, using the quasi-lattice concept for aqueous melts and some results derived from Blander's generalized model of ionic association,[5] we make the following temptative attempt to interpret the data in Tables 1 and 2.

The quasi-lattice of a melt like $Ca[NO_3]_2{\cdot}xOH_2$ consists of the interpenetrating cation and anion sub-lattices. The cations ($Ca^{2+}$, $Cd^{2+}$, and $K^+$) occupy sites on the cation sub-lattice, and are surrounded by $Z$ sites of the anion sub-lattice; $Z$ is the average co-ordination number. The anions, $[NO_3]^-$ and $Cl^-$, occupy sites on the anion sub-lattice, as do all the water molecules up to a content $x = Z$. In other words, we assume that only the small bivalent cations are hydrated up to $Ca[NO_3]_2{\cdot}ZOH_2$, and we neglect hydration of the large univalent ions $[NO_3]^-$, $Cl^-$, and $K^+$ in the range $0 \leqslant x \leqslant Z$. The anion sites are surrounded by cation sites as nearest neighbours, but as the melt is of unsymmetrical charge distribution we must assume different numbers of sites in the two sub-lattices and/or cation vacancies.

TABLE 3

Stability constants * for $[CdCl]^+$ and $CdCl_2$ in $Ca[NO_3]_2{\cdot}xOH_2$

| $T$/K | $x$ | $K_1$ | $K_2$ |
|---|---|---|---|
| 323 | 4.0 | 1 080 | 500 |
| | 5.0 | 725 | 330 |
| | 6.0 | 565 | 200 |
| | 7.0 | 440 | 135 |
| 338 | 3.5 | 1 200 | 580 |
| | 4.0 | 940 | 495 |
| | 5.0 | 660 | 340 |
| | 6.0 | 500 | 235 |
| 353 | 3.5 | 1 020 | 585 |
| | 4.0 | 890 | 600 |
| | 5.0 | 550 | 210 |
| | 6.0 | 420 | 160 |

* On the mole fraction scale.

Let us consider now a very dilute solution of $Cd^{2+}$ and $Cl^-$ in $Ca[NO_3]_2{\cdot}xOH_2$. The hydration number of $Ca^{2+}$ is $x$, and that of $Cd^{2+}$ is $y$. The formation of $[CdCl]^+$ can be described, according to our model, in two ways

$$[Cd(NO_3)_{Z-y}(OH_2)_y] + Ca_{Z'}Cl \longrightarrow [CdCl(NO_3)_{Z-y-1}(OH_2)_y] + Ca_{Z'}(NO_3) \quad (1)$$

[equations (1) and (2)]. Equations (1) and (2) use the quasi-lattice concept in that a $Cd^{2+}$ ion is surrounded by $Z$ anion sites, $y$ of which are occupied by $H_2O$ molecules

$$[Cd(NO_3)_{Z-y}(OH_2)_y] + Ca_{Z'}Cl \longrightarrow [CdCl(NO_3)_{Z-y}(OH_2)_{y-1}] + Ca_{Z'}(OH_2) \quad (2)$$

and $(Z - y)$ by nitrate ions. A $Cl^-$ ion is on the anion sub-lattice surrounded by cations and according to our model is not hydrated. The formation of $[CdCl]^+$ can take place in two distinct ways: either $Cl^-$ replaces a $[NO_3]^-$ anion in the co-ordination sphere of $Cd^{2+}$ [equation (1)] or replaces a water molecule [equation (2)]. As in earlier quasi-lattice models,[5-7] we assume only pairwise interactions between nearest neighbours in equations (1) and (2) (independent of the surrounding).

The energy increases in reactions (1) and (2) are expressed through pairwise bond-energy ($E_{x-y}$) differences as in (3) and (4). If the two reactions take place at

$$\Delta E_1 = E_{Cd\text{-}Cl} + E_{NO_3\text{-}Ca} - E_{Cd\text{-}NO_3} - E_{Ca\text{-}Cl} \quad (3)$$

constant temperature and pressure, the energy differences are equal to the standard enthalpy changes: $\Delta E_1 = \Delta H_1^{\ominus}$ and $\Delta E_2 = \Delta H_2^{\ominus}$. The standard entropy changes

$$\Delta E_2 = E_{Cd\text{-}Cl} + E_{H_2O\text{-}Ca} - E_{Cd\text{-}H_2O} - E_{Ca\text{-}Cl} \quad (4)$$

can be easily calculated if all specific-entropy contributions due to internal degrees of freedom are neglected. Such an approximation was assumed in Blander's [5] and Braunstein's [6] models, and it implies that the vibrational entropy does not change appreciably when $Cl^-$ and $[NO_3]^-$ (or $H_2O$) exchange their sites in the anion sub-lattice. Thus, the only entropy contribution to the reactions (1) and (2) is due to the statistical factors $(Z - y)$ and $y$, *i.e.* the numbers of available sites at cadmium for a $Cl^-$ ligand: $\Delta S_1^{\ominus} = R\ln\,(Z - y)$ and $\Delta S_2^{\ominus} = R\ln y$. These expressions are analogous to $\Delta S^{\ominus} = R\ln Z$ for the anhydrous molten salt.[3] Taking into account that

$$\Delta G_1^{\ominus} = \Delta E_1 - RT\ln\,(Z - y) \quad (5)$$

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$, the standard Gibbs free-energy, changes for reactions (1) and (2) are as in (5) and (6).

$$\Delta G_2^{\ominus} = \Delta E_2 - RT\ln y \quad (6)$$

Both reactions contribute to the experimentally measured free-energy change [equation (7)]. Here, $K_1$ is the

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[11] C. A. Angell, *J. Electrochem. Soc.*, 1965, **112**, 1224.

experimentally determined stability constant of $[CdCl]^+$, and $n$ is a statistical fraction ($0 \leqslant n \leqslant 1$) which determines the contribution of equations 1 and 2 to the overall

$$\Delta G^\ominus = -RT \ln K_1 = (1-n)\Delta G_1^\ominus + n\Delta G_2^\ominus \qquad (7)$$

equilibrium. This fraction can be estimated by assuming that $n/(1-n)$ is equal to the ratio of the number of $Cl^-$ ions which replace $H_2O$ molecules and that which replace $[NO_3]^-$ ions at cadmium.

Using Boltzmann's statistical distribution and taking into account that the two kinds of $Cl^-$ ions are at energy levels $\Delta E_1$ and $\Delta E_2$ relative to $Cl^-$ ions bound to calcium, whereas the corresponding multiplicities of the sites are $(Z-y)$ and $y$, respectively, equations (8) and (9) follow. Combining equations (5)—(7) and (9), equation (10) is obtained. In an anhydrous melt, when $y = 0$,

$$\frac{n}{1-n} = \frac{y[\exp(-\Delta E_2/RT)]}{(Z-y)[\exp(-\Delta E_1/RT)]} \qquad (8)$$

$$n = \frac{y[\exp(-\Delta E_2/RT)]}{y[\exp(-\Delta E_2/RT)] + (Z-y)[\exp(-\Delta E_1/RT)]} \qquad (9)$$

$$\begin{aligned}\Delta G^\ominus = \Delta E_1 + {} & \frac{(\Delta E_2 - \Delta E_1)\,y}{(Z-y)\exp\left(\dfrac{\Delta E_2 - \Delta E_1}{RT}\right) + y} - \\ & RT\Bigg[\frac{(Z-y)\ln(Z-y)}{(Z-y+y\exp\left(\dfrac{\Delta E_1 - \Delta E_2}{RT}\right)} + \\ & \qquad \frac{y \ln y}{y + (Z-y)\exp\left(\dfrac{\Delta E_2 - \Delta E_1}{RT}\right)}\Bigg] \qquad (10)\end{aligned}$$

the above equation gives (11) [lim $(y \ln y) = 0$] which is practically identical to Blander's expression for $K_1$.[3]

$$\Delta G^\ominus(y=0) = -RT \ln K_1(y=0) = \Delta E_1 - RT \ln Z \qquad (11)$$

$$\Delta G^\ominus(y=z) = -RT \ln K_1(y=z) = \Delta E_2 - RT \ln Z \qquad (12)$$

For a water content corresponding to $y = Z$, equation (10) gives (12). The model is obviously valid in the range $0 \leqslant y \leqslant Z$, and equations (11) and (12) give the Gibbs free energies for the limits of this range.

Equation (10) is a three-parameter system: it has two energy parameters, $\Delta E_1$ and $\Delta E_2$, and the parameter $y$ which is the hydration number of cadmium. All the parameters have definite physical meaning and can be determined independently. Thus, $\Delta E_1$ may be determined according to equation (11) by measuring $K_1$ in the anhydrous melt at any temperature, because, as in Blander's model, it is assumed that $\Delta E_1$ is independent of temperature; $\Delta E_2$ may be determined from equation (12) by measuring $K_1$ at such a water content of the melt that $Cd^{2+}$ is fully aquated ($y = Z$). In our interpretation of the data, we adopted the value $Z = 6$ (usual for nitrate melts), and $\Delta E_2$ was calculated from $K_1$ in the melts $Ca[NO_3]_2 \cdot 6OH_2$ and $Ca[NO_3]_2 \cdot K[NO_3] \cdot 6OH_2$ assuming the hydration number of cadmium ($y$) to be very close to that of calcium ($x$) because the Pauling radii of these bivalent cations are similar, 0.097 and 0.099 nm, respectively. We introduced a small correction, assuming that the ratio of the two numbers $y/x$ varies inversely with the square of the ratio of the corresponding radii [equation (13)]. As is seen from equation (13), the

$$y/x = (r_{Ca^{2+}}/r_{Cd^{2+}})^2 = 1.04 \qquad (13)$$

corrected hydration number $y$ is indeed very close to $x$, the anticipated hydration number of $Ca^{2+}$ in the aqueous melt $Ca[NO_3]_2 \cdot xOH_2$. This equation is based on the fact that ion–dipole interactions depend on the electrostatic field strength of the ion, which varies inversely as the square of the ionic radius.

Equations (10)—(13) were applied also to the $Ca[NO_3]_2 \cdot K[NO_3] \cdot xOH_2$ melts, assuming again that for $y \leqslant Z$ only $Ca^{2+}$ and $Cd^{2+}$ ions are hydrated. The hydration of potassium ions was neglected, which might be an approximation near $y = Z$ but has little influence on the $\Delta E_2$ value if the $K^+$ ions are only slightly hydrated and the pairwise bond-energy differences [as in equations (3) and (4)] are only slightly dependent on 'next-nearest neighbours' interactions. For $Ca[NO_3]_2 \cdot K[NO_3] \cdot xOH_2$ melts we used the experimentally derived value of $\Delta E_1 = -19.25$ kJ mol$^{-1}$, mentioned earlier.[10] This value is based on $K_1$ determined in anhydrous $Ca[NO_3]_2 \cdot K[NO_3]$, assuming $\Delta E_1$ to be independent of temperature. For $Ca[NO_3]_2 \cdot xOH_2$ melts a slightly smaller value of $\Delta E_1 = -18.83$ kJ mol$^{-1}$ was adopted as the best fit for all three temperatures. No experimentally determined $K_1$ value is available in pure anhydrous $Ca[NO_3]_2$ because of the dissociation and side reactions of nitrate ions at high temperature.[12]

TABLE 4

Comparison of experimental and calculated values of $\Delta G^\ominus$ for $[CdCl]^+$ complex formation in $Ca[NO_3]_2 \cdot xOH_2$

| | | $\Delta G^\ominus (= -RT \ln K_1)$/ kJ mol$^{-1}$ | | |
|---|---|---|---|---|
| $T$/K | $x$ | Expt. (Table 3) | Calc. [equation (10)] | Parameters [equation (10)] |
| 353 | 0.0 | | −24.1 | $Z = 6$ |
| | 3.5 | −20.3 | −20.6 | $y = 1.04\,x$ |
| | 4.0 | −19.9 | −19.8 | $\Delta E_1 = -18.83$ kJ mol$^{-1}$ |
| | 5.0 | −18.5 | −18.1 | $\Delta E_2 = -12.51$ kJ mol$^{-1}$ |
| | 6.0 | −17.7 | (−17.7) | |
| 338 | 0.0 | | −23.8 | $Z = 6$ |
| | 3.5 | −19.9 | −20.5 | $y = 1.04\,x$ |
| | 4.0 | −19.2 | −19.7 | $\Delta E_1 = -18.83$ kJ mol$^{-1}$ |
| | 5.0 | −18.2 | −17.7 | $\Delta E_2 = -12.42$ kJ mol$^{-1}$ |
| | 6.0 | −17.4 | (−17.4) | |
| 323 | 0.0 | | −23.6 | $Z = 6$ |
| | 4.0 | −18.7 | −19.5 | $y = 1.04\,x$ |
| | 5.0 | −17.7 | −17.7 | $\Delta E_1 = -18.83$ kJ mol$^{-1}$ |
| | 6.0 | −17.0 | (−17.0) | $\Delta E_2 = -12.20$ kJ mol$^{-1}$ |

A comparison of experimental and calculated $\Delta G^\ominus$ values for $[CdCl]^+$ formation is presented in Tables 4 and 5. As is seen from these Tables, the agreement between the experimental values of $\Delta G^\ominus$ and those calculated

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[12] R. N. Kust and F. R. Duke, *J. Amer. Chem. Soc.*, 1963, **85**, 3338.

TABLE 5

Comparison of experimental and calculated values of $\Delta G^\ominus$ for $[CdCl]^+$ formation in $Ca[NO_3]_2{\cdot}K[NO_3]{\cdot}xOH_2$

| | | $\Delta G^\ominus(=-RT\ln K_1)$/ kJ $mol^{-1}$ | | |
|---|---|---|---|---|
| $T$/K | $x$ | Expt. (Table 2) | Calc. [equation (10)] | Parameters [equation (10)] |
| 353 | 0.0 | | −24.5 | $Z = 6$ |
| | 3.5 | −20.5 | −20.9 | $y = 1.04\,x$ |
| | 4.0 | −20.2 | −20.2 | $\Delta E_1 = -19.25$ kJ $mol^{-1}$ |
| | 5.0 | −19.6 | −18.7 | $\Delta E_2 = -13.80$ kJ $mol^{-1}$ |
| | 6.0 | −19.1 | (−19.1) | |
| 338 | 0.0 | | −24.3 | $Z = 6$ |
| | 4.0 | −20.0 | −20.1 | $y = 1.04\,x$ |
| | 5.0 | −19.2 | −18.6 | $\Delta E_1 = -19.25$ kJ $mol^{-1}$ |
| | 6.0 | −18.6 | (−18.6) | $\Delta E_2 = -13.60$ kJ $mol^{-1}$ |
| 323 | 0.0 | | −24.1 | $Z = 6$ |
| | 4.0 | −19.5 | −20.0 | $y = 1.04\,x$ |
| | 5.0 | −18.8 | −18.3 | $\Delta E_1 = -19.25$ kJ $mol^{-1}$ |
| | 6.0 | −18.2 | (−18.2) | $\Delta E_2 = -13.39$ kJ $mol^{-1}$ |

according to our model is fairly good. The model is self consistent: $\Delta E_1$ is independent of temperature as required by the general quasi-lattice model of anhydrous melts,[5] and the hydration number of $Cd^{2+}$ ($y$) depends on the water content of the melt (*i.e.* on $x$, which is the anticipated hydration number of $Ca^{2+}$); $\Delta E_2$ is only slightly temperature dependent, and so is the standard enthalpy change [equation (14)]. The latter is true even

$$\Delta H^\ominus = (1 - n)\,\Delta E_1 + n\Delta E_2 \qquad (14)$$

if $\Delta E_2$ is independent of temperature, because $n$ is dependent on temperature [equation (9)].

Some preliminary calculations indicate that the proposed model can be also applied to other data on metal complexes in aqueous melts, which will be discussed in our next paper.

[5/648 *Received, 7th April*, 1975]