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Thermodynamics of (Ag,Na)IO_3 Solid Solutions and Silver Iodate Complexation in Molten (K,Na)NO_3. A Potentiometric and Solubility Study

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Complex formation between Ag(I) and IO_3^- in equimolar (K,Na)NO_3 has been studied by emf measurements at five temperatures between 523 and 623 K and by solubility measurements at 553 K. (Ag,Na)IO_3 solid solutions, exhibiting positive deviations from thermodynamic ideality, are formed when $AgIO_3$ is equilibrated with melts rich in iodate, and a transition to a new phase with $x_{NaIO_3} = 0.38 \pm 0.01$ is detected by thermodynamic methods and by X-ray powder diffraction analysis. All data can be rationalized by a model of stepwise formation of the complexes $AgIO_3$, $Ag(IO_3)_2^-$, and $Ag_2IO_3^+$. From the temperature dependence of the stability constant β_{11} for $AgIO_3$, $\Delta H_1^\circ = 2.3 \pm 1.6$ kJ mol^{-1} and $\Delta S_1^\circ = 31 \pm 3$ J K^{-1} mol^{-1} have been estimated. The entropy gain is thus responsible for the thermodynamic stability of the $AgIO_3$ complex. A critical comparison of ΔS_1° with predictions from quasi-lattice theory is made.

Introduction

This paper is part of a series of oxoanion–silver(I) complexation studies in molten equimolar (K,Na)NO_3 aiming at a rationalization of the influence of parameters such as ionic size, charge, and nature of the central atom of the oxoanion on the thermodynamics of the complexation. Ag(I) association with a number of divalent oxoanions in various molten nitrates has been studied by different authors.[1] In these works the pair association energy of the quasi-lattice theory is calculated for the 1:1 association processes, and its temperature dependence or independence is discussed. So far, however, monovalent oxoanions have received little attention as ligands in ionic melts. We have recently given results from a study of the Ag(I)–nitrite system in 1:1 KNO_3–$NaNO_3$,[2] and ionic association between IO_3^- and Ca^{2+} in the same solvent has been considered by Holmberg.[3]

The iodate ion is an attractive ligand in molten nitrate solvents since it has approximately the same size, although different geometry, and the same ionic charge as the solvent nitrate ion. These properties delete entropy contributions from configurational changes as ions of higher charge are introduced into a melt of monovalent ions only.

Habboush and Kerridge found the iodate ion to be stable up to 500 °C in (K,Li)NO_3. The nitrite formed by thermal decomposition of nitrate was said to reduce IO_3^- to a measurable extent above this temperature.[4] According to Sacchetto and co-workers[5] IO_3^- is unstable in unspecified nitrate melts containing Ag(I). Precipitation of AgI was observed and the presence of Ag(I) is thus expected to facilitate the iodate decomposition. We have paid special attention to this problem by studying separately the thermal stability of IO_3^- in (K,Na)NO_3–$AgNO_3$ melts in the range 250–350 °C.

Two independent methods, emf and solubility measurements, have been used to investigate the Ag(I)–iodate complexation. Emf measurements were performed with silver(I) concentration cells at various temperatures in an interval of 100 K, while the solubility study was made at one reference temperature, 280 °C.

It was observed in preliminary experiments that alkali metal iodate is dissolved into $AgIO_3$ when the solid is equilibrated with melts rich in iodate. This tendency of the highly concentrated ions of the solvent to replace ions in the solid phase appears to be a much more frequent problem in solubility studies of complex formation in ionic melts than in similar studies involving molecular solvents at ambient temperatures. Nevertheless solubility data can be used to determine stability constants for complex ions by means of a simultaneous thermodynamic treatment of all heterogeneous and homogeneous equilibria considered. This calculation method has been outlined previously by Holmberg.[6]

Experimental Section

Silver nitrate, sodium nitrate, and potassium nitrate (Merck p.a.) were pretreated and stored as described previously.[7] Alkali metal iodate was added as an equimolar mixture of sodium iodate and potassium iodate (Merck p.a.). These salts were dried separately, ground together, and then dried again at 120 °C for several days prior to use. Silver iodate was either a preparation made by us from $AgNO_3$ and $NaIO_3$ or a commercial preparation from BDH Chemicals Ltd. In some cases silver iodate was precipitated directly in the melt from added alkali iodate and silver nitrate.

Furnaces, temperature control and measurement, and the construction of the cell for emf measurements have been described elsewhere.[2,7,8]

Solubility Measurements. Systems with approximately 1 g of $AgIO_3$, 75 g of (K,Na)NO_3, and varying amounts of $AgNO_3$ or (K,Na)IO_3 were agitated for at least 50 h in Pyrex-glass tubes (series A). Maximum concentrations were 1.0 mol kg^{-1} $AgNO_3$ and 0.8 mol kg^{-1} (K,Na)IO_3. Samples from the nitrate phase were analyzed for silver and iodate. Total iodate was determined to ±0.4% by the conventional iodometric procedure using sodium thiosulfate solutions, standardized against potassium iodate. Silver was determined by electroanalytical precipitation of Ag on a rotating platinum cathode from hot aqueous cyanide solutions. In a separate series (B) 10 g of $AgIO_3$ was used in order to make it possible to calculate the composition of the solid from the difference between added and found amounts of various ions in the nitrate melt after equilibration.

Emf Measurements. The following cell was used:

$$\mathrm{Ag}\left|\begin{array}{l} C_{IO_3}\ \mathrm{(K,Na)IO_3} \\ C_{Ag}\ \mathrm{AgNO_3} \\ \quad\ \mathrm{(K,Na)NO_3} \end{array}\middle\|\begin{array}{l} C^\circ_{Ag}\ \mathrm{AgNO_3} \\ \quad\ \mathrm{(K,Na)NO_3} \end{array}\right|\mathrm{Ag}$$

The cell was usually set up with 250 g of (K,Na)NO_3 and 0.003 mol kg^{-1} $AgNO_3$ in both cell compartments and left while being vigorously stirred for about 18 h. Successive additions of (K,Na)IO_3 were then made, and the emf was measured repeatedly at constant temperature over four different electrode combinations after each addition by means of a Digiscan 10 PRC data-logging unit from Mess+System Technik, München. The *E* values were measured to ±0.05 mV. Stable readings were as a rule obtained within 30 min after each addition of iodate. In order to decide whether polynuclear species are present or not in melts with an excess of iodate over silver, we ran some series with $C_{Ag} = 0.001$ and 0.03 mol kg^{-1} as well. Eight different compositions

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(1) E.g.: Vallet, C. E.; Braunstein, J. *J. Phys. Chem.* **1973**, *77*, 2672. Sacchetto, G. A.; Macca, C.; Bombi, G. G. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *36*, 319.

(2) Holmberg, B.; Thomé, G. *Inorg. Chem.* **1980**, *19*, 980.

(3) Holmberg, B. *J. Inorg. Nucl. Chem.*, in press.

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(5) Bombi, G. G.; Sacchetto, G. A.; Macca, C. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *42*, 373.

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(7) Holmberg, B. *Acta Chem. Scand., Ser. A* **1974**, *A28*, 284.

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Table I. Tests of the Iodate Stability in Equimolar $(K,Na)NO_3$

		results from weighed in amounts		analytical results	
melt	$t/°C$	C_{Ag}/ mol kg^{-1}	C_{IO_3}/ mol kg^{-1}	time/ h	C_{IO_3}/ mol kg^{-1}
A	280		0.1034	24	0.1031
				48	0.1031
				96	0.1030
B	280	0.026	0.803	25	0.805
				50	0.807
C	280	0.100	0.0584	24	0.0579
				48	0.0584
				72	0.0579
D	350	0.029	0.302	1	0.301
				3	0.302
				5	0.301

were as a rule studied in every series; maximum concentrations of iodate was 0.3 mol kg^{-1}. All series of measurements were duplicated at least once. Data were recorded at five different temperatures in the range 250–350 °C.

The Stability of Iodate. The solubility of iodate is larger than 1.3 mol kg^{-1} at 280 °C when added as a 1:1 mixture of KIO_3 and $NaIO_3$ to the pure $(K,Na)NO_3$ solvent. The thermal stability was checked in a number of melts listed in Table I. Decomposition of IO_3^- does not occur in pure $(K,Na)NO_3$ according to the analyses of melt A made after several days at 280 °C. Melt B was high in iodate and rather low in silver concentration to avoid precipitation of $AgIO_3$. It was made to check if the observed difference between added and found iodate contents in the melts equilibrated with solid $AgIO_3$, which we have attributed to the ion-exchange reaction

$$AgIO_3(ss) + Na^+ \rightleftarrows NaIO_3(ss) + Ag^+$$

might in part be due to iodate decomposition. No changes were found within 50 h, the normal running time for systems used in solubility studies.

It has been claimed[5] that IO_3^- is unstable in nitrate melts containing Ag(I); therefore, melt C with even higher silver content was studied. No variation in C_{IO_3} with time could be detected and no precipitation of AgI was observed. Melt D was prepared with an iodate concentration corresponding to the largest one used in the emf measurements and was equilibrated at the highest temperature used. The iodate concentration in this melt remained constant for at least 5 h, which is more than the normal time for one emf titration series.

It is thus safely concluded that the reaction

$$IO_3^- \rightarrow I^- + {}^3/{}_2O_2$$

does not occur to any measurable extent under the conditions used in the present study up to 350 °C.

Emf Measurements

Stability constants defined by

$$\beta_{mn} = [Ag_m(IO_3)_n{}^{m-n}]/[Ag^+]^m[IO_3^-]^n \qquad (1)$$

were determined by use of the stoichiometric requirement

$$C_{Ag} = [Ag^+] + \sum_m\sum_n m[Ag_m(IO_3)_n{}^{m-n}] \qquad (2)$$

Since junction potentials are negligible in these dilute ionic melts, it holds that

$$\Delta E = (RT/F)\ \ln\ (C_{Ag}/[Ag^+]) \qquad (3)$$

where ΔE is the emf at the iodate concentration considered minus the emf at $C_{IO_3} = 0$ in the left-hand compartment of the cell. Combination of eq 1–3 yields eq 4.

$$\exp\left(\frac{(\Delta E)F}{RT}\right) = 1 + \sum_m\sum_n m\beta_{mn}[Ag^+]^{m-1}[IO_3^-]^n \qquad (4)$$

It appeared that the left-hand member of eq 4 could be accurately described by a second-degree polynomial in $[IO_3^-]$ independent of the Ag(I) content of the melts. Hence, the complexes $AgIO_3$ and $Ag(IO_3)_2^-$ are the only species that have to be considered in melts having iodate in excess over silver. This is exemplified by Figure 1, displaying results from three series of measurements at 280 °C.

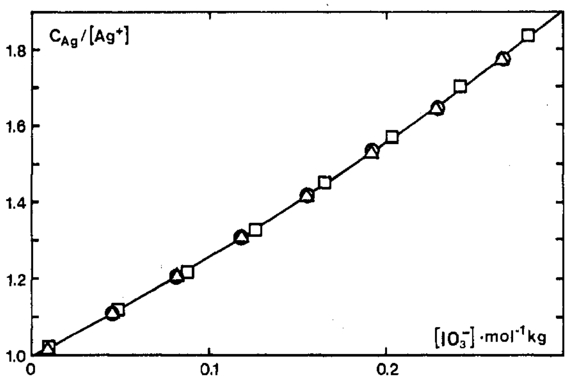

Figure 1. $C_{Ag}/[Ag^+]$ vs. $[IO_3^-]$ from three different emf titrations in 1:1 KNO_3–$NaNO_3$ at 553 K. $C_{Ag} = 3.02 \times 10^{-3}$ mol kg^{-1} (□), 3.06×10^{-2} mol kg^{-1} (○), and 3.08×10^{-2} mol kg^{-1} (△).

Table II. Overall Stability Constants β_{11} and β_{12} for Ag^+-IO_3^- Complexes in Molten 1:1 KNO_3-$NaNO_3$ from Emf Measurements[a]

T/K	$\beta_{11}/mol^{-1}\ kg$	$\beta_{12}/mol^{-2}\ kg^2$
524	2.27 ± 0.12	3.7 ± 0.6
538	2.26 ± 0.15	2.0 ± 0.7
553	2.28 ± 0.14	2.4 ± 0.7
588	2.34 ± 0.15	1.4 ± 0.7
622	2.43 ± 0.07	

[a] The limits of error correspond to 95% confidence limits.

The final treatment of data was made by use of a computer program yielding the best fitting parameters β_{mn} from eq 4 by minimizing the sum of squared errors $(\Delta E_{obsd} - \Delta E_{calcd})^2$. Table II gives stability constants from the emf measurements at five different temperatures. As can be seen from the table the data recorded at 622 K did not permit any meaningful estimate of β_{12} at this temperature. This is obviously due to the fact that the stability of $Ag(IO_3)_2^-$ decreases rapidly with increasing T.

The thermodynamic parameters $\Delta H_1°$ and $\Delta S_1°$ for the first step of complexation, schematically written as

$$Ag^+ + IO_3^- \rightarrow AgIO_3 \qquad (5)$$

have been estimated from a study of $\Delta G_1° = -RT \ln \beta_{11}$ as a function of temperature. The standard state chosen relates to unity ionic fractions. $\Delta G_1°$ is a good linear function of T, so $\Delta H_1°$ and $\Delta S_1°$ have been estimated by linear regression analysis. In doing so, every data point was given an individual weight proportional to $(\sigma_1(T))^{-2}$, where $\sigma_1(T)$ is given by eq 6. Here $\sigma(\beta_{11})$ is the estimated standard deviation in β_{11} at

$$\sigma_1(T) = RT\frac{\sigma(\beta_{11})}{\beta_{11}} \qquad (6)$$

the temperature in question. Resulting parameters are $\Delta H_1° = 2.3 \pm 1.6$ kJ mol^{-1} and $\Delta S_1° = 31 \pm 3$ J K^{-1} mol^{-1}. Stated errors are one estimated standard deviation.

Data for the second step of complexation are not accurate enough to make a similar estimate of $\Delta H_2°$ and $\Delta S_2°$ meaningful.

Solubility Measurements

The Solid Phase. The calculations, based on analytical results pertaining to the melts and the known total composition of two-phase systems in series B, clearly indicated that silver ions of the solid phase are partially replaced by alkali metal ions from the melt in systems with $C_{IO_3} > C_{Ag}$. For a determination of whether Na^+, K^+, or both are involved in the

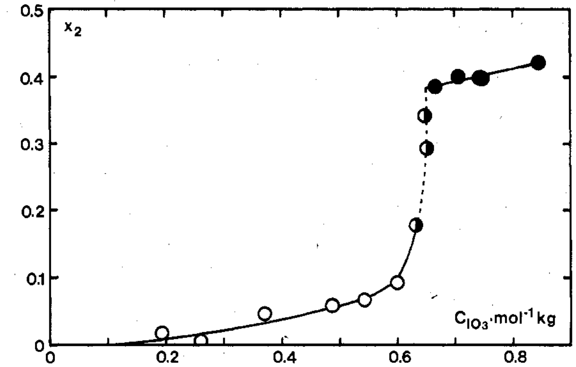

Figure 2. Mole fraction of $NaIO_3$, x_2, in the solid phase as a function of C_{IO_3} in the melt. Filled symbols represent the Na-rich phase, and half-filled symbols represent systems with a mixture of the two solid solutions (as indicated from X-ray diffraction at room temperature).

ion-exchange reaction, melts with pure KNO_3 and pure $NaNO_3$ as solvents were prepared with 1.2 mol kg^{-1} KIO_3 and $NaIO_3$, respectively, and were equilibrated with solid $AgIO_3$ at 350 °C. The mole fraction of $AgIO_3$, x_1, in the solid phase after equilibration was 0.52 in the sodium system and 0.96 in the potassium system, indicating that sodium is responsible for the paramount part of the ion exchange. x_2 $(=1 - x_1)$ raises slowly as C_{IO_3} is increased from 0 to 0.65 mol kg^{-1}. Here x_2 increases very steeply to 0.38 ± 0.01, indicating a phase transition. After this point, x_2 of the new "Na-rich" phase increases slowly with C_{IO_3} again. Figure 2 gives the composition of the solid as a function of C_{IO_3} in the melt.

X-ray powder diffraction studies were made at room temperature on solids with x_2 = 0.06, 0.18, 0.29, and 0.40 as well as on pure $AgIO_3$ and $NaIO_3$. The diffraction patterns for x_2 = 0.06 and for pure $AgIO_3$ were identical. New lines, different from those of $NaIO_3$, appeared for the next two powders, x_2 = 0.18 and 0.29. For x_2 = 0.40 the lines typical of $AgIO_3$ had disappeared. The half-filled symbols of Figure 2 thus represent systems with formal values of x_2 corresponding to mixtures of two solid solutions with different crystal structures.

The diffraction pattern of the new Na-rich phase could be properly indexed on the basis of an orthorhombic symmetry, like that of $AgIO_3$[9] and $NaIO_3$.[10] Cell parameters for x_2 = 0.40 are a = 6.801 (4) Å, b = 12.29 (1) Å, and c = 6.127 (3) Å. It is to be noted that b falls very close to the weighted average of the corresponding edge lengths for $AgIO_3$ (15.13 Å) and $NaIO_3$ (8.10 Å) which is 12.32 Å, whereas no similar relation is found for a and c.

The activity, a_1, of $AgIO_3$ in the solid phase has to be known in order that solubility data may be used for the determination of complex ion stabilities. a_1 is computed from (7) where R

$$a_{1j} = \exp\left[\int_{\ln R_0}^{\ln R_j} (x_2/x_1)\, \mathrm{d} \ln R\right] \qquad (7)$$

$= (y[IO_3^-])^{-1}$ and $y = [Na^+]/([Na^+] + [K^+])$.[6] The index j is used to denote different quantities referring to the same actual system, and R_0 refers to a system with $x_1 = 1$ and $a_1 = 1$, i.e., the standard state chosen for $AgIO_3$. Hence, the activity of $AgIO_3$ in the Na-rich phase also relates to pure $AgIO_3$. Figure 3 gives a_1 as a function of x_1 in the two solid phases. Both kinds of solid solutions exhibit positive deviations from thermodynamic ideality.

$C_{IO_3} > C_{Ag}$. Figure 4 surveys the experimental materials of series A.

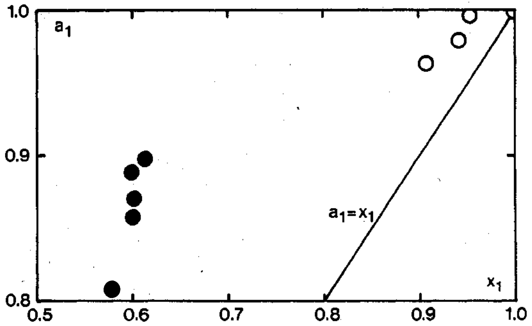

Figure 3. Activity of $AgIO_3$, a_1, as a function of the mole fraction x_1 of $AgIO_3$ in the solid $(Ag,Na)IO_3$ phase at 553 K. Filled symbols represent the Na-rich phase. a_1 is calculated from eq 7. The line $a_1 = x_1$, corresponding to a hypothetical ideal substitutional cationic solution, is included for the sake of comparison.

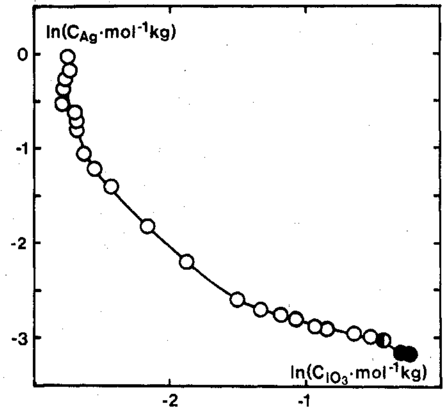

Figure 4. Solubility curve for $AgIO_3$ in 1:1 KNO_3–$NaNO_3$ at 553 K. Filled symbols represent melts in equilibrium with Na-rich solid solution after the phase transition.

It was observed that solubilities determined in series B were—to a small but significant extent—higher than the corresponding values obtained in series A. This difference can be attributed to the shift in the K:Na ratio of the nitrate melt brought about by the selective Ag–Na exchange reaction between the melt and the solid. Data from series A only were used in the determination of complex stabilities. In this way it was ensured that stability constants determined by emf and solubility methods refer to as similar cation composition of the solvent as possible. Values of x_1 and a_1 were transferred from series B to series A by means of interpolation in plots of x_1 and a_1 vs. $y[IO_3^-]$.

A general expression for the solubility "product" of $AgIO_3$ is

$$K_s = [Ag^+][IO_3^-]/a_1 \qquad (8)$$

By combination with eq 1 and 2

$$C_{Ag}[IO_3^-]a_1^{-1} = K_s(1 + \sum_m \sum_n m\beta_{mn}[Ag^+]^{m-1}[IO_3^-]^n) \qquad (9)$$

Inspection of the solubility curve shows that no species with more negative formal ionic charge than 1– are formed. Since emf measurements clearly show the absence of polynuclear complexes in this composition range, all data were treated according to eq 9 with the assumption that $AgIO_3$ and $Ag(IO_3)_2^-$ only were present. A second-degree polynomial in $[IO_3^-]$ that describes the experimental data $C_{Ag}[IO_3^-]a_1^{-1}$ can easily be found by iteration. K_s, $K_s\beta_{11}$, and $K_s\beta_{12}$ are thus determined.

$C_{Ag} > C_{IO_3}$. In analogy with eq 9, we have

$$C_{IO_3}[Ag^+]a_1^{-1} = K_s(1 + \sum_m \sum_n n\beta_{mn}[Ag^+]^m[IO_3^-]^{n-1}) \qquad (10)$$

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(9) Santana, D. *An. R. Soc. Esp. Fis. Quim. Ser. A* **1948**, *44*, 557 (as cited in *Struct. Mater. Rep.* (*Aust., Aeronaut. Res.*) **1951**, *11*, 366).

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Table III. Stability Constants and K_s for $AgIO_3$ in 1:1 KNO_3-$NaNO_3$ at 280 °C Determined by Different Experimental Methods[a]

10^3K_s/ mol^2 kg^{-2}	β_{11}/mol^{-1} kg	β_{12}/mol^{-2} kg^2	β_{21}/mol^{-2} kg^2	method
10 ± 2	3.5 ± 1.0		2.1 ± 1.0	sol, $C_{Ag} > C_{IO_3}$
10 ± 1	2.1 ± 0.7	2.2 ± 0.8		sol, $C_{IO_3} > C_{Ag}$
	2.3 ± 0.1	2.4 ± 0.7		emf

[a] The errors define 95% confidence limits.

where a_1 can be set to unity as the solid phase is pure $AgIO_3$ in all systems where Ag(I) is in excess over iodate in the melt. From the shape of the solubility curve it is clear that complex ions of a formal charge 1+ have to be taken into account in a proper description model. Any complex of the composition $Ag_m(IO_3)_{m-1}^+$ may be considered, but we have made the reasonable assumption that the simplest complex $Ag_2IO_3^+$ is formed. The experimental data $C_{IO_3}[Ag^+]$ are well described by a second-degree polynomial in $[Ag^+]$, employing an iterative least-squares calculation process that yields K_s, $K_s\beta_{11}$, and $K_s\beta_{21}$ at 280 °C.

Discussion

From aqueous solution chemistry, the complexes $AgIO_3$ and $Ag(IO_3)_2^-$ are well characterized,[11] and even cationic complexes have been proposed.[12] These are the same species as we have found in nitrate melts although the association does not by far proceed to the same extent in the ionic liquid. Table III displays a comparison between stability constants and K_s determined by different methods at 280 °C. The results from solubility and emf measurements agree very well within the estimated limits of error. It is clear, though, that emf measurements give the most precise estimate of β_{11}. Figure 5 shows the fraction α of the different silver-containing species as a function of $[IO_3^-]$ at 524 and 588 K. Ag^+ and $AgIO_3$ are the dominating species containing Ag(I), and $Ag(IO_3)_2^-$ contributes at most to only 16% of C_{Ag} at 524 K. This fraction decreases rapidly with increasing T, making $Ag(IO_3)_2^-$ practically undetectable at 622 K.

The enthalpy change for the first step of ionic association

$$Ag^+ + IO_3^- \rightarrow AgIO_3 \tag{11}$$

does not differ significantly from zero. This is about the expected value if only changes in electrostatic interactions between hard-sphere ions are considered in a model where process 11 is more rigorously treated at a 1:1 exchange of NO_3^- for IO_3^- between two different quasi-static cationic environments.[3] The thermodynamic stability of $AgIO_3$ is thus exclusively due to a comparably large entropy gain on association of Ag^+ with IO_3^-.

A comparison between IO_3^- and NO_2^{-2} as ligands for Ag^+ in molten $(K,Na)NO_3$ is instructive, since both ligands are monovalent polyatomic oxoanions. Although the stability constants for the 1:1 complexes, and hence $\Delta G_1°$, are almost identical at the reference temperature 280 °C, the $\Delta H_1°$ and $\Delta S_1°$ patterns are quite different. The nitrite association is favored by a large negative $\Delta H_1°$ term but disfavored by a substantial loss of entropy. This suggests that a schematic description of the association, such as (11), may represent quite different kinds of processes on the molecular level even in cases of total ionic charge equality.

The question therefore arises as to whether straightforward applications of lattice-like models are always justified. We calculated the specific pair association energy ΔA_1 for process 11 at five different temperatures by use of the general quasi-lattice theory of Blander.[13] The lattice coordination number Z was set to 5 in order to conform to previous calculations by Sacchetto and co-workers.[1,5,14]

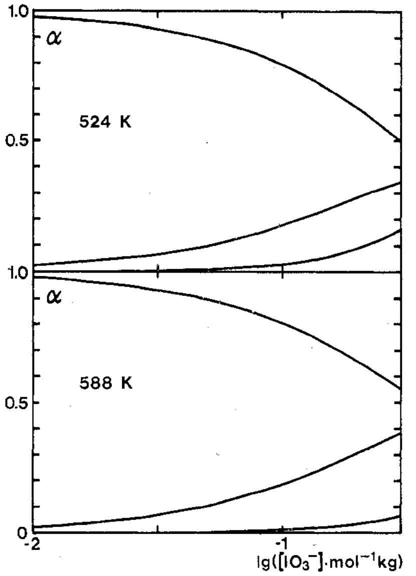

Figure 5. The fraction α of Ag(I) present in different species in molten 1:1 KNO_3-$NaNO_3$ at 524 and 588 K as a function of the iodate concentration in the limit $C_{Ag} \rightarrow 0$. The graphs—calculated from the constants of Table II—represent from top to bottom Ag^+, $AgIO_3$, and $Ag(IO_3)_2^-$.

As $\Delta S_1°$ indicates, ΔA_1 has a considerable temperature dependence, which can be generalized as

$$\Delta A_1 = a + bT \tag{12}$$

since $\partial(\Delta A_1)/\partial T$ is virtually temperature independent. Linear regression yields $a = 1.7 \pm 0.6$ kJ mol^{-1} and $b = -18 \pm 1$ J K^{-1} mol^{-1}. The parameters refer to the same standard state as $\Delta H_1°$ and $\Delta S_1°$ and are given within 95% confidence limits.

Substantial values of b have previously been attributed to entropy effects due to changes in internal degrees of freedom for polyatomic solute and solvent ions[1] taking part in processes such as (13).

$$Ag^+(NO_3^-)_Z + IO_3^- \rightarrow Ag^+IO_3^-(NO_3^-)_{Z-1} + NO_3^- \tag{13}$$

The internal entropy change, $\Delta S°_{int}$, may be roughly estimated, however, from vibrational spectra of IO_3^- and NO_3^- in various cationic environments[15,16] and from the reasonable assumption that the entropy effects of restrictions on the rotation in the (K,Na) and (Ag,K,Na) environments are related to the products of principal moments of inertia in essentially the same way for NO_3^- and IO_3^-. $\Delta S°_{int}$ should thus probably fall between −2 and −18 J K^{-1} mol^{-1}, which gives a configurational contribution $\Delta S°_{conf} = 41 \pm 11$ J K^{-1} mol^{-1}. Despite the large uncertainty in these figures, they clearly show that the ideal value of the quasi-lattice model, $\Delta S°_{conf} = 14 \pm 3$ J K^{-1} mol^{-1} (for reasonable values of Z around 5), is not obtained, which rules out the "internal entropy explanation" to $\partial(\Delta A_1)/\partial T$.

The negative sign of b is at least in qualitative agreement with the prediction by Bombi and Sacchetto[14] of the temperature dependence of ΔA_1, which is entirely attributed to a nonrandom distribution of solvent cations in a mixed-solvent system. The magnitude, however, would require an unreal-

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(16) Wait, S. C.; Ward, A. T.; Janz, G. J. *J. Chem. Phys.* **1966**, *45*, 133.

istically large difference between ΔA_1 in pure $NaNO_3$ and in pure KNO_3 in order to be accounted for in this way. In our opinion the apparent temperature dependence of ΔA_1 is largely due to configurational entropy contributions in excess of those predicted by the quasi-lattice model.

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Registry No. KNO_3, 7757-79-1; $NaNO_3$, 7631-99-4; $NaIO_3$, 7681-55-2; $AgIO_3$, 7783-97-3; $Ag(IO_3)_2^-$, 74096-65-4.

Supplementary Material Available: Tables IV–VI, giving all experimental data from solubility and emf measurements (10 pages). Ordering information is given on any current masthead page.

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Evidence of a Chromium(II) Intermediate in the Photolysis of Tris(2,2′-bipyridyl)chromium(III) in Dimethylformamide

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The mechanism for the photochemical reaction of $[Cr(bpy)_3]^{3+}$ in DMF has been found to be strikingly different from that obtained in aqueous solution. The primary difference stems from the initial formation of a Cr(II) intermediate in DMF which does not occur in water. This leads to a large photochemical quantum yield in DMF. Experimental evidence supports an autocatalytic chain reaction with a Cr(II)–bipyridine complex as the chain carrier. The luminescence lifetime and quantum yield are smaller in DMF than in water, and, in mixed H_2O–DMF systems, they have been found to vary monotonically with solvent composition.

Introduction

The study of excited states of tris(bipyridyl) transition-metal complexes in nonaqueous solvents has demonstrated that the nature of the solvent can exert large effects on the processes observed. These effects can arise without change in the energy of the lowest excited state(s) with variation in solvent properties.

In some relatively simple cases, the solvent effects can be traced to variations in the kinetics of nonradiative decay of the excited state. For example, the luminescence lifetime and quantum yield, the racemization quantum yield, and the photochemical quantum yield of $[Ru(bpy)_3]^{2+}$ are all found to be greater in D_2O than in H_2O.[1-4] In this case the effect has been attributed to a decrease in the efficiency of nonradiative deactivation of the excited state via O–D vibrations vis-à-vis O–H vibrations. On the other hand, no such deuterium isotope effect has been observed for the excited-state decay of $[Cr(bpy)_3]^{3+}$.[5,6]

The use of nonhydroxylic solvents can lead to a more complicated situation. Inasmuch as O–H vibrations are important in radiationless decay, there will naturally be an alteration of the lifetime and quantum yields. Furthermore, differences in the chemical properties of various solvents (ligating ability, redox potential, etc.) can provide pathways for photochemical reactions which are inaccessible in water. The recent literature provides several examples of the effect of nonhydroxylic solvents on the photo processes of $[Ru(bpy)_3]^{2+}$. In aqueous solution the photochemical quantum yield of this complex is too small to be detected ($<10^{-5}$) at room temperature. As the temperature is raised, the quantum yield increases, although it remains small ($\Phi = 5.3 \times 10^{-4}$ at 90 °C in 0.1 M HCl).[3] On the other hand, photosubstitution of $[Ru(bpy)_3]^{2+}$ proceeds much more readily in nonhydroxylic solvents. In chlorinated hydrocarbons, $Ru(bpy)_2Cl_2$ is formed at room temperature with $\Phi = 0.02$.[7] In neat DMF, photosolvation of $[Ru(bpy)_3]^{2+}$ occurs at room temperature with $\Phi \approx 10^{-4}$ and the complex also undergoes photoanation with an increase in quantum yield when NCS^- is added.[8] The increase in photochemical quantum yield for $[Ru(bpy)_3]^{2+}$ in nonhydroxylic solvents is accompanied by an increase in the luminescence lifetime; for example, at 25 °C $\tau = 0.60$, 0.80, 0.82, and 1.03 μs in H_2O, CH_3CN, DMF, and Me_2SO, respectively.[2,9]

When $[Cr(bpy)_3]^{3+}$ is irradiated in neat argon-saturated DMF at room temperature, a number of effects are observed which indicate that the excited-state processes of this complex are quite different from those which occur in aqueous solution. These effects are more dramatic than those reported for the Ru(II) analogue. The luminescence lifetime and quantum yield of $[Cr(bpy)_3]^{3+}$ in DMF are a factor of 15 smaller than they are in water.[10] The photochemical quantum yield for disappearance of substrate in DMF is greater than it is in water ($\Phi_{aq} = 0.18$ at pH 9–10).[11]

The increase in photochemical quantum yield of $[Cr(bpy)_3]^{3+}$ in DMF is the focus of this report. Our data support the hypothesis that the kinetics of radiationless deactivation are solvent dependent. Furthermore, in DMF the initial photoreduction of the substrate to form a kinetically labile Cr(II) complex plays a major role in the overall reaction mechanism. Reduction of the excited $[Cr(bpy)_3]^{3+}$ complex by H_2O is also thermodynamically feasible, although it has never been reported. In aqueous solution $[Cr(bpy)_3]^{2+}$ has been observed in flash photolysis experiments using $[Cr(bpy)_3]^{3+}$ in the presence of reducing agents such as ferrous ion.[12] In that case, the ^2E $[Cr(bpy)_3]^{3+}$ excited state was quenched, and a transient absorption spectrum with maxima at 470 and 560 nm was observed and assigned as $[Cr(bpy)_3]^{2+}$.[12,13] Similar behavior of the Cr(III) complex has

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