Thermodynamics of Metal Complex Formation in Aqueous Melts of Calcium Dinitrate–Ammonium Nitrate. Part 2.[1] Cadmium(II) Bromides

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The formation constants of $[CdBr]^+$ and $CdBr_2$ in melts of $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]{\cdot}xH_2O$ (a = 1.5—11.5, x = 0—8), in the range 323—433 K, have been determined from e.m.f. measurements in suitable concentration cells. The results are discussed in terms of a previously developed model based on the quasi-lattice concept of aqueous melts.

IN Part 1 of this work[1] the formation of $[CdCl]^+$ and $CdCl_2$ in aqueous $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]{\cdot}xH_2O$ was investigated, and the application of a model[2] which predicts the dependence of $[CdCl]^+$ formation on temperature and water content of the melt has been tested. The present paper extends our study to cadmium(II) bromide complexes in the above charge-unsymmetrical aqueous melt. The data obtained can be used for an additional test of the quasi-lattice model and, as will be discussed later, allow an improvement of the evaluation of the average hydration numbers which appear as an independent variable in the free-energy equation employed.[2]

EXPERIMENTAL

Aqueous melts of the desired composition were prepared from weighed amounts of dry reagent-grade salts and water. Dry calcium nitrate and ammonium nitrate were obtained after prolonged heating at 220 and 85 °C, respectively, in a dry atmosphere.[3]

The preparation of the Ag–AgBr electrodes, the measuring cell, the null-balance millivoltmeter, and the testing of the validity of the Nernst equation are described in a previous paper.[4] The electromotive force (e.m.f.) measurements in suitable concentration cells have also been described.[1-4] The experimental part of the investigation and the calculation of the complex-formation constants of cadmium(II) bromide species from e.m.f. data are identical to the procedures described in Part 1.[1] The extensive e.m.f. data are available as Supplementary Publication No. SUP 22244 (26 pp.).†

The consecutive formation constants K_1 for $[CdBr]^+$ and K_2 for $CdBr_2$, at various salt compositions (a), water contents (x), and temperatures are listed in Table 1.

RESULTS AND DISCUSSION

Table 1 reveals a similar trend in the dependence of K_1 and K_2 on temperature and water content as in the case of cadmium chloride complexes,[1] but, as expected for bromo-complexes, the formation constants are larger. The quotient K_1/K_2 is always within 2.0—2.4 which is close to the statistical value for non-directional ligand co-ordination[5] in molten salts. Thus, if we assume the usual quasi-lattice co-ordination number $Z = 6$ for nitrate melts,[5,6] the statistical value of K_1/K_2 should equal[6] $2Z/(Z - 1) = 2.4$ (for $Z = 6$), whereas

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[1] I. J. Zsigrai, R. M. Nikolić, and I. J. Gal, *J.C.S. Dalton*, 1976, 879.

[2] I. J. Gal, R. M. Nikolić, and G. Heraković, *J.C.S. Dalton*, 1976, 104.

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

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

[5] M. Blander (ed.), 'Molten Salt Chemistry,' Interscience, New York, 1964, ch. 3.

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

in dilute aqueous solutions K_1/K_2 is much larger, *ca.* 8.[7] This fact and other evidence indicate that aqueous melts having low water contents could be adequately described in terms of a quasi-lattice structure. Such a concept was applied to anhydrous molten salts in the development of a general model of ionic association.[5,8]

TABLE 1

Consecutive formation constants K_1 and K_2 (ion-fraction scale)* of $[CdBr]^+$ and $CdBr_2$ in $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]{\cdot}xH_2O$ melts

a	x	T/K	K_1	K_2
11.50	0.00	433	1 485	749
	0.00	423	2 017	805
5.41	0.00	433	1 800	909
	7.81	353	1 260	531
	6.73		1 465	612
	5.77		1 674	756
	5.13		1 836	814
	4.49		2 017	906
	8.65	338	1 220	564
	7.81		1 355	610
	6.73		1 560	734
	6.09		1 653	736
2.33	5.77	353	1 358	682
	4.53		2 005	923
	4.06		2 340	1 070
	3.67		2 392	1 124
	3.33		2 860	1 310
	3.00		2 925	1 391
	2.67		3 432	1 612
	4.06	338	2 776	1 260
	6.77	323	1 355	581
	5.77		1 755	830
	5.07		2 020	959
	4.53		2 185	1 027
	4.06		2 977	1 426
	3.67		3 315	1 576
1.50	5.77	353	1 348	689
	4.36		2 023	836
	3.75		2 478	1 175
	3.38		3 300	1 460

* B. Temkin, *Acta Physicochim. U.S.S.R.*, 1945, **20**, 411.

The first model for ionic association (complex formation) in aqueous melts was developed by Braunstein,[9] but is valid only at low water contents. In one of our previous papers [2] we proposed an ionic-association model for melts of higher water content. It was tested in charge-unsymmetrical melts of the type $Ca[NO_3]_2{\cdot}aM[NO_3]{\cdot}xH_2O$ ($M = K$ or NH_4, $x = 0$—6).[1,2] According to our model the first formation constant K_1 can be calculated from equation (1). Here Z is the quasi-lattice co-ordination number (6), y is the average hydration number of the complex-forming cation (in our case, Cd^{2+}), and ΔE_1 and ΔE_2 are bond-energy increases (in terms of pairwise interactions) when a ligand (say, Br^-) replaces a nitrate ion and a water molecule, respectively, in the co-ordination sphere of the cation. The energy parameters can, in principle, be determined independently, since equation (1) reduces to (2) in the case of an

$$\Delta G_1^{\ominus} = -RT\ln K_1 = \Delta E_1 + \frac{(\Delta E_2 - \Delta E_1)y}{(Z-y)\exp[(\Delta E_2 - \Delta E_1)/RT] + y} - RT\left\{\frac{(Z-y)\ln(Z-y)}{Z - y + y\exp[(\Delta E_1 - \Delta E_2)/RT]} + \frac{y\ln y}{(Z-y)\exp[(\Delta E_2 - \Delta E_1)/RT] + y}\right\} \quad (1)$$

$$-RT\ln K_1 = \Delta E_1 - RT\ln Z\ (y = 0) \quad (2)$$

anhydrous melt, and to (3) in the case of an aqueous melt

$$-RT\ln K_1 = \Delta E_2 - RT\ln Z\ (y = Z) \quad (3)$$

whose water content corresponds to an average hydration number $y = Z$ (when all the sites around Cd^{2+} are occupied by water molecules). Thus, ΔE_1 and ΔE_2, which are temperature independent over a wide temperature range, can be obtained from equations (2) and (3), if the K_1 values are known (at any temperature) in the anhydrous melt and in an aqueous melt whose water content corresponds to $y = Z = 6$.

An inspection of equation (1) reveals that the practical application of the model depends on the evaluation of the hydration number, y, which is dependent on the water content x in the melt $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]{\cdot}xH_2O$. (In the absence of Br^- ligand, or at low ligand concentration, y is the number of water molecules and $Z - y$ the number of $[NO_3]^-$ ions around a Cd^{2+} ion in the melt.) In the previous paper [1] we evaluated the y values approximately: Cd^{2+} and Ca^{2+} are ions having the same charge and size; their hydration numbers should be approximately equal, and since small bivalent ions are preferentially hydrated we simply neglect the hydration of large univalent ions such as $[NH_4]^+$ and $[NO_3]^-$. Thus, $y = x$, and in equation (1) we insert instead of y the value of x from the melt formula $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]{\cdot}xH_2O$. This approximation is fairly reasonable for melts having low water contents, but less good at high water contents.

In the present paper we introduce a better procedure for evaluating the hydration number y. If K_1 values for two different ligands are available, say for Cl^- and Br^-, and the energy parameters are known, we can insert the experimentally obtained K_1 values for $[CdCl]^+$ into equation (1) and obtain the value of y. (All the calculations can be made using a simple computer program.) In this way we can obtain a plot of y against x based on the chloride data. Since the hydration number y is independent of the type of ligand, the same plot can be now be used for the bromide data, for various water contents x of the melt. Finally, from equation (1) the K_1 values for $[CdBr]^+$ can be calculated and the model can be tested by comparing the calculated and experimental formation constants of $[CdBr]^+$. In the Figure plots of y against x are presented for the melts $Ca[NO_3]_2{\cdot}2.33[NH_4][NO_3]{\cdot}xH_2O$ and $Ca[NO_3]_2{\cdot}1.50[NH_4][NO_3]{\cdot}xH_2O$. These plots are obtained from our $[CdCl]^+$ data.[1] It can be seen that the hydration number y is slightly dependent on temperature, although ΔE_1 and

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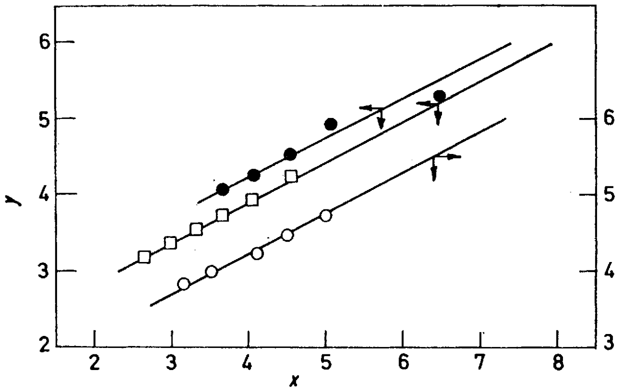
[7] L. Eriksson, *Acta Chem. Scand.*, 1953, **7**, 1146.

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

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

ΔE_2 are practically independent of temperature.* In order to calculate the K_1 values for $[CdBr]^+$, beside the y values we must know the two energy parameters. ΔE_2 is easily obtained from equation (3) when $y = Z = 6$ (the corresponding water content x of the melt being obtained from the plots in the Figure). To evaluate ΔE_1 we must know the K_1 value in the anhydrous melt. Unfortunately, for melts with $[NH_4^+]/[Ca^{2+}] < 5$ this requires e.m.f. measurements at >180 °C, where $[NH_4][NO_3]$ is appreciably decomposed.[1] Therefore we have evaluated the ΔE_1 value as follows. According to the model, the difference $\Delta E_1 - \Delta E_2$ should be independent of the type of ligand [see equations (3) and (4) of ref. 2], and according to our data [1,2] for $[CdCl]^+$ in $Ca[NO_3]_2 \cdot a[NH_4][NO_3] \cdot xH_2O$ and $Ca[NO_3]_2 \cdot K[NO_3] \cdot xH_2O$ melts this difference is usually *ca.* 5—7 kJ mol^{-1}. Thus, a first approximate value, $\Delta E_1 \approx (\Delta E_2 - 6)$ kJ mol^{-1}, can be assumed, and this can be refined for each melt of given $[NH_4^+]/[Ca^{2+}]$ by fitting the ΔE_1 value to all the experimental K_1 values, at all temperatures and water contents of the melt. (This can again be done using a simple computer program.)



Plots of hydration numbers (y) of Cd^{2+} against water content (x) of the melt (based on data from ref. 1): $Ca[NO_3]_2 \cdot 2.33[NH_4][NO_3] \cdot xH_2O$ at 323 (●) and 353 K (□); $Ca[NO_3]_2 \cdot 1.50[NH_4][NO_3] \cdot xH_3O$ at 353 K (○)

In Table 2 the experimentally obtained $\Delta G_1^{\ominus}$ values (derived from Table 1) are compared with values calculated from equation (1) of the model, using the two energy parameters in the last column. In order to test the model, only two melts having sufficient experimental data have been analysed in the Table. As seen from Table 2, there is good agreement between the experimental and calculated $\Delta G^{\ominus}$ values. The difference is always within ±0.5 kJ mol^{-1}, except in one case when it is 0.8 kJ mol^{-1}. The model is self-consistent: (i) the hydration number y is a variable independent of the type of ligand; (ii) the bond-energy parameters ΔE_1 and ΔE_2 are practically temperature independent, are dependent on the salt composition, and independent of the water content of the melt; (iii) equation (1) reproduces the experimental $\Delta G_1^{\ominus}$ values (within an overall error of *ca.* ±0.5 kJ mol^{-1}).

It is interesting to know what results are obtained with the model if the simple approximation $y \approx x$ is used. In this case equation (1) reproduces the experimental $\Delta G^{\ominus}$ values nearly as well as previously, only the ΔE_2 values being somewhat changed: for $Ca[NO_3]_2 \cdot 2.33[NH_4][NO_3] \cdot xH_2O$ the energy parameters are then $\Delta E_1 = -21.05$ and $\Delta E_2 = -15.58$ kJ mol^{-1}, whereas for $Ca[NO_3]_2 \cdot 1.50[NH_4][NO_3] \cdot xH_2O$ the corresponding values are −21.76 and −15.89 kJ mol^{-1}. Thus it can be concluded that $\Delta G^{\ominus}$ from equation (1) is not very sensitive to y when the relative difference $(\Delta E_1 - \Delta E_2)/\Delta E_1$ is, say, <0.4.

TABLE 2

Comparison of experimental and calculated values of $\Delta G^{\ominus}$

			$-\Delta G^{\ominus} = RT \ln K_1$/kJ mol^{-1}		
x	y	T/K	expt.	calc. from equation (1)	Parameters
(*a*) $Ca[NO_3]_2 \cdot 2.33[NH_4][NO_2] \cdot xH_2O$					
7.36	6.00	323	19.2	(19.2)	$\Delta E_1 = -21.05$ kJ mol^{-1}
6.77	5.70		19.4	20.2	$\Delta E_2 = -14.37$ kJ mol^{-1}
5.77	5.14		20.1	20.0	$Z = 6$
5.07	4.92		20.4	20.5	
4.53	4.50		20.6	21.4	
4.06	4.25		21.5	21.8	
3.67	4.06		21.8	22.1	
0.00	0.00			25.9	
4.06	4.10	338	22.3	22.1	
7.94	6.00	353	19.9	(19.9)	
5.77	4.74		21.2	21.0	
4.53	4.22		22.3	21.9	
4.06	3.95		22.8	22.4	
3.67	3.73		22.8	22.7	
3.33	3.53		23.4	23.0	
3·00	3.35		23.4	23.2	
2.67	3.18		23.9	23.4	
0.00	0.00			26.3	
(*b*) $Ca[NO_3]_2 \cdot 1.50[NH_4][NO_3] \cdot xH_2O$					
7.30	6.00	353	19.9	(19.9)	$\Delta E_1 = -22.20$ kJ mol^{-1}
5.77	5.20		21.2	20.9	$\Delta E_2 = -14.64$ kJ mol^{-1}
4.36	4.44		22.4	22.7	$Z = 6$
3.75	5.12		23.0	23.3	
3.38	3.93		23.8	23.6	
0.00	0.00			27.4	

The model, as represented by equation (1), is a two-variable (y,T) and three-parameter (ΔE_1, ΔE_2, Z) function of $\Delta G^{\ominus}$. The three parameters have precise physical meanings and can be, in principle, determined independently. Therefore the method adopted in the present work, by which ΔE_1 is obtained from the best fit to the experimental $\Delta G^{\ominus}$ values, can be criticised in that it does not prove unambiguously the validity of the model. This is, of course, true for the present case, but in our previous work on $[CdCl]^+$ formation in aqueous $Ca[NO_3]_2$–$K[NO_3]$ melts the ΔE_1 parameter was obtained by independent measurement in the anhydrous melt at high temperature, and the model was successfully tested with experimental data from aqueous melts (see Table 5 of ref. 2). Thus the fitting procedure is not an inherent part of the model. It has been used in the present work because in the anhydrous melt, at high temperature,

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* See Table 3 of ref. 1.

ammonium nitrate is decomposed and therefore a direct determination of ΔE_1 is not feasible. One purpose of the present paper is to show that in such a case the experimental data can be still successfully interpreted.

In this connection, two facts show the self-consistency of the model. First, the difference $\Delta E_1 - \Delta E_2$ for the chloro- and bromo-complex in the same melt should lie within a narrow energy range, since, as explained earlier, this difference is independent of the type of ligand. In our case, these differences are indeed comparable: -6.7 and -5.1 kJ mol^{-1} for the first melt and -7.6 and -5.7 kJ mol^{-1} for the second (see Table 2 of this paper and Table 3 of ref. 1). Secondly, the standard deviation for the 18 pairs of experimental and calculated $\Delta G^\ominus$ values compared in Table 2 is ± 0.39 kJ mol^{-1}, within the experimental accuracy of the data. This result, of course, must be weighted against the facts that the model operates in a relatively narrow range of 6—7 kJ mol^{-1} (from $y = 0$ to 6), and that one parameter has been obtained by the fitting procedure.

We are aware that the general validity of the model must be tested in many other melt systems, with various complexes over a wide range of temperature and composition. A serious obstacle is the scarcity of published data, especially those of equilibrium constants, which reflects the fact that aqueous melts belong to a field poorly understood and experimentally neglected.

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