Chloride and Bromide Complexes of Zinc(II) and Mercury(II) in Aqueous Ammonium Nitrate Melts

By **Ružica M. Nikolić** and **Ivan J. Gal,*** The Boris Kidrič Institute and Faculty of Sciences, The University, Belgrade, Yugoslavia

The stability constants of species $HgCl^+$, $HgCl_2$, in aqueous melts of NH_4NO_3,xH_2O (x = 2—5), and $ZnCl^+$, $ZnCl_2$, $ZnBr^+$, $ZnBr_2$ (x = 1—3) have been determined at 55—85 °C from e.m.f. measurements of suitable concentration cells. The results for Hg^{II} chlorides are essentially in agreement with a quasi-lattice model of aqueous melts, but the zinc halide species behave anomalously: the chloride complexes are more stable than bromide complexes, and the first consecutive stability constants for $ZnCl^+$ and $ZnBr^+$ increase with temperature, in contrast to the behaviour of other divalent metal halides.

In a previous paper[1] it was shown that the association of Cd^{2+} and Pb^{2+} with halide ligands in NH_4NO_3,xH_2O ($x = 1{\cdot}5$—3) could be interpreted in terms of a quasi-lattice model of aqueous melts,[2] which predicts the dependence of the first consecutive stability constant (K_1) on temperature and water content of the melt. In the present work, we have extended our investigation to Hg^{II} and Zn^{II} halides. It seemed interesting to test whether the same model could be applied to Hg^{II} halides with strong covalent bonds and to the relatively weak Zn^{II} halide complexes with bonds of a more ionic character.

No data on Hg^{II} and Zn^{II} complexes in aqueous melts could be found in the literature. In anhydrous $LiNO_3$–KNO_3, Zangen and Marcus[3] have determined the stability constants of higher (anionic) Hg^{II} halides, whereas Van Artsdalen[4] has studied cryoscopically Zn^{II} chlorides in anhydrous $NaNO_3$. Zangen[5] has also reported the stability constants of Zn^{II} halides in anhydrous $LiNO_3$–KNO_3. The latter data are surprisingly high in comparison with those obtained in aqueous solutions.[6]

We report here the stability constants of $HgCl^+$, $HgCl_2$, in NH_4NO_3,xH_2O (x = 2—5), and $ZnCl^+$, $ZnCl_2$, $ZnBr^+$, $ZnBr_2$, in the same melt, but x = 1—3. The constants have been calculated at 55, 70, and 85 °C from e.m.f. measurements of suitable concentration cells. Attempts to determine the stability constants of $HgBr^+$ and $HgBr_2$ were unsuccessful. The latter species are too stable and therefore unsuitable for the e.m.f. technique.

EXPERIMENTAL

The electromotive force of the following concentration cell has been measured:

$$\mathrm{Ag,\ AgX}\left|\begin{array}{l}\mathrm{NH_4NO_3},x\mathrm{H_2O}\\ \mathrm{NH_4X}\ (n_\mathrm{X})\\ \mathrm{M(NO_3)}\ (n_\mathrm{M})\end{array}\right|\left|\begin{array}{l}\mathrm{NH_4NO_3},x\mathrm{H_2O}\\ \mathrm{NH_4X}\ (n_\mathrm{X})\\ \\ \end{array}\right|\mathrm{AgX,\ Ag}$$

Here, Ag, AgX refers to the silver–silver halide electrode (X = Cl, Br) which has been prepared as described elsewhere,[7,8] n_X is the total halide concentration which is equal in both half-cells, n_M ($M^{2+} = Hg^{2+}$ or Zn^{2+}) is the total metal concentration, and x is water : nitrate ratio in NH_4NO_3,xH_2O. The concentrations and stability constants are expressed in mole fraction scale based on NH_4NO_3,xH_2O solvent as one component. The accuracy of e.m.f. measurements is $\pm 0{\cdot}1$ mV, the temperature constancy $\pm 0{\cdot}05$ °C. In all systems investigated the theoretical Nernst slope (when $n_M = 0$ and n_X differ in the two half-cells) was obtained within $\pm 2\%$, which indicates that NH_4X behaves ideally in NH_4NO_3,xH_2O in the concentration scale investigated, and justifies the neglect of liquid-junction potential. Experimental details and the interpretation of data are described in our previous paper.[1]

RESULTS

As our experimental data (n_M, n_X, ΔE) have been extended to three M^{2+}–X^- systems, varying the temperature and water content of the melt, they are too extensive to be tabulated in this paper. Therefore, they have been deposited in Supplementary Publication No. SUP 20936 (14 pp.).† Measurements for the system Zn^{2+}–Cl^-–$NH_4NO_3,2H_2O$ at 70 °C are presented in Table 1 as an example of the data. The stability constants K_1 and K_2 have been calculated

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

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

using a graphical[9] and an algebraic method as described previously.[1] In all cases a good agreement between the two methods has been obtained. The values of K_1 and K_2 are listed in Table 2. The estimated error in K_1 is *ca.* ±5% for Zn^{II} complexes and ±10% for Hg^{II} complexes. The accuracy of K_2 is *ca.* 15%. The error in K_1 for $HgCl^+$ is higher than in the case of $ZnCl^+$, owing to the very low concentration range of the chloride ligand. However, it has been verified that even at lowest chloride concentration, the free concentration of Cl^- ligand is still above the limit governed by the solubility product,[10] so that no dissolution of AgCl on the silver–silver halide electrode occurs.

As seen from Table 2, the behaviour of zinc is peculiar if the K_1 and K_2 values are compared with those of mercury, lead, and cadmium.[1] Thus, the stability constants of zinc halides increase with temperature, and the bromides are

---

† For details of the Supplementary Publications Scheme see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, index issue.

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

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

[3] M. Zangen and Y. Marcus, *Israel J. Chem.*, 1964, **2**, 49.

[4] E. R. Van Artsdalen, *J. Phys. Chem.*, 1956, **60**, 172.

[5] M. Zangen, *Inorg. Chem.*, 1968, **7**, 133.

[6] L. G. Sillén and A. E. Martell, 'Stability Constants,' The Chemical Society, London, 1964.

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

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

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

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

less stable than the chlorides. This behaviour is opposite to the 'normal' behaviour of halide complexes of most metals in anhydrous or aqueous melts. Anomalous behaviour of zinc chloride complexes compared to the bromide complexes has been noted in molten (Li,K)NO$_3$,[5] and in aqueous solutions.[6]

TABLE 1

E.m.f. measurements in the system Zn^{2+}–Cl^-–NH_4NO_3,-$2H_2O$ at 70 °C

$n_{Cl} = 5{\cdot}87 \times 10^{-4}$

$n_{Zn} \times 10^4$	ΔE/mV
2·15	0·2
5·57	0·7
9·83	1·2
15 16	1·9
20·47	2·6
30·92	3·9
51·94	6·2

$n_{Cl} = 10{\cdot}33 \times 10^{-4}$

$n_{Zn} \times 10^4$	ΔE/mV
2·21	0·3
5·75	0·8
10·15	1·4
15·67	2·1
21·12	2·8
31·93	4·2
53·54	6·5

$n_{Cl} = 12{\cdot}51 \times 10^{-4}$

$n_{Zn} \times 10^4$	ΔE/mV
2·35	0·5
4·69	0·9
7·04	1·3
9·98	1·8
12·95	2·4
18·80	3·3

$n_{Cl} = 13{\cdot}91 \times 10^{-4}$

$n_{Zn} \times 10^4$	ΔE/mV
2·26	0·3
5·87	0·9
10·37	1·4
14·99	2·0
20·46	2·8
31·60	4·1
53·58	6·7

$n_{Cl} = 31{\cdot}14 \times 10^{-4}$

$n_{Zn} \times 10^4$	ΔE/mV
2·12	0·4
5·51	1·0
9·74	1·6
15·00	2·4
20·26	3·2
30·73	4·8
51·39	7·7

$n_{Cl} = 58{\cdot}05 \times 10^{-4}$

$n_{Zn} \times 10^4$	ΔE/mV
2·26	0·5
5·86	1·4
10·36	2·4
15·97	3·5
21·54	4·4
32·64	6·3
54·60	9·8

TABLE 2

The equilibrium constants (mole fraction scale)

M^{2+}	X^-	x in NH_4NO_3,xH_2O	T/K	K_1	K_2
Hg^{2+}	Cl^-	2	328	$2{\cdot}0 \times 10^5$	$9{\cdot}9 \times 10^4$
Hg^{2+}	Cl^-	2	343	$1{\cdot}4 \times 10^5$	$7{\cdot}1 \times 10^4$
Hg^{2+}	Cl^-	2	358	$8{\cdot}3 \times 10^4$	$3{\cdot}8 \times 10^4$
Hg^{2+}	Cl^-	3	343	$9{\cdot}8 \times 10^4$	$5{\cdot}5 \times 10^4$
Hg^{2+}	Cl^-	4	343	$7{\cdot}4 \times 10^4$	$3{\cdot}9 \times 10^4$
Hg^{2+}	Cl^-	5	343	$6{\cdot}0 \times 10^4$	$2{\cdot}8 \times 10^4$
Zn^{2+}	Cl^-	2	328	33	99
Zn^{2+}	Cl^-	2	343	44	57
Zn^{2+}	Cl^-	1	343	195	58
Zn^{2+}	Cl^-	1·5	343	72	125
Zn^{2+}	Cl^-	3	343	24	84
Zn^{2+}	Br^-	2	328	23	
Zn^{2+}	Br^-	2	343	24	
Zn^{2+}	Br^-	2	358	26	

TABLE 3

Thermodynamic functions for the reactions:
$M^{2+} + Cl^- \rightleftharpoons MCl^+$ at 343 K

Reaction	ΔH°/ kJ mol^{-1}	ΔG°/ kJ mol^{-1}	ΔS°/ J mol^{-1} K^{-1}
$Hg^{2+} + Cl^- \rightleftharpoons HgCl^+$	−30·1	−33·9	10·4
$Zn^{2+} + Cl^- \rightleftharpoons ZnCl^+$	18·0	−10·9	84·1

From the temperature dependence of K_1 (at constant water content of the melt) the thermodynamic functions listed in Table 3 have been calculated in the usual way: $\Delta G^\circ = -RT \ln K_1$; $\Delta H^\circ = -R\dfrac{\partial \ln K_1}{\partial(1/T)}$; $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$. The anomalous behaviour of zinc is again reflected by a very large entropy change and a positive ΔH° value.

DISCUSSION

An expression for the first consecutive stability constant K_1 based on a quasi-lattice model for aqueous melts has been developed by Braunstein.[2] This expression gives the dependence of K_1 on temperature and water : salt ratio (x) in terms of two thermodynamic parameters, ΔA and Δh, which are assumed temperature independent:

$$\frac{z}{K_1 + 1 + \dfrac{Z-1}{1+x}} \simeq \frac{z}{K_1} = \exp\left(\frac{\Delta A}{RT}\right) + \exp\left(\frac{\Delta A - \Delta h}{RT}\right) \tag{3}$$

In the above equation, z is a quasi-lattice co-ordination number (usually taken 4—6 for nitrate melts), ΔA is the Helmholtz free energy increase for the metal–ligand bond, relative to metal–nitrate bond, whereas Δh is the Helmholtz free energy increase of hydration (M^{2+}–H_2O) relative to the hydration of the salt cation (*i.e.* NH_4^+–H_2O). Thus a plot of the left-hand side of the above equation against the water : salt ratio, x, makes it possible to test the model and calculate ΔA and Δh from the intercept and slope of the straight line. These plots are shown in Figures 1 and 2 for $HgCl^+$ and $ZnCl^+$ at 343 K, using the K_1 values from Table 1 and assuming co-ordination numbers $z = 4$—6. In the case of $ZnBr^+$, the K_1 values are too low and uncertain for testing the model. As seen from Figure 1, for $HgCl^+$ a straight line with a positive intercept is obtained. For $z = 6$ the following energy parameters were calculated:

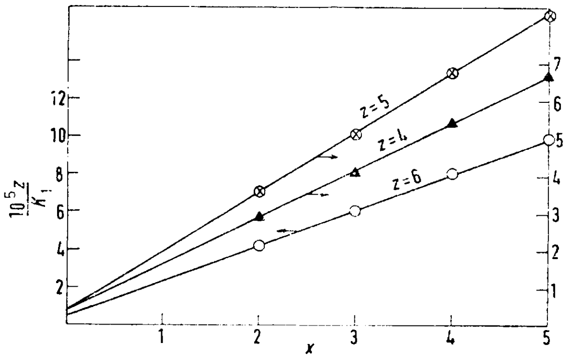

FIGURE 1 Plots of z/K_1 *vs.* x [equation (3)] for $HgCl^+$ complexes at 343 K

$$HgCl^+:\ \Delta A = -34{\cdot}7 \pm 0{\cdot}4 \text{ kJ mol}^{-1}$$

$$\Delta h = -3{\cdot}8 \pm 0{\cdot}4 \text{ kJ mol}^{-1}$$

With the two parameters ΔA and Δh for $HgCl^+$, the model can be further tested by calculating K_1 with equation (1) for various temperatures, and comparing the calculated values with the experimentally determined constants. This comparison is shown in Table 4. The agreement is good, indicating again that ΔA and Δh are practically temperature independent.

TABLE 4

Experimental stability constants for $HgCl^+$ compared with the values calculated from equation (3)

T/K	$K_{1(\text{exp.})}$	$K_{1(\text{calc.})}$
328	$2{\cdot}0 \times 10^5$	$2{\cdot}3 \times 10^5$
343	$1{\cdot}4 \times 10^4$	$1{\cdot}4 \times 10^5$
358	$8{\cdot}9 \times 10^4$	$8{\cdot}3 \times 10^4$

From the ΔA value of $HgCl^+$, the stability constant in the anhydrous melt can be calculated[11] as $K_{1,0} = z[\exp(-\Delta A/RT) - 1] = 1{\cdot}3 \times 10^6$ at 343 K.

The aqueous quasi-lattice model can be further tested by deriving expressions for the thermodynamic functions of Table 3 in terms of the two parameters, ΔA and Δh. Thus, assuming again these parameters temperature independent we obtain:

$$\Delta H^\circ = -R\frac{d(\ln K_1)}{d(1/T)} = \Delta A - \Delta h\,\frac{x\,.\,\exp\left(\dfrac{\Delta h}{RT}\right)}{1 + x\,.\,\exp\left(-\dfrac{\Delta h}{RT}\right)} \tag{4}$$

$$\Delta G^\circ = -RT\ln K_1 = -RT\left[\ln z - \frac{\Delta A}{RT} - \ln\left(1 + x\,.\,\exp\left(-\frac{\Delta h}{RT}\right)\right)\right] \tag{5}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = R\ln z - R\ln\left[1 + x\,.\,\exp\left(-\frac{\Delta h}{RT}\right)\right] - \frac{\Delta h}{T}\,\frac{x\,.\,\exp\left(-\dfrac{\Delta h}{RT}\right)}{1 + x\,.\,\exp\left(-\dfrac{\Delta h}{RT}\right)} \tag{6}$$

For $HgCl^+$ formation at 343 K, equations (4)—(6), assuming $z = 6$, give: $\Delta H^\circ = -31{\cdot}4$ kJ mol^{-1}, $\Delta G^\circ = -33{\cdot}9$ kJ mol^{-1}, $\Delta S^\circ = 6{\cdot}8$ J mol^{-1} K^{-1}, which is in good agreement with the experimentally determined values listed in Table 3.

Applying equation (3) to $ZnCl^+$, also fairly straight lines are obtained for $z = 4$—6 (Figure 2), but in all cases the intercept is negative which has no physical meaning. The Pauling radius of Zn^{2+} is much smaller than that of Hg^{2+}, Pb^{2+}, and Cd^{2+}, and correspondingly the replacement of a water molecule by halide ligands should be more difficult. On the other hand, in anhydrous melts, it has been noted that Zn^{2+}–NO_3^- interactions are rather strong, which is reflected in the formation of mixed zinc complexes with NO_3^- and Cl^- ligands.[12] Moreover, in dilute aqueous solutions the co-ordination number of zinc can be changed.[13,14] Unfortunately, ammonium nitrate is unstable above its melting point,[15] and therefore a direct determination of $K_{1\cdot0}$ in anhydrous NH_4NO_3 is hardly possible.

Braunstein and co-workers [16,17] found that the aqueous quasi-lattice model cannot be applied in melts as $KNO_3,Ca(NO_3)_2,xH_2O$ ($x = 2{\cdot}8$—10). However, they show that a simple relation exists between the association constant in the anhydrous melt ($K_{1,0}$), the association constant in the aqueous melt (K_1), the equilibrium constant for replacing nitrate ions around a cation by water molecules (K_h), and the activity of water (a_W) in the aqueous melt:[16]

$$\frac{1}{K_1} = \frac{1}{K_{1,0}} + \frac{K_h}{K_{1,0}}\,a_W{}^n \tag{7}$$

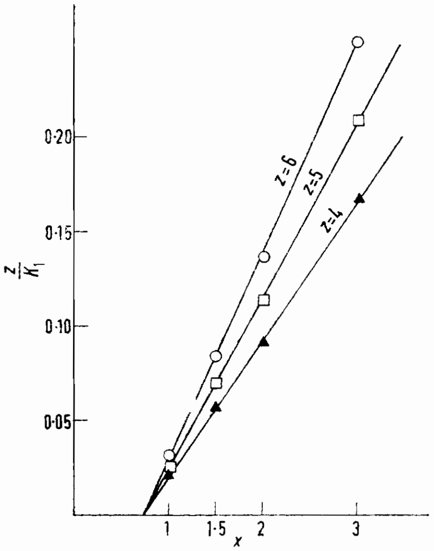

FIGURE 2 Plots of z/K_1 *vs.* x [equation (3)] for $ZnCl^+$ complexes at 343 K

Here, n is an 'average' hydration number of cation which forms the complex. Equation (7) does not assume a quasi-lattice model of the melt nor any other specific model concerning the structure of the liquid. It is based rather on a chemical equilibrium between two competing processes: co-ordination of water and co-ordination of other (ionic) ligands around a metal ion.

If equation (7) is applied to $ZnCl^+$ formation in our melts (which contain 1—3 moles of water per mole of nitrate salt), plots of $1/K_1$ *vs.* $a_W{}^n$ are linear for $n = 4$. (The a_W values are taken from reference 18.) This is

---

[11] M. Blander, *J. Phys. Chem.*, 1959, **63**, 1262.

[12] R. E. Hester, *Progr. Co-ordination Chem.*, 1968, 766.

[13] D. F. C. Morris, E. L. Short, and D. N. Waters, *J. Inorg. Nuclear Chem.*, 1963, **25**, 975.

[14] H. Freiser, *Progr. Co-ordination Chem.*, 1968, 649.

[15] C. D. Hodgman, 'Handbook of Chemistry and Physics,' 2nd edn., Chemical Rubber Publ. Co., Cleveland, 1964.

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

[17] H. Braunstein, J. Braunstein, and P. T. Hardesty, *J. Phys. Chem.*, in the press.

[18] A. N. Campbell, J. B. Fishman, G. Rutherford, T. P. Shaefer, and L. Ross, *Canad. J. Chem.*, 1956, **34**, 151.

shown in Figure 3, which refers to our data obtained at 70 °C. From the intercept and slope of the straight line the values $K_{1.0} = 3 \times 10^4$ and $K_h = 6{\cdot}7 \times 10^3$ are obtained, which shows that in the anhydrous melt the association constant for $ZnCl^+$ formation is 150—1300 times higher than in melts containing 1—3 moles of water. Similar comparison have been made for $HgCl^+$ and for $CdCl^+$ and $PbCl^+$.[1] However, in these cases the association constant in anhydrous melt is 10—20 times higher than in aqueous melts containing 1—3 moles of water per mole of nitrate salt, which indicates that hydration of Zn^{2+} cations competes more significantly with ion-association in aqueous melts.

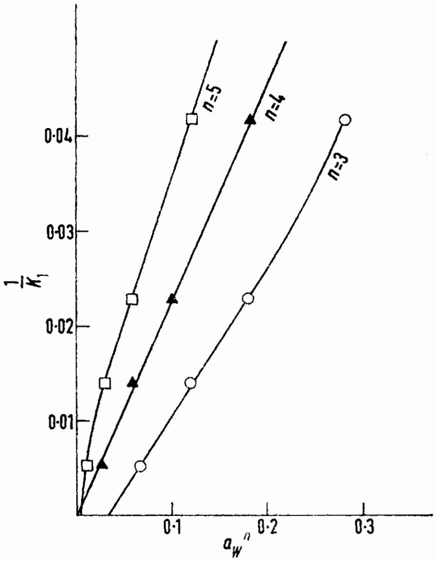

FIGURE 3 Plots of $1/K_1$ *vs.* a_W^n [equation (7)] for $ZnCl^+$ complexes at 343 K

If the quasi-lattice model is applied to the $K_{1.0}$ value obtained from equation (7) and Figure 3 (this value refers to the anhydrous melt), then the expression [11]

$$K_{1.0} = z[\exp(-\Delta A/RT) - 1] \qquad (8)$$

with $\Delta A = -24{\cdot}2$ kJ mol^{-1} is valid for $ZnCl^+$, whereas

$$K_h^{-1} = p[\exp(-\Delta h/RT)] \qquad (9)$$

with $\Delta h = -41{\cdot}8$ kJ mol^{-1} and $p = 3 \times 10^{-4}$ (p is a parameter which correlates K_h determined from the mass action law and from the quasi-lattice model).[17] The ΔA and Δh values obtained, when inserted in equation (4) give $\Delta H^\circ = 17{\cdot}6$ kJ mol^{-1}, in good agreement with the experimental value 18·0 kJ mol^{-1} from Table 3.

It is interesting to compare equation (3) (quasi-lattice model) and equation (7) for the case of $HgCl^+$ formation. The average hydration number n for the Hg^{2+} ion is expected to be smaller than that of Zn^{2+}, if the Pauling radii are compared. Thus, equation (7) applied to $HgCl^+$ shows that for $n = 3$—4 fairly straight lines are obtained, as shown in Figure 4. From the plot of equation (7) for $n = 3$ in Figure 4, $K_{1.0}$ is calculated which, if inserted in equation (8), gives $\Delta A = -34{\cdot}3$ kJ mol^{-1}, in good agreement with the value obtained from the aqueous quasi-lattice model ($\Delta A = -34{\cdot}7$ kJ mol^{-1}).

We conclude that equation (3), based on a very simple aqueous quasi-lattice model, cannot be applied for all types of ion association, especially if the water content of the system is high. This conclusion does not necessarily imply that the quasi-lattice concept of aqueous melts is inapplicable or of limited value, but rather that no realistic models are at present available.

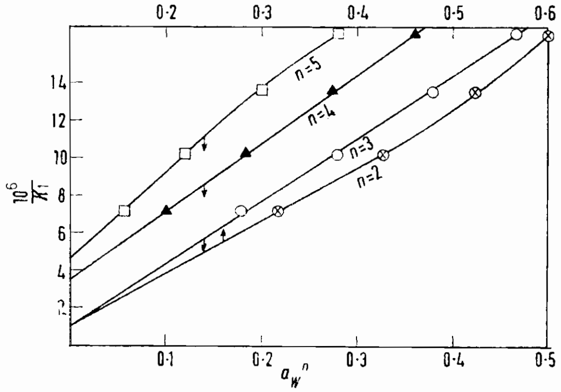

FIGURE 4 Plots of $1/K_1$ *vs.* a_W^n [equation (7)] for $HgCl^+$ complexes at 343 K

[3/2109 *Received, 15th October,* 1973]