occurred with the chromium compounds. It may be that the thermal instability in all cases is due to anisotropic contractions of the lattice.

The spectrum of $W_2Cl_9^{3-}$ has been previously discussed.[10] The first observed absorption, which appears at 13,200 cm^{-1} (ϵ 50), would not correspond to a reasonable estimate of the wave numbers of the same absorption in the unknown WCl_6^{3-}. For this reason, it was believed that the absorptions are the result of transitions between d orbitals which are delocalized between the two metal atoms.

Possible Chemical Significance.—A comparison of the properties of $Cr_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ reveals three distinct differences: structural, magnetic, and spectroscopic. It is not difficult to believe that these differences occur because of electron localization in the former and electron delocalization in the latter. The effect of these properties on the chemical reactivity of each ion is a subject which is currently receiving our attention. However, several points related to this subject can be discussed. In salts of $Cr_2Cl_9^{3-}$, the energy associated with the intraionic coupling of spins is not chemically significant, and it is not expected that the long-range spin coupling alone will prevent the degradation of the dinuclear ion into mononuclear units during the course of a chemical reaction. On the other hand, bonding between the adjacent metal atoms in $W_2Cl_9^{3-}$ could reasonably be expected to deter, if not prevent, the conversion to mononuclear complexes of trivalent tungsten. The products of the reactions of $Cr_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ with pyridine are in full accord with this reasoning. When $K_3Cr_2Cl_9$ is allowed to react with hot pyridine, mononuclear $CrCl_3(py)_3$ is obtained. However, in the corresponding reaction with $K_3W_2Cl_9$, it was shown[10] that at least one-third of the product was diamagnetic $W_2Cl_6(py)_4$, in which it was presumed that adjacent octahedra were joined by two chlorine bridges. The three-dimensional X-ray study of Jackson and Streib[21] confirmed this hypothesis and showed that the metal–metal internuclear distance had increased to only 2.6 Å. Thus, the product retains a considerable amount of interaction between the metal atoms in their adjacent octahedra. It may be that kinetic factors alone are responsible for the different products. However, the special nature of $W_2Cl_9^{3-}$ can be further exemplified. The remarkable stability of this ion toward degradation was recently demonstrated[22] in the mass spectrum of $K_3W_2Cl_9$, wherein $W_2Cl_6^+$ and $W_2Cl_5^+$ were observed. Although mass spectroscopic data for $Cr_2Cl_9^{3-}$ are not available, similar ions were not found in the mass spectrum of $MoCl_3$. Furthermore, it is noteworthy that the only reported reactions of $W_2Cl_9^{3-}$ which lead to mononuclear compounds are those involving oxidation or the loss of some of the electrons which are thought to be extensively involved in metal–metal bonding. Thus, the reaction of this ion with the cyanide ligand[23] leads to $W(CN)_8^{4-}$, while the pyrolysis of $(NH_4)_3W_2Cl_9$ with 8-hydroxyquinoline yields[24] the eight-coordinate tetrakis derivative of W(IV).

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Solubility of Silver Chloride and Bromide and the Formation of Silver Halide Complexes in Molten Ammonium Nitrate Dihydrate

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The solubilities of silver chloride and bromide as a function of the corresponding ammonium halide concentration were determined in molten $NH_4NO_3 \cdot 2H_2O$, at 55, 70, and 85°. Solubility measurements were made using a radioactive-tracer technique with ^{110}Ag. The solubility product K_{sp} and the consecutive stability constants of the complexes AgX, AgX_2^-, and AgX_3^- ($X^- = Cl^-, Br^-$) were computed. The results are discussed in terms of a quasi-lattice model of molten salts.

Introduction

The solubility of silver chloride[1-5] and bromide[2,4,6-8] in water at various halide ion concentrations has been extensively studied. From solubility data it was conconclued that soluble silver complexes of the type $AgX_n^{-(n-1)}$ were formed (X^- denotes the halide ion, $n = 1$–4) and in some cases the stability constants of the complexes were calculated. The association of silver(I) ions with halide ions was also studied at high

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temperature in anhydrous ionic molten salts,[9-15] mostly by emf measurements at low halide concentration. Formally, the formation of silver halide complexes proceeds along the same path in water and ionic melt and the same species were identified in both media. However, one would expect a different mechanism in the coordination of ligands. In a dilute aqueous solution the siliver cation is surrounded by polar water molecules, while in a molten salt it is incorporated in the ionic quasi-lattice and surrounded by the anions of the solvent salt. Indeed, a difference is revealed by comparing the consecutive stability constants of the species AgX and AgX_2^-. Thus, the ratio K_1/K_2 differs appreciably in the two media, which indicates different statistics of ligand coordination.

The equilibrium constants of some metal complexes in ionic melts are often in good agreement with a quasi-lattice model for reciprocal salt systems.[16,17] This model was also applied to complexes in aqueous melts,[18-20] and recently the theory was extended to molten salt systems containing variable amounts of water.[21]

The present work investigates the formation of silver chloride and bromide complexes in molten $NH_4NO_3 \cdot 2H_2O$ by the solubility method. The solvent $NH_4NO_3 \cdot 2H_2O$, which is liquid above 35°, is intermediate between concentrated aqueous electrolyte solutions and anhydrous molten salts (it is nearly a 28 *m* solution of ammonium nitrate). So far no data on silver complexes in aqueous melts or concentrated electrolyte solutions have been available and, in general, little information on metal complexes in such media can be found. The purpose of the present paper is to provide some new information about chemical reactions in this type of solvent.

Experimental Section

The solvent $NH_4NO_3 \cdot 2H_2O$ was prepared from dry, reagent grade ammonium nitrate and distilled water. Inactive silver nitrate was mixed with radioactive $^{110}AgNO_3$ (specific activity about 12 mCi/g) and dissolved in molten $NH_4NO_3 \cdot 2H_2O$, thus obtaining melts of initial silver concentration 10^{-4}–10^{-3} *M* and of known specific activity.

Active melt samples (0.1–0.2 g) were weighed in tared vials. The sample was dissolved in 3 ml of 6 *M* aqueous ammonia and then counted in a well-type γ-scintillation counter. From these data and a standard silver sample counted under the same conditions, the molal concentration of silver in the melt was determined.

The experimental procedure consisted of equilibrating known amounts of $AgNO_3$, $NH_4NO_3 \cdot 2H_2O$, and NH_4Cl (or NH_4Br) in 50-ml stoppered glass tubes in a thermostat for at least 1 week. In all cases the aged, well-formed precipitate was visible on the bottom of the tube. With preheated disposable glass pipets, samples of the clear supernatant were withdrawn, placed in counting vials, weighed, and counted as described above. The solubility of silver halide was calculated from the counting data, the sample weight, and the activity of a standard silver sample. The equilibrium concentration of halide was obtained from the initial ammonium halide concentration and the initial and equilibrium concentration of silver, assuming the precipitate is pure AgX.

Solubility determinations of silver chloride and bromide were made at three temperatures in dependence on the halide concentration of the melt. The experimental data are presented in Figures 1 and 2 as solublity *S vs.* halide concentration m_X.[22]

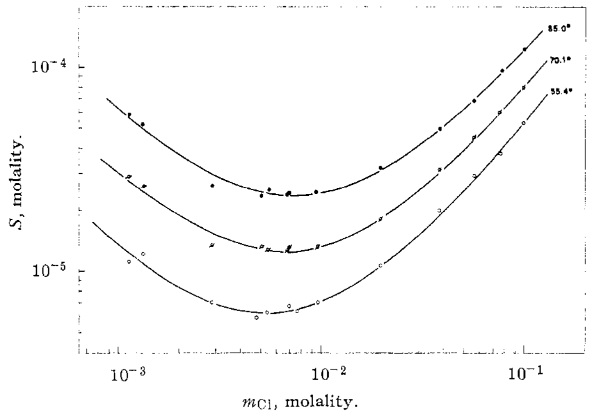

Figure 1.—The dependence of silver chloride solubility (*S*) in $NH_4NO_3 \cdot 2H_2O$ on ammonium chloride concentration (m_{Cl}). The curves were calculated from eq 6 with the constants given in Table I.

Results

The solubility *S* of silver halide can be defined by

$$S = m_0 + m_1 + m_2 + m_3 + \ldots \qquad (1)$$

where m_i is the molal concentration of a soluble silver species while the indices 0, 1, 2, 3, ... refer to the species Ag^+, AgX, AgX_2^-, AgX_3^{2-}, respectively. Under the experimental conditions (excess of halide over silver) the formation of polynuclear silver complexes is improbable. The solubility product K_{sp} and the consecutive formation constants (K_i) of silver halide complexes are defined in terms of thermodynamic activities ($a_i = m_i\gamma_i$) of the indicated species

$$K_{sp} = m_0 m_X \gamma_0 \gamma_X \qquad (2)$$

$$K_1 = m_1\gamma_1/m_0 m_X \gamma_0 \gamma_X \qquad (3)$$

$$K_2 = m_2\gamma_2/m_1 m_X \gamma_1 \gamma_X \qquad (4)$$

$$K_4 = m_3\gamma_3/m_2 m_X \gamma_2 \gamma_X \qquad (5)$$

Here, γ_i is the activity coefficient of the species *i*, and m_X is the molal concentration of ammonium halide.

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TABLE I

THE EQUILIBRIUM CONSTANTS

Ligand	Temp, °C	K_{sp}		K_1		K_2		K_3		$(DS)_S$, %	K_1/K_2
		m^a	x^b	m^a	x^b	m^a	x^b	m^a	x^b		
Cl^-	55.4	1.00×10^{-8}	1.35×10^{-10}	253	2180	141	1215	4.86	41.7	±5.1	1.8
	70.1	2.44×10^{-8}	3.29×10^{-10}	216	1860	108	930	3.80	32.4	±4.8	2.0
	85.0	4.90×10^{-8}	6.60×10^{-10}	205	1760	89.3	769	2.96	25.5	±5.8	2.3
Br^-	55.7	4.86×10^{-11}	6.55×10^{-13}	5450	4.69×10^4	693	5970	20.8	179	±4.9	7.9
	70.0	7.74×10^{-11}	1.04×10^{-12}	5280	4.55×10^4	754	6490	15.1	130	±3.1	7.0
	85.0	2.15×10^{-10}	2.90×10^{-12}	4440	3.85×10^4	510	4390	7.4	64	±3.4	8.7

[a] Molal scale. [b] Mole fraction scale (based on $NH_4NO_3 \cdot 2H_2O$ as *one* component).

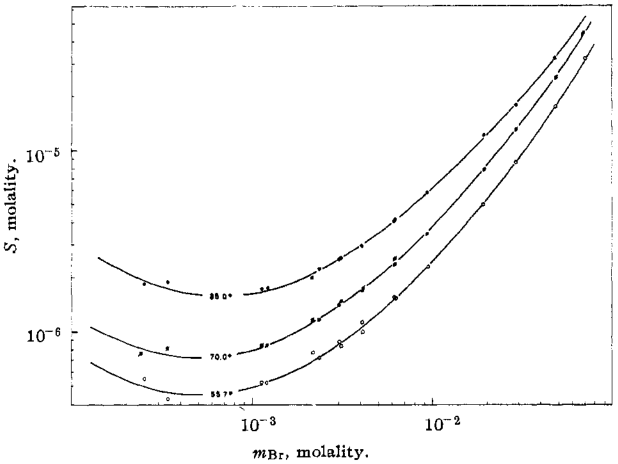

Figure 2.—The dependence of silver bromide solubility (S) in $NH_4NO_3 \cdot 2H_2O$ on ammonium bromide concentration (m_{Br}). The curves were calculated from eq 6 with the constants given in Table I.

For the activity coefficients, as usual, the infinite dilution in the solvent $NH_4NO_3 \cdot 2H_2O$ is chosen as a reference state; *i.e.*, these coefficients approach unity at low concentration of all solutes.

The activity coefficients in $NH_4NO_3 \cdot 2H_2O$ are not known and no theoretical limiting law, such as that of Debye–Hückel for dilute aqueous solutions, can be used. However, emf measurements of $NH_4NO_3 \cdot 2H_2O$ solutions containing 1:2 and 1:1 solute salts[19] proved that in this solvent solutes follow Henry's law up to a mole ratio (solute/NH_4NO_3) of 6×10^{-3}. This limit corresponds to a molal concentration of 0.05. Comparable ranges of ideal solute behavior were observed in anhydrous melts,[17] and in aqueous solutions the activity coefficients are also fairly constant up to this solute concentration if the ionic strength is kept constant with a large excess of a suitable electrolyte. All solubility measurements in the present work were made at a halide concentration below 0.1 *m*. Moreover, only one point on the bromide solubility curve (Figure 2) and two points on the chloride solubility curve (Figure 1) were above 0.056 *m* halide concentration. Therefore, it seems reasonable to assume that the activity coefficients in eq 2–5 are constant and, according to the reference state chosen, equal to unity. In this case eq 1–5 give

$$S = K_{sp}m_x^{-1}(1 + K_1m_x + K_1K_2m_x^2 + K_1K_2K_3m_x^3) \quad (6)$$

The experimental results, S *vs.* m_x, were interpreted according to eq 6 in a digital computer by a modified nonlinear least-squares program.[23] A relative-deviation least-squares treatment was applied so that deviations at low concentration of halide have the same statistical weight as those at high concentration. Values for K_{sp}, K_1, K_2, and K_3 and the standard deviation of the solubility, $(SD)_S$, were obtained. The results are summarized in Table I. Equation 6 was tested with and without the cubic term in m_x. However, even in the case of chloride, when K_3 values are low, the fit is significantly better with the cubic term, although the numerical values for K_1 and K_2 only slightly change if this term is omitted. Hence, it is concluded that the AgX_3^{2-} species is not very important in the m_x range of 0.01–0.1, but it cannot be neglected.

As seen from Table I, K_{sp} increases with temperature, and an opposite trend is valid for the consecutive stability constants. The only apparent exception is the K_2 value for $AgBr_2^-$ at 70°, although it seems more probable that the value at 55° is too low.

Discussion

The ratios K_1/K_2 in Table I provide valuable information on the statistics of ligand coordination. This ratio is actually the equilibrium constant for the disproportionation reaction: $2AgX = Ag^+ + AgX_2^-$, which is independent of the concentration scale used. Thus, the K_1/K_2 ratio can be readily compared for various media. In the case of silver chloride complexes, K_1/K_2 in Table I is between 1.8 and 2.3, while for dilute aqueous solutions values of 24[1] and 11[3] are reported. In anhydrous ionic melts, irrespective of the temperature, this ratio is about 2.5,[11,12] which is close to the value obtained in the present work at 70 and 85°. For silver bromide complexes, the K_1/K_2 ratio is rather high in dilute aqueous solutions, *i.e.*, 26 according to Berne and Leden[6] or even 50 according to Lieser.[4] In anhydrous molten salts values between 2 and 4 are reported,[11,15] while according to Table I this ratio is higher in $NH_4NO_3 \cdot 2H_2O$ but still much lower than in dilute aqueous solutions.

Qualitatively, this survey of data indicates that AgX_2^- should be a linear species in dilute aqueous solutions. (Only one possible site in the coordination sphere of Ag is available to the second ligand; thus K_2 is low compared with K_1). In anhydrous ionic melts the lattice structure probably provides a greater chance for the second ligand to replace any of the available nitrate ions around Ag^+, so that AgX_2^- is not necessarily a linear grouping. Consequently, $K_1/$

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(23) I. J. Gal and M. Jeftović, to be submitted for publication.

K_2 is lower, approaching eventually the statistical ratio of Bjerrum[24] and Adams[25] if the two bonds are of equal strength. In a solvent like $NH_4NO_3 \cdot 2H_2O$ the formation of silver halide complexes is apparently similar to a coordination mechanism valid for anhydrous melts, especially in the case of silver chloride.

A more quantitative test is provided by the quasi-lattice model of Blander.[16] According to this model developed for reciprocal molten salt systems, the stability constants (on a mole fraction scale) can be expressed as

$$K_1 = Z(\beta_1 - 1) \tag{7}$$

$$K_2 = [(Z - 1)/2]\{\beta_2 - 1 + [(\beta_2 - \beta_1)/(\beta_1 - 1)]\} \tag{8}$$

Here, Z is the coordination number of cations in the "lattice," usually 4–6, and

$$\beta_1 = \exp(-\Delta A_1/RT) \tag{9}$$

$$\beta_2 = \exp(-\Delta A_2/RT) \tag{10}$$

where ΔA_1 and ΔA_2 are the Helmholtz free energies of the first and second metal–ligand bond, respectively. Equation 8 is based on the assumption that the second ligand has available $Z - 1$ sites around the central cation. If only a linear grouping can be formed, K_2 is lower and eq 8 should be replaced by[16]

$$K_2' = {}^1/_2\{\beta_2 - Z + [(\beta_2 - 1)/(\beta_1 - 1)]\} \tag{11}$$

Taking the values for K_1 and K_2 from Table I and $Z = 6$, the free energies of the bonds were calculated assuming eq 7–11 valid in the $NH_4NO_3 \cdot 2H_2O$ melt. Thus for ΔA_2 two values are obtained: from eq 8 (nonlinear grouping) and from eq 11 (linear grouping). The results are listed in Table II.

TABLE II

THE BOND FREE ENERGIES

Ligand	Temp, °K	$-\Delta A_1$, kcal	$-\Delta A_2$, kcal Nonlinear (eq 8)	linear (eq 11)
Cl^-	328.5	3.87	4.04	4.91
	343.2	3.94	4.03	5.02
	358.1	4.05	4.07	5.19
Br^-	328.8	5.87	5.09	7.01
	343.1	6.10	5.36	7.40
	358.1	6.24	5.32	7.38

As seen from this table, when chloride ion is the ligand, the free energies ΔA_1 and ΔA_2 (nonlinear) are within a few per cent independent of the temperature and nearly equal. This is in agreement with the results obtained in molten salts,[9–12,17] although the free energies are higher in anhydrous melts. The linear model seems to be less suitable. (As seen from Table II, for chloride, ΔA_2 (linear) increases with the temperature.)

In the case of bromide ligands ΔA_1 is larger than ΔA_2 (nonlinear) and depends strongly on temperature. This differs from the behavior in anhydrous KNO_3[15] where the temperature dependence of K_1 is correctly predicted by eq 8.

Recently, Braunstein extended the quasi-lattice model to reciprocal molten salt systems containing water.[21] His theoretical expression for K_1 has two ΔA_1 terms because a ligand can replace either water or a salt anion from the coordination sphere of the cation. Unfortunately, this interesting model cannot be tested at this time because the stability constants in anhydrous melt and in melts of different water content are required. An extension of the present investigation in this direction is under way.

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