Chloride and Bromide Complexes of Cadmium and Lead in Aqueous Melts of NH_4NO_3,xH_2O

By **R. M. Nikolić** and **I. J. Gal,*** The Boris Kidrič Institute of Nuclear Sciences, Belgrade, Yugoslavia

The formation constants of species $CdCl^+$, $CdCl_2$, $CdBr^+$, $CdBr_2$, $PbCl^+$, $PbCl_2$, $PbBr^+$, and $PbBr_2$ in aqueous melts of composition NH_4NO_3,xH_2O (x = 1·5, 2, and 3) are evaluated from e.m.f. measurements of suitable concentration cells in the temperature range 40—70 °C. The results are interpreted in terms of a quasi-lattice model of aqueous melts. Standard enthalpy changes for complex formation are calculated and compared with data obtained in sodium nitrate melts.

AQUEOUS melts of inorganic salts are relatively low-melting solvents characterised by incomplete hydration shells around the ions. They are intermediate between aqueous electrolyte solutions and anhydrous ionic molten salts and, in general, little information on chemical equilibria in such media can be found. It has been recognized that a better understanding of ionic interactions in concentrated aqueous electrolyte solutions requires an approach from the molten salt side of the concentration scale.[1,2] Thus it is interesting to study ionic association equilibria in molten salts containing a small, variable amount of water and discuss the experimental data in terms of a statistical–mechanical model developed for reciprocal molten salt systems [3] and later extended to systems containing water.[4]

This paper reports the formation constants of $CdCl^+$, $CdCl_2$, $CdBr^+$, $CdBr_2$, $PbCl^+$, $PbCl_2$, $PbBr^+$, and $PbBr_2$ in aqueous melts NH_4NO_3,xH_2O (x = 1·5, 2, and 3) obtained by e.m.f. measurement of concentration cells of suitable composition, in the temperature range 40—70 °C. The data will be discussed in terms of a quasi-lattice model for aqueous melts which predicts the dependence of the formation constants on temperature and water content of the system.[4]

EXPERIMENTAL

The electromotive force of the type of concentration cell (I) (with variable values of x, n_X, and n_M) has been measured.

	NH_4NO_3,xH_2O	NH_4NO_3,xH_2O	
Ag,AgX	NH_4X (n_X)	NH_4X (n_X)	AgX,Ag
(I)	$M(NO_3)_2$ (n_M)		

Here (Ag,AgX) refers to the silver–silver halide electrode (X^- = Cl^-, Br^-), n_X is the total concentration of the halide ligand kept equal in both half-cells, and n_M is the total bivalent metal-ion concentration in the left-hand half-cell (M^{2+} = Cd^{2+}, Pb^{2+}), both expressed in mol-fractions. The silver–silver chloride and bromide electrodes were prepared as described elsewhere.[5,6] The cell consisted of a Pyrex glass vessel with two compartments divided by a small sintered-glass disc. The vessel has been provided with ground glass joints for electrodes and thermometer. The complete cell was immersed in a thermostat bath and kept at desired temperature within ±0·05 °C. The e.m.f. of the cell was measured with a Beckman Research pH-meter, model 1019, operated as a null-balance millivoltmeter. The accuracy of measurements was ±0·1 mV.

Melts of desired composition were prepared from known amounts of carefully dried salts and distilled water. In preliminary experiments the validity of the Nernst equation

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[1] R. M. Fuoss and F. Accascina, 'Electrolytic Conductance,' Interscience, New York, 1959.

[2] B. R. Sundheim, 'Fused Salts,' McGraw-Hill, New York, 1964.

[3] M. Blander, *J. Chem. Phys.*, 1961, **34**, 432; see also 'Molten Salt Chemistry,' ed. M. Blander, Interscience, New York, 1964, chap. 3.

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

[5] A. I. Levin and A. V. Pomosov, 'Laboratornii Praktikum po Elektrohimii,' Metalurgizdat, Moscow, 1966.

[6] P. C. Lammers and J. Braunstein, *J. Phys. Chem.*, 1967, **71**, 2626.

for chloride and bromide concentration cells at various water content of the melt [when $M(NO_3)_2$ is absent] was tested. In one half-cell an ammonium halide concentration of 1×10^{-3} molal was kept constant, while in the other half-cell the ammonium halide concentration was varied up to 4×10^{-2} molal. These experiments were repeated with different water content of the melt, for both bromide and chloride concentration cells at several temperatures. In all systems, the theoretical Nernst slope was obtained within ±2%. This agreement indicates that halide salts in NH_4NO_3,xH_2O behave ideally in the concentration range tested and justifies the neglect of the liquid-junction potential.

RESULTS

As our e.m.f. measurements have been extended to 20 systems [ten for Cd^{2+}–$Cl^-(Br^-)$–NH_4NO_3,xH_2O and ten for Pb^{2+}–$Cl^-(Br^-)$–NH_4NO_3,xH_2O, varying the temperature and water content], the data have been published in Supplementary Publication No. SUP 20240 (15 pp., 1 microfiche).* As an example, in Table 1 only the measurements in the system Cd^{2+}–Br^-–$NH_4NO_3,2H_2O$ at 40 °C are presented. For all systems investigated (see Table 2) the following data are reported: the water content of the melt (x), temperature, total halide concentration (n_X), total cadmium or lead concentration (n_M), and e.m.f., ΔE. From these data the formation constants (1) and (2) have been calculated as explained below. The e.m.f. of the cell is given by equation (3) where Y is the 'free' halide concentration in

$$K_1 = (MX^+)/(M^{2+})(X^-) \qquad (1)$$

$$K_2 = (MX_2)/(MX^+)(X^-) \qquad (2)$$

$$\Delta E = \frac{2{\cdot}303RT}{F}\log\frac{Y}{n_X} \qquad (3)$$

the left-hand half-cell. Owing to the association of halide ions with Cd^{2+} (or Pb^{2+}), $Y \leqslant n_X$. Equations 1—3 assume ideal behaviour of the species in the melt. The total halide and metal concentrations are given by expressions (4) and (5), where z is the 'free' metal ion (M^{2+}) concentration.

$$\begin{aligned} n_X &= (X^-) + (MX^+) + 2(MX_2) + \ldots \\ &= Y + K_1Yz + 2K_1K_2Y^2z + \ldots \qquad (4) \end{aligned}$$

$$\begin{aligned} n_M &= (M^{2+}) + (MX^+) + (MX_2) + \ldots \\ &= z + K_1Yz + K_1K_2Y^2z + \ldots \qquad (5) \end{aligned}$$

Polynuclear complexes of the type M_2X^{3+} are highly improbable from the purely electrostatic viewpoint, and so far have not been reported in the case of small bivalent cations. The last two equations give equation (6). Expanding the left-hand side of equation (7) (for small values

$$\left(\frac{n_X}{Y} - 1\right) = n_M\left(\frac{K_1 + 2K_1K_2Y + 3K_1K_2K_3Y^2 + \ldots}{1 + K_1Y + K_1K_2Y^2 + \ldots}\right) \qquad (6)$$

$$\frac{1}{1 + K_1Y + K_1K_2Y^2 + \ldots} = 1 - K_1Y + K_1^2Y^2 - K_1K_2Y^2 + \ldots \qquad (7)$$

of Y, $\Sigma(K_1 \cdots K_i)Y^i < 1$), and combining equation (7) and (3) and (6), we obtain equation (8). The formation

$$\exp\left(-\frac{F\Delta E}{RT}\right) - 1 = n_M[K_1 + (2K_1K_2 - K_1^2)Y + (3K_1K_2K_3 - 3K_1^2K_2 + K_1^3)Y^2 + \ldots] \qquad (8)$$

TABLE 1

E.m.f. measurements in the system Cd^{2+}–Br^-–$NH_4NO_3,2H_2O$ at 40 °C [n_X and n_M are NH_4Br and $Cd(NO_3)_2$ concentrations, respectively, in mol-fractions based on solvent $NH_4NO_3,2H_2O$ as *one* component; ΔE in V]

$n_X = 1{\cdot}46 \times 10^{-4}$		$n_X = 2{\cdot}77 \times 10^{-4}$	
10^4n_M	$10^3\Delta E$	10^4n_M	$10^3\Delta E$
1·76	2·5	1·76	2·3
5·28	7·0	5·29	6·4
8·81	10·8	8·82	10·4
12·33	14·3	12·35	13·7
17·62	18·8	17·65	18·3
24·67	24·0	24·70	22·8
33·49	29·2	33·53	28·2
$n_X = 5{\cdot}43 \times 10^{-4}$		$n_X = 7{\cdot}96 \times 10^{-4}$	
10^4n_M	$10^3\Delta E$	10^4n_M	$10^3\Delta E$
1·60	2·1	1·73	2·0
4·80	5·8	5·21	6·1
8·00	8·6	8·69	10·1
11·20	12·3	12·17	13·0
16·00	16·5	17·39	17·6
22·40	21·0	24·34	22·5
30·41	26·2	33·05	28·5
$n_X = 10{\cdot}46 \times 10^{-4}$		$n_X = 13{\cdot}75 \times 10^{-4}$	
10^4n_M	$10^3\Delta E$	10^4n_M	$10^3\Delta E$
1·75	2·1	1·57	1·7
5·25	6·1	4·72	5·0
8·75	9·7	7·86	8·7
12·25	13·1	11·01	11·5
17·51	17·6	15·73	15·5
24·52	22·0	22·02	20·2
33·27	28·0	29·89	25·7

constants K_1 and K_2 have been obtained from equation (8) by two methods. The first is a graphical method developed by Braunstein, Blander, and Lindgren.[7] It is based on the relations (9) and (10). The second method is a simple

$$\lim_{\substack{n_M \to 0 \\ n_X \to 0}} \frac{\partial}{\partial n_M}[\exp(-F\Delta E/RT) - 1] = K_1 \qquad (9)$$

$$\lim_{\substack{n_M \to 0 \\ n_X \to 0}} \frac{\partial^2}{\partial n_M \partial n_X}[\exp(-F\Delta E/RT) - 1] = 2K_1K_2 - K_1^2 \qquad (10)$$

curve-fitting. Equation (8) can be written in the form (11)

$$\phi = K_1 + (2K_1K_2 - K_1^2)Y + (3K_1K_2K_3 - 3K_1^2K_2 + K_1^3)Y^2 + \ldots \qquad (11)$$

where $\phi = [\exp(-F\Delta E/RT) - 1]n_M^{-1}$ and Y are known quantities. In the present case, it was found that the linear relationship (12) was adequate for the concentration range investigated. No significantly better fit was obtained by introducing the square term and higher terms of

$$\phi = K_1 + (2K_1K_2 - K_1^2)Y \qquad (12)$$

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

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

Y. The constants K_1 and K_2 have been derived from equation (12) by the least-squares method. In all cases a good agreement with the graphical method was obtained. The formation constants are listed in Table 2.

TABLE 2

The association constants K_1 and K_2 *

M^{2+}	X^-	x in NH_4NO_3,xH_2O	T/K	K_1 †	K_2 †
Cd	Cl	2	313	341	115
Cd	Cl	2	328	313	127
Cd	Cl	2	343	307	118
Cd	Cl	1·5	343	410	175
Cd	Cl	3	343	235	92
Cd	Br	2	313	559	220
Cd	Br	2	328	498	206
Cd	Br	2	343	475	186
Cd	Br	1·5	343	604	272
Cd	Br	3	343	380	157
Pb	Cl	2	313	72	43
Pb	Cl	2	328	72	38
Pb	Cl	2	343	71	34
Pb	Cl	1·5	343	89	33
Pb	Cl	3	343	54	39
Pb	Br	2	313	123	32
Pb	Br	2	328	110	46
Pb	Br	2	343	101	48
Pb	Br	1·5	343	121	83
Pb	Br	3	343	77	58

* Mol-fraction scale (based on NH_4NO_3,xH_2O solvent as one component). † The estimated errors in K_1 are ±5—10%, in K_2 *ca.* ±15%.

DISCUSSION

Little information on metal complexes in aqueous melts are reported. Thus, no data for lead halide complexes in such systems are available. In the case of cadmium, the formation constants of halides in $Ca(NO_3)_2,4H_2O$ [8,9] and of $CdCl^+$ in $NH_4NO_3,2H_2O$ ($K_1 = 340 \pm 20$ at 40 °C) [10] have been reported. The latter constant is in good agreement with our value in Table 2. Lammers and Braunstein [6] reported also K_1 values for $CdBr^+$ in aqueous $LiNO_3$–KNO_3 melts.

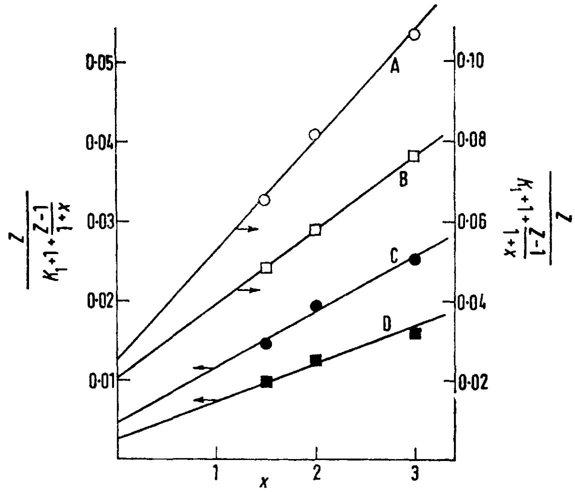
With the K_1 values of Table 2, the quasi-lattice model for aqueous melts can be tested. This model [4] leads to expression (13) for K_1. Here, K_1 is the first consecutive

$$Z\left(K_1 + 1 + \frac{Z-1}{1+x}\right)^{-1} = \exp\left(\frac{\Delta A}{RT}\right) + x\left[\exp\left(\frac{\Delta A - \Delta h}{RT}\right)\right] \quad (13)$$

complex-formation constant in mol-fraction scale, Z is the quasi-lattice co-ordination number (usually taken $Z = 6$), x is the mole ratio of water to nitrate salt (*e.g.*, NH_4NO_3,xH_2O), ΔA is the Helmholtz free energy increase of the metal–ligand bond (M^{2+}–X^-) relative to the metal–salt anion bond (M^{2+}–NO_3^-), Δh is the Helmholtz free-energy increase of the metal–water interaction (M^{2+}–H_2O) relative to the salt cation–water interaction (NH_4^+–H_2O), while R and T have their usual meaning. For anhydrous melts, $x = 0$, and equation (13) is reduced to (14). Equation (14) was obtained by Blander [3] using statistical–mechanical calculations based on a generalized quasi-lattice model of reciprocal molten salt systems.

$$K_1 = Z[\exp(-\Delta A/RT) - 1] \quad (14)$$

According to equation (13), at constant temperature a linear relationship exists between $Z/\{K_1 + 1 + [(Z-1)/(1+x)]\}$ and the water : nitrate salt ratio, x. This relationship applied to the K_1 values of $CdCl^+$, $CdBr^+$, $PbCl^+$, and $PbBr^+$ at 343 K (see Table 2) for $x = 1{\cdot}5$, 2, and 3 and $Z = 6$ is shown in the Figure.



Plots of $Z\left(K_1 + 1 + \frac{Z-1}{1+x}\right)^{-1}$ against x at 70 °C for A, $PbCl^+$; B, $PbBr^+$; C, $CdCl^+$; D, $CdBr^+$

From the intercepts and slopes of the lines, calculated with the least-squares method, the ΔA and Δh values listed in Table 3 are obtained.

TABLE 3

Equation (13) applied to the K_1 values of Table 2 (343 K, $Z = 6$)

Complex	$-\Delta A$/kcal mol^{-1}	Δh/kcal mol^{-1}
$CdCl^+$	3·7 ± 0·1	0·4 ± 0·1
$CdBr^+$	4·0 ± 0·1	0·5 ± 0·1
$PbCl^+$	2·5 ± 0·1	0·0 ± 0·1
$PbBr^+$	2·6 ± 0·1	−0·1 ± 0·1

The Figure and Table 3 show that within a deviation of ±0·1 kcal mol^{-1} in ΔA and Δh, the aqueous quasi-lattice model, as expressed by equation (13), fits our experimental data. Two additional facts support this conclusion. First, the Δh values are within ±0·1 kcal mol^{-1} equal for the bromide and chloride complexes, which is in agreement with the model in that the hydration parameters Δh should be independent of the type of ligand. Secondly, the ratios $K_1 : K_2$ (see Table 2) are always between 2—3, in agreement with the expected statistics of ligand co-ordination in a quasi-lattice,[3,11] according to which the species MX_2 do not necessarily form a linear grouping as in dilute aqueous solutions. Only in two cases (lead chloride in

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[8] J. Braunstein, A. R. Alverez-Funes, and H. Braunstein, *J. Phys. Chem.*, 1966, **70**, 2734.

[9] D. G. Lovering and D. J. Alner, *Chem. Comm.*, 1970, 570.

[10] J. M. C. Hess, J. Braunstein, and H. Braunstein, *J. Inorg. Nuclear Chem.*, 1964, **26**, 811.

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

$NH_4NO_3{,}3H_2O$ and lead bromide in $NH_4NO_3{,}1{\cdot}5H_2O$) is this ratio apparently below 2, but this might be due to the uncertainty in K_2.

A further test of the model can be made by calculating the K_1 values in $NH_4NO_3{,}2H_2O$ at different temperatures, by use of equation (13) and the energy parameters of Table **3**. These calculated values can be compared with the experimental constants of Table 2. Such a comparison is made for $CdCl^+$, $CdBr^+$, and $PbBr^+$ in Table 4. In the case of $PbCl^+$, the experimental K_1 values are too uncertain for evaluating the temperature effect. As seen from Table 4, the agreement between the experimental and calculated values is generally within the expected accuracy of ΔA, Δh, and the experimental K_1.

The basic assumption of the model that ΔA is temperature-independent implies that ΔA is practically equal to the standard enthalpy increase (ΔH°) of the association reaction ($M^{2+} + X^- = MX^+$) in the anhydrous molten salt. Thus, starting with equation (14) which refers to the anhydrous salt, one obtains equation (15). It is interesting to compare the association enthalpies calculated for anhydrous NH_4NO_3 with the values reported for alkali-metal nitrate melts. In anhydrous molten salts, sodium nitrate is a better analogue to ammonium nitrate than potassium nitrate,[12] in contrast to dilute aqueous systems in which K^+ and NH_4^+ have practically the same effective radii and mobilities. In Table 5, our values of ΔH° are compared with those reported for anhydrous molten $NaNO_3$. It can be seen that the ΔH° values in molten NH_4NO_3 are always lower than the corresponding values in molten $NaNO_3$. In the case of bromide complexes, the difference between ΔH° values is large. According to some new data obtained by Braunstein [15] it seems that the ΔH° values for $CdCl^+$ and $PbCl^+$ in $NaNO_3$ [7,15] (listed in Table 5) are too low, so that also for the chloride species most probably the difference between ΔH° in NH_4NO_3 and $NaNO_3$ is much larger. In that case, we must assume that ammonium and sodium ions behave quite differently in the nitrate melt. For instance, it is possible that even at low water content of the melt, ammonium ion takes part in hydrogen bonding, but not sodium ion. This effect as well as the specific effect of anion–water interaction are, of course, neglected in the simple model used in this work.

$$\Delta H^\circ = -R\,\frac{\partial \ln K_1}{\partial(1/T)} = \Delta A\,\frac{\exp\left(-\Delta A/RT\right)}{\exp\left(-\Delta A/RT\right) - 1} \simeq \Delta A \qquad (15)$$

TABLE 4

Comparison of experimental and calculated log K_1 values

Complex	T/K	log K_1 Found	log K_1 Calc.*
$CdCl^+$	313	2·53	2·62
	328	2·50	2·52
	343	2·49	2·42
$CdBr^+$	313	2·75	2·83
	328	2·70	2·72
	343	2·68	2·61
$PbBr^+$	313	2·09	2·11
	328	2·04	2·03
	343	2·00	1·95

* With equation (13) using for cadmium $\Delta A_{Cl} = -3{\cdot}7$ kcal mol^{-1}, $\Delta A_{Br} = -4{\cdot}0$ kcal mol^{-1}, $\Delta h = -0{\cdot}5$ kcal mol^{-1}, and for lead $\Delta A_{Br} = -2{\cdot}6$ kcal mol^{-1}, $\Delta h = 0$.

TABLE 5

Enthalpies of association in NH_4NO_3 and $NaNO_3$

Reaction	$-\Delta H^\circ$ ($\approx -\Delta A$)/kcal mol^{-1} In NH_4NO_3	$-\Delta H^\circ$ ($\approx -\Delta A$)/kcal mol^{-1} In $NaNO_3$
$Cd^{++} + Cl^- = CdCl^+$	3·7	4·0 *
$Cd^{++} + Br^- = CdBr^+$	4·0	5·6 †
$Pb^{++} + Cl^- = PbCl^+$	2·5	2·8 *
$Pb^{++} + Br^- = PbBr^+$	2·6	3·9 ‡

* Ref. 7. † Ref. 13. ‡ Extrapolated value from ref. 14.

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[13] H. Braunstein, J. Braunstein, and D. Inman, *J. Phys. Chem.*, 1966, **70**, 2726.

[14] D. L. Manning, M. Blander, and J. Braunstein, *Inorg. Chem.*, 1963, **2**, 345.

[15] J. Braunstein, personal communication.