Solubility of Silver Chloride and Silver Bromide and Their Complexes in Anhydrous Calcium Nitrate–Potassium Nitrate (1/1·9) Melt

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The solubility of silver chloride and bromide as a function of the corresponding halide concentration has been measured in molten $Ca(NO_3)_2,1{\cdot}925KNO_3$, in the temperature range 160—200 °C, by use of ^{110}Ag as radioactive tracer. The solubility products and the consecutive stability constants for metal halide complex species were determined and the ΔG°, ΔH°, and ΔS° values of the corresponding equilibria evaluated. The results are compared with data obtained in other nitrate melts and discussed in terms of a quasi-lattice model for reciprocal molten salt systems.

QUASI-LATTICE models[1-3] of reciprocal molten salt systems[4,5] are useful in the interpretation of ionic association equilibria in anhydrous and aqueous 1–1 molten salts. We are studying metal halide complexes in molten $Ca(NO_3)_2,xKNO_3,yH_2O$, where the coefficients x and y are variable. The molten salt system $Ca(NO_3)_2$–KNO_3 is a charge-unsymmetrical melt and it is interesting to investigate how ionic equilibria (*e.g.*, formation of metal halide complexes) depend on the $Ca^{++}:K^+$ ratio and water content, and whether a simple quasi-lattice model can describe the thermodynamics of complex formation.

For the anhydrous melt $Ca(NO_3)_2,1{\cdot}925KNO_3$ (34·2 mol % calcium nitrate, the eutectic composition,[6] m.p. 144 °C) we now report the solubility products of silver chloride and bromide and the formation constants of AgCl, $AgCl_2^-$, AgBr, and $AgBr_2^-$ complexes in the range 160—200 °C. The thermodynamic data for the formation of complexes are compared with the published data for silver chloride at lower calcium nitrate content,[7] and for silver chloride and bromide in pure potassium nitrate.[8,9] The data are discussed in terms of Blander's generalised quasi-lattice model of molten salts.[4]

EXPERIMENTAL

Reagent grade $Ca(NO_3)_2,4H_2O$, KNO_3, KCl, KBr, and $AgNO_3$ were used after prolonged drying (calcium nitrate was dehydrated at 270 °C). Melt samples of composition $Ca(NO_3)_2,1{\cdot}925KNO_3$ containing a small amount of $AgNO_3$ and variable amounts of KCl (or KBr) were prepared. The silver nitrate in the melt was traced with radioactive $^{110}AgNO_3$ so that in each sample a desired total amount of silver of known specific activity was present. Melt samples of known weight and composition were placed in 50 ml stoppered Pyrex tubes and left in a thermostat at the desired temperature (±1 °C) for several days. In all tubes a well-formed AgCl (or AgBr) precipitate settled at the bottom of the clear melt. The experimental technique and measurement of silver halide solubility with radioactive ^{110}Ag have been described.[1,2]

RESULTS

The solubilities of AgCl and AgBr in molten $Ca(NO_3)_2$,$1{\cdot}925KNO_3$ have been measured as a function of equilibrium halide concentration at different temperatures. The solubility S of silver halide can be defined by equation (1) where

$$S = [Ag^+] + [AgX] + [AgX_2^-] + \ldots + [AgX_n^{(n-1)-}] + \ldots \quad (1)$$

X = Cl or Br. Introducing the solubility product [equation (2)] and the consecutive formation constants [equation (3)]

$$K_{sp} = [Ag^+][X^-] \quad (2)$$

$$K_i = [AgX_1^{(i-1)-}]/[AgX_{i-1}^{(i-2)-}][X^-] \quad (3)$$

we can express equation (1) as (4), where $m_X = [X^-]$ is the

$$Sm_X = K_{sp} + K_{sp}K_1m_X + K_{sp}K_1K_2m_X^2 + \ldots \quad (4)$$

equilibrium halide concentration which can be obtained from the total halide and silver concentration and the amount of silver precipitate in the melt, assuming that the precipitate is pure AgX.[1,2] The experimental results, S as a function of m_X at different temperatures, are in Table 1.

Equations (1)—(4) are based on two assumptions. First it is assumed that polynuclear silver complexes like Ag_2X^+ can be neglected, because the Ag^+ concentration is very low and there is always present an excess of free halide relative to silver. Secondly, the activity coefficients of all solute species are assumed equal to unity, as in the reference state at infinite dilution. This assumption is justified in that in molten nitrates most 1–1 salt solutes follow Henry's law up to a molality of *ca.* 0·1.[1,2]

The results of Table 1 were interpreted according to equation (4) with a digital computer by a polynomial-fitting programme in which the sum of relative square deviations $\Sigma[\Delta(Sm_X)/Sm_X]^2$ were minimised, so that deviations at low halide concentration have the same statistical weight as those at high concentration. Values of K_{sp}, K_1, and K_2 were obtained. Higher complexes such as AgX_3^{2-} were neglected. The numerical values of the equilibrium constants (on the mol fraction scale) are in Table 2. K_1 and K_2 decrease with temperature, as usual in anhydrous and aqueous melts, although some exceptions, as for ZnX^+ and ZnX_2, have been noted.[10]

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Table 1

Silver chloride and bromide solubilities (S and m_x in mol kg^{-1})

Ligand	10^5S	10^3m_x	10^5S	10^3m_x	10^5S	10^3m_x
	(163 °C)		(178 °C)		(198 °C)	
Cl	18·3	0·420	27·8	0·515	47·1	0·708
	5·92	0·896	11·7	0·954	25·3	1·09
	5·57	1·45	9·89	1·50	22·1	1·62
	3·46	2·71	6·81	2·75	14·6	2·82
	3·30	3·41	6·34	3·17	13·3	3·24
	2·74	6·45	5·99	3·45	13·2	3·52
	2·65	9·39	4·58	6·47	9·31	6·52
	2·62	9·69	4·24	9·41	8·33	9·45
	2·85	13·4	4·13	9·71	8·03	9·75
	3·82	24·4	4·35	13·4	7·83	13·4
	5·90	43·7	5·32	23·2	9·10	23·3
	7·61	60·3	5·55	24·4	9·46	24·5
	11·7	85·0	7·83	43·7	12·0	43·8
			9·98	60·4	13·9	60·4
			14·9	85·0	18·3	81·1
					19·7	84·1
	(168 °C)		(183 °C)		(198 °C)	
Br	0·381	0·403	0·626	0·405	2·79	0·445
	0·310	0·420	0·622	0·423	2·05	0·754
	0·269	0·786	0·454	0·788	1·82	1·44
	0·347	0·807	0·624	2·27	1·73	1·62
	0·314	1·41	0·755	3·36	1·68	2·28
	0·412	2·26	0·535	3·42	1·71	3·43
	0·712	6·94	0·889	6·94	1·78	6·95
	1·67	21·2	0·928	7·30	3·02	21·9
	3·60	44·8	2·01	21·2	4·70	33·6
	8·18	77·4	3·51	33·6	6·12	44·7
	16·4	127·0	4·58	44·8	11·6	77·4
			9·36	77·4	21·7	127·0
			19·9	127·0		

Table 2

Equilibrium constants *

Ligand	T/K	K_{sp}	K_1	K_2
Cl	436	$8·48 \times 10^{-10}$	$1·47 \times 10^3$	897
	451	$1·74 \times 10^{-9}$	$1·24 \times 10^3$	628
	471	$4·18 \times 10^{-9}$	$1·11 \times 10^3$	383
Br	441	$9·88 \times 10^{-12}$	$1·82 \times 10^4$	$4·85 \times 10^3$
	456	$2·30 \times 10^{-11}$	$1·11 \times 10^4$	$4·03 \times 10^3$
	471	$7·90 \times 10^{-11}$	$0·90 \times 10^4$	$1·88 \times 10^3$

* Mol fraction scale based on the solvent $Ca(NO_3)_2,1·925 KNO_3$. Estimated errors in K_{sp} and K_1 are 5—10%, in K_2 15—20%.

DISCUSSION

With the K_{sp} and K_1 values of Table 2 the standard Gibbs free energy changes for the dissolution equilibria

$$AgX\ (solid) = Ag^+ + X^- \qquad (5)$$

and for the complex formation (6) can be calculated

$$Ag^+ + X^- = AgX \qquad (6)$$

($\Delta G° = -RT \ln K$). The corresponding standard enthalpy changes can be derived from relation (7) by

$$\frac{\partial \ln K}{\partial (1/T)} = -\frac{\Delta H°}{R} \qquad (7)$$

plotting $\ln K$ against $1/T$, and the standard entropy changes from $T\Delta S° = \Delta H° - \Delta G°$. These data are in Table **3**, rounded to two significant figures. The thermodynamic data for AgX_2^- formation are omitted, because the K_2 values are too uncertain for a meaningful evaluation of $\Delta H°$.

The $\Delta H°$ values for the dissolution equilibria are close to the corresponding values [11] in molten 1–1 nitrates and in molten $Ca(NO_3)_2,4H_2O$. Thus, for AgCl dissolution in molten $(Na,K)NO_3$ (250 °C) the standard enthalpy change is 18·3 kcal mol^{-1} (1 cal = 4·184 J), whereas in molten $Ca(NO_3)_2,4H_2O$ (40—80 °C) a value of 18·1 kcal mol^{-1} has been obtained. For AgBr dissolution, these values are 21·3 and 22·5 kcal mol^{-1}, respectively, which is somewhat lower than our value of 25 kcal mol^{-1}. The $\Delta S°$ values for the dissolution equilibria in Table **3** show an increase for AgBr relative to AgCl, in contrast to the behaviour in molten $Ca(NO_3)_2,4H_2O$ where the two values are nearly identical [11] (6·7 and 7·0 cal mol^{-1} K^{-1}). However, in aqueous calcium nitrate melt a halide anion is surrounded by large, hydrated $[Ca(H_2O)_4]^{++}$ cations, whereas in anhydrous molten $Ca(NO_3)_2$–KNO_3 it is partially surrounded by small bare Ca^{++} ions. In the latter case, the difference in size between chloride and bromide ions might be important in that a stronger Coulomb interaction between Ca^{++}–Cl^- than Ca^{++}–Br^- could decrease the partial entropy of solvation of the chloride ion relative to the bromide ion.

Table 3

Thermodynamic quantities (471 K)

Equilibrium	X	$\Delta G°$ kcal mol^{-1}	$\Delta H°$ kcal mol^{-1}	$\Delta S°$ cal mol^{-1} K^{-1}
Dissolution: AgX (solid) = $Ag^+ + X$	Cl	18	19	2·1
	Br	22	25	6·4
Complex formation: $Ag^+ + X^- = AgX$	Cl	$-6·5$	$-4·4$	4·5
	Br	$-8·5$	$-7·2$	2·8

The data in Tables 2 and 3 which refer to the formation of AgX and AgX_2^- complexes in the melt can be analysed in terms of a generalised quasi-lattice model of ionic melts.[4] According to this model, the stability constants can be expressed as in equations (8) and (9).

$$K_1 = Z(\beta_1 - 1) \qquad (8)$$

$$K_2 = [(Z - 1)/2]\{\beta_2 - 1 + [(\beta_2 - \beta_1)/(\beta_1 - 1)]\} \qquad (9)$$

Here, Z is the quasi-lattice co-ordination number, usually 5—6, and β_1 and β_2 are given by equations (10) and (11),

$$\beta_1 = \exp\ (-\ \Delta A_1/RT) \qquad (10)$$

$$\beta_2 = \exp\ (-\ \Delta A_2/RT) \qquad (11)$$

where ΔA_1 and ΔA_2 are the Helmholtz free-energy changes for the first and second metal–ligand bond formation (in AgX and AgX_2^-), when the ligand X^- replaces NO_3^- in the co-ordination sphere of a silver ion. With equations (8)—(11), $Z = 6$, and the data of Table 2, the ΔA values in Table 4 are obtained.

According to the model, the ΔA values should be temperature-independent. This seems to be valid for

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the ΔA_1 values, but the ΔA_2 values show a tendency to decrease with increasing temperature. A further test of the validity of the model in our charge-unsymmetrical melt can be made as follows. As ΔA_1 values are temperature-independent within the experimental error, equations (7), (8), and (10) give equation (12). Further,

$$\Delta H^\circ = \Delta A_1 \frac{\exp(-\Delta A_1/RT)}{\exp(-\Delta A_1/RT) - 1} \simeq \Delta A_1 \quad (12)$$

as $K_1 \gg Z$, equations (8) and (10) lead to equations (13) and (14), and consequently to (15).

$$K_1 \simeq Z \exp(-\Delta A_1/RT) \quad (13)$$

$$\Delta G^\circ = -RT \ln K_1 = -RT \ln Z + \Delta A_1 \quad (14)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T = R \ln Z \quad (15)$$

TABLE 4

The bond energy parameters ΔA/kcal mol^{-1} for $Z = 6$

Ligand	T/K	$-\Delta A_1$	$-\Delta A_2$
Cl^-	436	4·8	5·1
	451	4·8	4·9
	471	4·9	4·7
Br^-	441	7·0	6·8
	456	6·8	6·5
	471	6·9	6·2

According to equation (15) ΔS° is independent of the type of ligand X. This is perfectly in agreement with the model, which neglects all specific entropy contribution (due to internal degrees of freedom) when a ligand (X^-) and a salt anion (NO_3^-) exchange their sites in the quasi-lattice. Thus, when a complex AgX is formed, the only entropy contribution is due to the co-ordination number Z, which is a statistical factor.

Equations (12) and (15) can readily be tested. A comparison of the ΔA_1 values (Table 4) with the ΔH° values for AgX formation (Table 3) shows that equation (12) holds within 0·3—0·5 kcal mol^{-1}. Similarly, with $Z = 6$, equation (15) gives $\Delta S^\circ = 3{\cdot}5$ cal mol^{-1} K^{-1}, whereas the experimental values (Table 3) are 4·5 and 2·8 for AgCl and AgBr, respectively. The agreement is reasonable, within ± 1 cal mol^{-1} K^{-1}. With equation (15) it is, of course, impossible to discriminate between, say, a co-ordination number 5 and 6. Thus, $Z = 5$ gives $\Delta S^\circ = 3{\cdot}2$ cal mol^{-1} K^{-1}, which means that a more precise determination of Z requires a precision of *ca.* $\pm 0{\cdot}1$ cal mol^{-1} K^{-1}.

An important consequence of the quasi-lattice concept of molten salts is the influence of the reciprocal Coulomb effect on the ΔA values.[12] For a mixture of 1–1 and 2–1 salts, Braunstein and Brill [7] developed an expression which illustrates how ΔA_1 varies with the composition of the melt, assuming that the Coulomb interactions are based on hard-sphere ions with certain effective radii. Their relation applied to our system is given by equation (16).

$$\Delta A_1\,[\text{in } x\mathrm{Ca(NO_3)_2} + (1-x)\mathrm{KNO_3}] = \Delta A_1\,(\text{in pure } \mathrm{KNO_3}) - xNe^2 \left\{ \frac{2(r_X - r_{NO_3})}{(r_{Ca} + r_{NO_3})(r_{Ca} + r_X)} - \frac{r_X - r_{NO_3}}{(r_K + r_{NO_3})(r_K + r_X)} \right\} \quad (16)$$

Here x is the mol fraction of $Ca(NO_3)_2$, N the Avogadro constant, e the elementary charge, and r_{Ca}, r_K, r_{NO_3}, and r_X the effective radii of Ca^{++}, K^+, NO_3^-, and X^- (halide) ions. Equation (16) predicts that ΔA_1 in $Ca(NO_3)_2$–KNO_3 melts increases relative to the value in pure KNO_3 melt, if the halide radius r_X is smaller than the nitrate radius r_{NO_3}. Moreover, the change in ΔA_1 is assumed to be linear with x, as found in many 1–1 salt mixtures.[12] Equation (16) neglects several important factors, but it does predict the correct trend, as shown in Table 5.

TABLE 5

Comparison of ΔA_1 values ($Z = 6$)

Temp. range/°C	Melt composition (mol %) KNO$_3$	Ca(NO$_3$)$_2$	$-\Delta A_1$ kcal mol^{-1} AgCl	AgBr	Ref.
350—500	100	—	5·6	6·8	8, 9
320—350	80	20	5·3	No data	7
160—200	65·8	34·2	4·8	6·9	This work
—	—	100	(3·9)*	No data	7

* Estimated by extrapolation.

Table 5 shows that ΔA_1 for AgCl increases from $-5{\cdot}6$ kcal mol^{-1} in pure KNO_3 to $-4{\cdot}8$ kcal mol^{-1} in a mixture containing 34·2 mol % calcium nitrate. This trend is in agreement with equation (16) if $r_{Cl} < r_{NO_3}$. On the other hand, ΔA_1 for AgBr does not change appreciably, which according to equation (16) indicates that $r_{NO_3} \simeq r_{Br}$. However, a quantitative application of (16), as, for example, predicting ΔA_1 values in salt mixtures from the Pauling radii of ions, is not possible. This is understandable, because equation (16) neglects long-range Coulomb interactions (in solid crystals this is taken into account through the Madelung constant) and the polarisability of ions. It is also questionable which value of effective radius should be assigned to the planar NO_3^- ion, and whether a unique value for its radius can be used in a wide range of composition if the solvent is a charge-unsymmetrical molten salt mixture.

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