

## Silver Iodide Complexes in Fused Potassium-Sodium Nitrate

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The complex formation between silver and iodide ions in an equimolar melt of potassium-sodium nitrate at  $(280 \pm 1)^\circ\text{C}$  has been studied using both solubility measurements and potentiometric measurements with silver electrodes in melts saturated or unsaturated with solid silver iodide.

Evidence has been found for the existence of the species  $\text{Ag}^+$ ,  $\text{AgI}$ ,  $\text{AgI}_2^-$  and  $\text{AgI}_3^{2-}$  in the melt. Because of experimental difficulties it has not been possible to prove or disprove the presence of species containing more than three iodide ligands.

### SOLUBILITY MEASUREMENTS

The solubility of solid silver iodide in an equimolar melt of sodium nitrate and potassium nitrate has been studied at  $(280 \pm 1)^\circ\text{C}$  as a function of the concentration of iodide ions, which were added to the melt as an equimolar mixture of sodium iodide and potassium iodide. The silver iodide was labelled with  $^{110\text{m}}\text{Ag}$  and most of the solubilities were determined by a radio assay technique. Solubilities above 1 mmole/kg were also determined by electro-analyses from aqueous solutions containing an excess of cyanide.

### EXPERIMENTAL

The method of measurement has been described by Cigén and Mannerstrand,<sup>1</sup> and only a few further details will be given here.

About 10 mg (more at high solubilities) silver iodide was added to 50 g of the melt. The mixture was stirred until equilibration was established, which needed from two hours to two days, depending on the iodide concentration.

No oxidation of the iodide to iodate or iodine could be detected. The concentration of iodide in the melt was unchanged after four days.

A sample of the melt was separated from the precipitate with a preheated filter-stick. The sample was then poured into a beaker of pyrex glass in order to cool, after which it was dissolved in an aqueous cyanide solution and radio-analyzed or electro-analyzed for silver.

Table 1 contains the results of the solubility measurements.

Table 1. The solubility,  $S$ , of silver iodide at various concentrations of added alkali iodide,  $C_I$ .

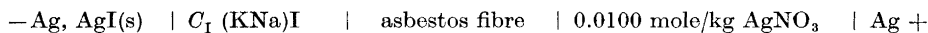
$C_I \times 10^3/\text{mole kg}^{-1}$ ,  $S \times 10^5/\text{mole kg}^{-1}$ ;

0, 2.70; 0.0268, 1.78; 0.0539, 1.27; 0.0983, 0.865; 0.176, 0.669; 0.320, 0.517; 0.590, 0.503; 0.980, 0.524; 2.10, 0.759; 4.97, 1.43; 10.05, 2.64; 21.8, 5.81; 49.7, 15.9; 99.7, 42.3; 191, 121; 350, 370; 600, 1180; 799, 2240.

*Chemicals.* Potassium iodide (BDH AnalaR) and sodium iodide (Mallinckrodt *p.a.*) were dried and used without further purification. Labelled silver iodide was prepared by dissolving 0.2 g silver metal,  $^{110m}\text{Ag}$  (9 mC/g) from AERE, Harwell, England in 3.5 M nitric acid. After dilution of this solution silver iodide was precipitated at 90°C by adding a hot dilute solution of potassium iodide (*cf.* Vogel<sup>2</sup>). The precipitate was washed with 1 % nitric acid and water, dried at 110°C and was then stored protected from light. No darkening of the silver iodide could be observed.

### POTENTIOMETRY

The emf's of cells with the following composition were measured to determine the solubility product,  $K_{s,0}$ , of silver iodide



Stable emf's (within  $\pm 0.5$  mV) were obtained in less than an hour when  $C_I > 1$  mmole/kg. For lower concentrations of iodide no stable emf's could be obtained. Table 2 contains the results for these cells with melts saturated with silver iodide.

For the computation of  $K_{s,0}$  Cigén and Mannerstrand's<sup>3</sup> value of  $RTF^{-1} \ln 10 = 108.1$  mV, was used, since their value was determined with the same equipment as ours. It corresponds to a temperature a little lower than 280°C. Probably heat leakage through the metal connections of the silver electrodes causes a somewhat lower temperature at the surface of the electrodes than in the bulk of the melt. In all melts (except the last one in Table 2), where stable emf's could be obtained, the difference between  $C_I$  and the concentration of free iodide ions is less than 1 %, because of the low solubility of silver iodide. However, a small correction of  $C_I$  to  $[\text{I}^-]$  has been introduced when computing  $K_{s,0}$  (*cf.* Ref. 3). The result is compared with values from the literature in Table 3.

Table 2. Potentiometric measurements in saturated solutions.

$$[\text{Ag}^+]_{\text{ref}} = 10.0 \text{ mmole/kg.}$$

$C_I \times 10^3/\text{mole kg}^{-1}$ ,  $E/\text{mV}$ ,  $K_{s,0} \times 10^{10}/(\text{mole kg}^{-1})^2$ ;

0, (269), (10.4); 1.049, (457), (6.2); 3.09, 509.2, 6.01; 7.99, 554.8, 5.88; 20.28, 599.5, 5.76; 61.2, 651.5, 5.72; 163.9, 697.4, 5.74; 791, 768.6, 5.72.

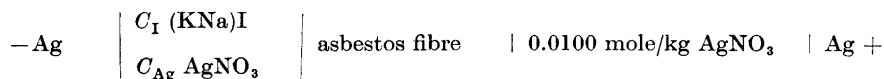
$$K_{s,0,\text{average}} = (5.8 \pm 0.1) \times 10^{-10} (\text{mole/kg})^2$$

Table 3. Review of measurements of the solubility product  $K_{s,0}$  in equimolar mixtures of  $\text{KNO}_3$  and  $\text{NaNO}_3$ .

Author	Ref.	Method	Temp. °C	$\frac{K_{s,0} \times 10^{10}}{(\text{mole/kg})^2}$
Flengas, Rideal	4	Pot.	250	1.86
» »	4	Calc.	280	8.7 <sup>a</sup>
Blander, Luchsinger	5	Pot.	250	1.62
» »	5	Calc.	280	6.9 <sup>a</sup>
Swofford	6	Pot.	248	4.0
This paper		Sol.	280	6.2
» »		Pot.	280	5.8

<sup>a</sup> Calculated from the measured value at 250°C and the values of the enthalpy change given in the paper.

A few potentiometric measurements were also carried out in unsaturated melts. Emf's of the following cell were measured



Because of the low solubility of silver iodide,  $C_{\text{Ag}}$  must not exceed 2 mmole/kg and the range of  $C_{\text{I}}$  was 0.2 mole/kg  $< C_{\text{I}} < 0.8$  mole/kg.

The reproducibility of the measurements is not very good at such small silver concentrations (*cf.* Mannerstrand and Cigén<sup>3</sup>) and the absolute uncertainty is probably as large as 5 mV. When the measurements are performed

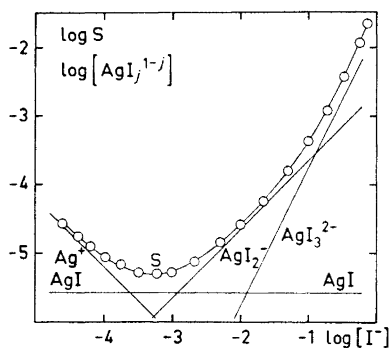


Fig. 1. The solubility curve for silver iodide calculated from the first set of  $k_j$ -values in Table 5. The four straight lines show the concentrations of  $\text{Ag}^+$ ,  $\text{AgI}$ ,  $\text{AgI}_2^-$  and  $\text{AgI}_3^{2-}$  in melts saturated with solid silver iodide.

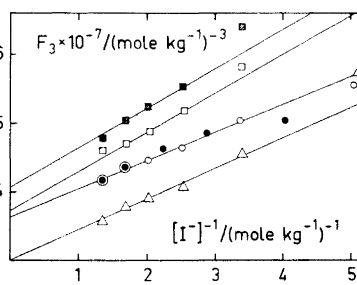


Fig. 2. The function  $F_3([I^-]^{-1})$  from potentiometric measurements in unsaturated melts. The lines are drawn to show how much slope and intercept diverge from one titration series to another. The symbols are defined in Table 4.

as potentiometric titrations with constant  $C_{\text{Ag}}$  and increasing  $C_{\text{I}}$  the relative accuracy within one such series is a little better, perhaps 1 or 2 mV. Table 4 contains five examples of such titrations performed at three different values of  $C_{\text{Ag}}$ .

Table 4. Potentiometric measurements in unsaturated solutions.  $[\text{Ag}^+]_{\text{ref}} = 10.0$  mmole/kg. The symbols in the table have been used in Fig. 2 to distinguish the titrations with various  $C_{\text{Ag}}$ .

	$C_{\text{I}}/\text{mole kg}^{-1}$ , $E/\text{mV}$ ;
△:	$C_{\text{Ag}} = 0.624$ mmole/kg. 0.1967, 739.0; 0.2962, 786.0; 0.3956, 821.7; 0.4950, 851.4; 0.5942, 875.7; 0.7440, 904.7.
●:	$C_{\text{Ag}} = 1.00$ mmole/kg. 0.2511, 745.2; 0.3506, 791.0; 0.4500, 824.0; 0.5988, 861.7; 0.7481, 891.1.
○:	$C_{\text{Ag}} = 1.00$ mmole/kg. 0.2009, 717.2; 0.3005, 770.0; 0.3998, 806.6; 0.4987, 836.0; 0.5974, 860.3; 0.7462, 889.9.
□:	$C_{\text{Ag}} = 2.04$ mmole/kg. 0.3000, 741.4; 0.3982, 776.4; 0.4965, 805.0; 0.5952, 829.0; 0.7461, 860.1.
■:	$C_{\text{Ag}} = 2.04$ mmole/kg. 0.3004, 746.0; 0.4002, 780.0; 0.5000, 809.1; 0.5987, 833.0; 0.7494, 862.5.

## RESULTS AND DISCUSSION

The solubility,  $S$ , of silver iodide may be described as a polynomial function of the iodide concentration.

$$S = \sum_{j=-1}^{3 \text{ or } 4} k_j [\text{I}^-]^j \quad (1)$$

where  $-j$  is the charge of the silver species  $\text{Ag}_m \text{I}_n^{-j}$ . Hence  $j = n - m$ . If there is only one species of each charge in the melt the constants  $k_j$  may be written as

$$k_j = K_{s,0}^m \times \beta_{n,m} \quad (2)$$

If there are several species of the same charge,  $k_j$  is a sum of terms similar to that in eqn. 2, *vide e.g.* Leden<sup>7</sup> or Johansson.<sup>8</sup> The latter paper gives an exhaustive review of various possibilities to study complex formation by solubility methods. In our case

$$K_{s,0} = [\text{Ag}^+][\text{I}^-] \quad (3)$$

and

$$\beta_{n,m} = [\text{Ag}_m \text{I}_n^{-j}] \times [\text{Ag}^+]^{-m} \times [\text{I}^-]^{-n} \quad (4)$$

The constants  $k_j$  in eqn. (1) were calculated by graphical and least squares methods as described by Cigén and Mannerstrand.<sup>1</sup> To get a curve which fits the results it was necessary to use at least five terms in the right hand side of eqn. (1), *viz.* terms corresponding to  $j = -1, 0, 1, 2$ , and 3 or  $j = -1, 0, 1, 2$ , and 4. Of course the results can also be described by an equation containing six terms in the right hand side of eqn. (1).

The calculated constants are given in Table 5. Because of the low solubility the concentration of free iodide,  $[I^-]$ , is very close to  $C_I$  in almost the whole range studied. One exception is the solubility of silver iodide in pure alkali nitrate melt,  $C_I=0$ , and a second exception is found at the highest values of  $C_I$ , where the solubility is high enough to cause a substantial difference between  $C_I$  and  $[I^-]$ . Hence the constant  $k_3$  (and similarly for  $k_4$ ) is somewhat dependent on which species with charge  $-3$  exist in the melt, *e.g.*  $AgI_4^{3-}$  or  $Ag_2I_5^{3-}$  (*cf.* Johansson<sup>8</sup>). The constants  $k_{-1}$ ,  $k_0$ ,  $k_1$ , and  $k_2$  on the other hand do not depend on which species are formed with the corresponding charges,  $+1$ ,  $0$ ,  $-1$ , and  $-2$ , because of the low solubility in the range where these species predominate. The potentiometric measurements, however, favour the choice  $Ag^+$ ,  $AgI_2^-$  and  $AgI_3^{2-}$  and it is then reasonable to assume that the uncharged species in the melt is  $AgI$ .

In Fig. 1 it is shown how eqn. (1) fits the experimental solubilities, if the set of constants for the mononuclear case in Table 5 is used. The two other sets of constants in Table 5 describe the solubility measurements about equally well.

From the constants  $k_j$  in Table 5 the corresponding stability constants  $\beta_{n,m}$  have been calculated from eqn. (2) (*vide* Table 6). For  $K_{s,0}$  the value

Table 5. Three sets of constants,  $k_j$ , each of which may be used to describe the solubilities.

$k_j$	1 Only mononuclear complexes	2 Mononucle. compl. and $Ag_2I_5^{3-}$	3 Mononucle. compl. and $Ag_2I_6^{4-}$
$k_{-1} \times 10^{10}/(\text{mole kg}^{-1})^2$	$6.2 \pm 0.1$	$6.2 \pm 0.1$	$6.1 \pm 0.1$
$k_0 \times 10^6/\text{mole kg}^{-1}$	$2.6 \pm 0.1$	$2.6 \pm 0.1$	$2.7 \pm 0.1$
$k_1 \times 10^3$	$2.21 \pm 0.04$	$2.19 \pm 0.04$	$2.12 \pm 0.04$
$k_2 \times 10^2/(\text{mole kg}^{-1})^{-1}$	$1.7 \pm 0.1$	$1.8 \pm 0.1$	$2.2 \pm 0.1$
$k_3 \times 10^2/(\text{mole kg}^{-1})^{-2}$	$2.6 \pm 0.2$	$2.3 \pm 0.2$	—
$k_4 \times 10^2/(\text{mole kg}^{-1})^{-3}$	—	—	$2.7 \pm 0.2$

$(6.0 \pm 0.2) \times 10^{-10}$  (mole/kg)<sup>2</sup> has been used, which is the average of the values from the potentiometric and solubility determinations,  $(5.8 \pm 0.1) \times 10^{-10}$  (mole/kg)<sup>2</sup>, and  $(6.2 \pm 0.1) \times 10^{-10}$  (mole/kg)<sup>2</sup>, respectively. Hence it has been assumed that  $K_{s,0}$  remains constant, *i.e.* that the solid phase is pure  $AgI$  in all cases. At iodide concentrations above 0.8 mole/kg the solid melts to a liquid phase of a higher density and a much deeper colour than the nitrate melt. At such high iodide concentrations the system hence consists of two liquid phases. Holmberg<sup>9</sup> has studied systems around the point of phase transformation and found that the composition of the solid is not quite constant in a narrow range of iodide concentration below this point. This invalidates to an unknown extent the use of eqn. (2) for the highest iodide concentrations which makes any conclusion drawn from solubility measurements hazardous for all species containing more than three iodide ligands.

The melts from the potentiometric measurements in unsaturated solutions may be treated in the following way.

The concentration of free silver ions,  $[Ag^+]$ , is computed from the eqn.

$$E = 108.1 \text{ mV} \times \log (0.01 \text{ m}/[Ag^+]) \quad (5)$$

Then

$$F_3 = C_{Ag}/[Ag^+][I^-]^3 \quad (6)$$

is computed and plotted as a function of  $[I^-]^{-1}$ , where  $[I^-] = C_I$  with sufficient accuracy, since  $C_{Ag} \ll C_I$  in the range studied. The result is shown in Fig. 2, from which it can be seen that  $F_3([I^-]^{-1})$  may be approximately described by one straight line for each titration series.

If only mononuclear complexes existed in the melt all the experimental points should fall on the same line. Polynuclear complexes cause one separate line for each  $C_{Ag}$ . These lines would approach each other and a mononuclear limit curve when  $C_{Ag}$  decreases. From Fig. 2 it is obvious, however, that the curves for the two lowest values of  $C_{Ag}$  are instead more separated than the curves for the two highest  $C_{Ag}$ . This result cannot be described by any kind of complex species and must at least partly be caused by experimental difficulties, which increase with decreasing silver concentrations. Hence the only conclusion to be drawn from Fig. 2 is that mainly two species exist in this range, *viz.*  $AgI_2^-$  and  $AgI_3^{2-}$ . If this is true, it follows that

$$C_{Ag} = [AgI_2^-] + [AgI_3^{2-}] = \beta_{2,1}[Ag^+][I^-]^2 + \beta_{3,1}[Ag^+][I^-]^3 \quad (7)$$

Hence from eqn. (6) and eqn. (7).

$$F_3 = \beta_{3,1} + \beta_{2,1}[I^-]^{-1} \quad (8)$$

The lines in Fig. 2 then give as an average  $\beta_3 = (3.5 \pm 0.5) \times 10^7$  (mole/kg)<sup>-3</sup> as the ordinate for  $[I^-]^{-1} = 0$ , and  $\beta_2 = (4.5 \pm 1) \times 10^6$  (mole/kg)<sup>-2</sup> as the slope of the lines. These values are compared with the constants from the solubility measurements in Table 6, from which it is seen that the two pairs of values coincide within the limits of uncertainty, which are, unfortunately, rather broad.

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Table 6. The complexity constants for  $AgI$ ,  $AgI_2^-$  and  $AgI_3^{2-}$  calculated from the solubility and potentiometric measurements.

$\beta_{m+n,n}$	Sol.	Pot.
$\beta_{1,1} \times 10^{-3}/\text{mole kg}^{-1}$	$4.2 \pm 0.3$	—
$\beta_{2,1} \times 10^{-6}/(\text{mole kg}^{-1})^2$	$3.6 \pm 0.2$	$4.5 \pm 1$
$\beta_{3,1} \times 10^{-7}/(\text{mole kg}^{-1})^3$	$2.9 \pm 0.3$	$3.5 \pm 0.5$

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