

## Complex Formation between Silver and Iodide Ions in Fused Potassium—Sodium Nitrate. I. A Potentiometric Investigation of the Complex Formation at High Iodide Concentrations

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The stepwise formation of complexes  $\text{Ag}_m\text{I}_n^{(n-m)-}$  in fused equimolar  $(\text{K},\text{Na})\text{NO}_3$  at  $280^\circ\text{C}$  has been followed by means of potentiometric determination of the free silver ion concentration at varied concentrations of  $(\text{K},\text{Na})\text{I}$ , *viz.* in the range  $0.3 \text{ mol kg}^{-1} \leq C_{\text{I}} \leq 1.5 \text{ mol kg}^{-1}$ . From separate potentiometric measurements in melts saturated with  $(\text{K},\text{Na})\text{I}$  it has been shown, that only mono- and dinuclear species are present in significant amounts. In the concentration range investigated the complexes  $\text{AgI}_2^-$ ,  $\text{AgI}_3^{2-}$ , and  $\text{Ag}_2\text{I}_4^{4-}$  have been proved to exist, and the corresponding stability constants have been calculated. Evidence has also been found for the existence of a fourth mononuclear complex,  $\text{AgI}_4^{3-}$ , and an approximate value of the stability constant  $\beta_{41}$  has been estimated.

The complex formation between  $\text{Ag}^+$  and  $\text{I}^-$  in fused salt media has lately been studied by solubility<sup>1</sup> and electromotive force<sup>1-5</sup> measurements. As compared to the silver chloride and bromide systems our knowledge of the iodide system is rather scarce. This may to some extent be due to the small solubility of  $\text{AgI}$  in most ionic melts, causing the concentration range available for thermodynamic measurements to be narrow and unfavourably situated. In most works carried out hitherto no higher complexes than  $\text{AgI}_2^-$  have been reported. Elding and Leden,<sup>1</sup> however, recently proved the existence of  $\text{AgI}_3^{2-}$  in fused equimolar  $(\text{K},\text{Na})\text{NO}_3$  at  $280^\circ\text{C}$  by solubility measurements.

As for the bromide system no higher mononuclear complex than  $\text{AgBr}_3^{2-}$  could be detected in the same medium by Cigén and Mannerstrand,<sup>6</sup> employing both solubility and emf measurements.

One aim of the present investigation has been to make clear what higher complexes are formed in the iodide system. It is of particular interest to determine whether silver co-ordinates at most three halide ions or the complex

formation proceeds to  $\text{AgI}_4^{3-}$  in the iodide system as is the case in aqueous solution.<sup>7</sup>

This paper reports results from emf measurements with cells of the following three types:

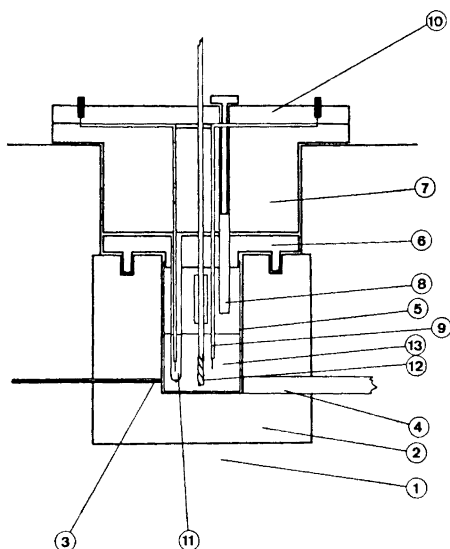
I:	Ag	$C_{\text{Ag}} \text{AgNO}_3$	asbestos fibre	$C_{\text{Ag}}^\circ \text{AgNO}_3$	Ag
II:	Ag	$C_{\text{Ag}} \text{AgNO}_3$ (K,Na)I, saturated	asbestos fibre	$C_{\text{Ag}}^\circ \text{AgNO}_3$ (K,Na)I, saturated	Ag
III:	Ag	$C_{\text{Ag}} \text{AgNO}_3$ $C_{\text{I}} \text{(K,Na)I}$	asbestos fibre	$C_{\text{Ag}}^\circ \text{AgNO}_3$ $C_{\text{I}}^\circ \text{(K,Na)I}$	Ag

In order to avoid the experimental difficulties in the emf measurements, reported by Elding and Leden,<sup>1</sup> a different kind of high-temperature thermostat for potentiometric work has been constructed and tested. The elimination of temperature gradients in the test melt has been of major concern.

#### EXPERIMENTAL

*Chemicals used.* Potassium nitrate and sodium nitrate (Merck, *p.a.*) were powdered and dried at 120°C for two weeks. Silver nitrate (Engelhard, *p.a.*) was used without further treatment. Potassium iodide (Merck, *p.a.*) and sodium iodide (Mallinckrodt, *p.a.*) were dried at 140°C before use.

*Apparatus.* The thermostated cell compartment is shown schematically in Fig. 1. The aluminium block is furnished with two tubes for temperature measurement with Pt-resistance thermometers and two tubes for occasional illumination and observation of the melt. The block is thermostated by a proportional temperature regulator (SWEMA,



*Fig. 1.* Schematic view of the thermostated cell. 1. Insulation. 2. Aluminium block. 3. Platinum resistance thermometer. 4. Observation tube. 5. Pyrex vessel. 6. Aluminium lid. 7. Asbestos plug. 8. Immersed teflon-plugged addition funnel. 9. Bent electrode. 10. Top asbestos lid. 11. Reference half-cell. 12. Stirrer. 13. Test melt.

TK 65). In order to effect heating of the melt from above, a removable aluminium lid is resting at the top of the block. The electrodes and the upper part of the reference half-cell vessels are closely fixed to this hot lid.

Four electrodes and the stirrer run through narrow apertures in an 80 mm thick asbestos plug over the hot lid. The screw-formed Pyrex glass stirrer has two parallel wings along the axis, making the air circulate over the melt. At their upper end the electrodes are bent at right angles, and the horizontal part is fixed in tracks under the insulating top asbestos lid. This construction provides a well closed system with good temperature uniformity.

The temperature is measured by a Pt-resistance thermometer connected to a bridge (KNAUER), which is furnished with an external variable comparison arm. Since the working Pt-sensor is located in the aluminium block at a distance of ca 4 mm from the melt, it has been calibrated against a standard Pt-resistance thermometer (calibrated by National Physical Laboratory, Teddington) immersed in the test melt. By the same procedure the maximum temperature differences in the bulk melt were recorded. At constant temperature in the aluminium block the maximum differences amounted to 0.04°C. The temperature was maintained at 280.0°C with maximal over-all variations of  $\pm 0.1^\circ\text{C}$  during the emf measurements. Work at further modifications of the furnace construction is in progress.

Two reference electrodes and two indicator electrodes have been used simultaneously. The electrodes were made from spectrographically pure silver wire of 1 mm diameter (Johnson, Matthey & Co., London). They were spotwelded to a platinum wire (0.3 mm diameter) which was sealed into the end of a glass tubing. The electrodes were bent at right angles about 50 mm from their upper end, where the platinum wire ran freely out of the glass tubing. The ends of the platinum wires were connected to plugs in the top asbestos lid. The electrodes were silver-plated before use. Reference electrode vessels were of the same kind as described by Cigén and Mannerstrand.<sup>8</sup>

For the emf measurements a valve potentiometer, PHM4d from Radiometer, Copenhagen, was used. The accuracy of the emf measurements was  $\pm 0.1$  mV.

*Procedure.* In all series of measurements the test melt contained 250.0 g of equimolar (K,Na)NO<sub>3</sub>. Successive weighed amounts of solidified stock melts of AgNO<sub>3</sub> in (K,Na)NO<sub>3</sub> (cells of type I), of pure AgNO<sub>3</sub> (type I and II), or equimolar (K,Na)I (type III) were added through a Pyrex glass addition funnel, which was temporarily immersed through the asbestos plug and the hot aluminium lid.

For cells containing unsaturated solutions stable emf's were obtained within 10 min after each addition. For saturated solutions (cells of type II) stabilization times of about 1 h were required, probably due to slow attainment of equilibrium between solid phase and solution. Occasional checks showed, that the measured emf was stable to  $\pm 0.3$  mV for at least 24 h. The measurements could as a rule be reproduced to within 0.5 mV (or better for cells of type I).

*Cells of type I.* These cells were used to elucidate the validity of the Nernst equation in the form

$$E = E_0 - RTF^{-1} \ln 10 \log C_{\text{Ag}} \quad (1)$$

Reference half-cells with  $C_{\text{Ag}}^\circ = 6.03 \times 10^{-3}$  mol kg<sup>-1</sup> (*i.e.* mol per kg solvent, (K,Na)NO<sub>3</sub>) and  $C_{\text{Ag}}^\circ = 6.02 \times 10^{-4}$  mol kg<sup>-1</sup> were used. Repeated series of measurements were performed in the range  $10^{-5}$  mol kg<sup>-1</sup>  $< C_{\text{Ag}} < 3 \times 10^{-1}$  mol kg<sup>-1</sup>.

*Cells of type II.* The number of silver atoms in polynuclear species has been directly determined from measurements of the emf of cells of type II. In the reference half-cell  $C_{\text{Ag}}^\circ$  was kept at  $8.19 \times 10^{-2}$  mol kg<sup>-1</sup>. Melts, saturated with (K,Na)I, have been investigated in the range  $1 \times 10^{-2}$  mol kg<sup>-1</sup>  $< C_{\text{Ag}} < 12 \times 10^{-2}$  mol kg<sup>-1</sup>.

*Cells of type III.* Unsaturated solutions have been investigated by emf measurements with cells of type III. The composition of the reference half-cell solution was 0.0300 mol kg<sup>-1</sup> AgNO<sub>3</sub> and 1.300 mol kg<sup>-1</sup> (K,Na)I. In the test melt  $C_{\text{Ag}}$  was kept constant and  $C_{\text{I}}$  was varied in each series of measurements. The following values of  $C_{\text{Ag}}$  were used: (1, 3, 10, 20, 40 and 80)  $\times 10^{-3}$  mol kg<sup>-1</sup>. For each  $C_{\text{Ag}}$  the maximal possible range of  $C_{\text{I}}$  was utilized. Thus, most of the concentration range available<sup>8</sup> has been studied.

## VALIDITY OF THE NERNST EQUATION

The measurements of the emf for concentration cells of type I indicate, that eqn. (1) is applicable in the range  $C_{\text{Ag}} > 10^{-4}$  mol kg<sup>-1</sup>. Fig. 2 shows the results from a typical series of measurements. The total amount of experimental data yields a value  $109.2 \pm 0.2$  mV for the factor  $RTF^{-1} \ln 10$ . This value has been used in the further calculations from the emf data. The temperature 280.0°C, however, should give a somewhat higher value, 109.7 mV.

The approximate validity of the Nernst equation for silver concentration cells in different fused nitrate media and at different temperatures has been verified by several authors.<sup>4,6,9-18</sup> For those cases, where the experimental value of the coefficient  $RTF^{-1} \ln 10$  has been given explicitly, this value is lower than the theoretical one at the actual temperature. This remarkable feature has been paid attention to by Cigén and Mannerstrand<sup>6</sup> and by Elding and Leden.<sup>1</sup> They assume, that their low experimental value, 108.1 mV, is caused by a local cooling of the electrode metal surface due to heat leakage through the connection wires. This assumption is strongly supported by the result from this work, where a more thorough care for the thermostating of the system has effected a decrease of the distance from the theoretical value 109.7 mV with 2/3 as compared to the experimental value of Cigén and Mannerstrand.

The linear dependence of  $E$  on  $\log C_{\text{Ag}}$ , indicating constant activity factors and negligible liquid junction potentials in these systems, ceases at  $C_{\text{Ag}} < 10^{-4}$  mol kg<sup>-1</sup> (*vide* Fig. 2). Similar deflections at such low silver nitrate concentrations have been observed before by different authors.<sup>4,6</sup> This may be due in part to the appearance of a mixed electrode function caused by the presence of additional redox systems in minor concentrations. Furthermore, corrosion of the silver electrodes would give a too high concentration of silver ions close to the electrode. This might influence the results to some extent in the most dilute solutions (*cf.* Ref. 15).

Obviously concentrations on the molality scale may be used for activities in the range where eqn. (1) holds, and these melts may — in this respect — be regarded as ideal solutions. On the other hand, no conclusions about solvation phenomena (*cf.* Ref. 19) can be drawn, since measurements of this kind do not give any information on, *e.g.*, species  $\text{Ag}(\text{NO}_3)_n^{(n-1)-}$ . As a matter of fact evidence for Ag—O bonds of covalent character in fused nitrate medium has emerged from data on excess volumes of mixtures,<sup>20</sup> enthalpies of mixing,<sup>21,22</sup> and Raman spectroscopy.<sup>23</sup>

## SOLUTIONS SATURATED WITH ALKALI METAL IODIDE

The rather limited solubility of alkali metal iodide in fused (K,Na)NO<sub>3</sub> offers a unique opportunity of studying the formation of polynuclear silver-iodide complexes under in many respects optimal conditions. In principle one is enabled to determine the number of central atoms in the complexes present by measuring the emf of cells of type II at different  $C_{\text{Ag}}$ . There are at least three obvious advantages associated with this method:

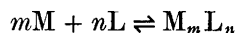
*a.* The reference half-cell solution and the test solution can be made rather similar in composition. Thus, the effects of junction potentials of unknown magnitude may be minimized.

*b.* At maximum concentration of free ligand the total central ion concentration may be varied over the largest range. This is of course a favourable situation when polynuclear complexes are studied.

*c.* There is no need for calculations of the free ligand concentration, based on assumptions about the existence of certain complexes and their stability, since the free ligand concentration has a known constant value,  $1.577 \pm 0.004$  mol kg<sup>-1</sup>, independent of  $C_{Ag}$ . This is important when solutions with high total central ion concentrations are used.

### Calculations and results

The complex formation between the central ion M and the ligand L is described by the equilibria

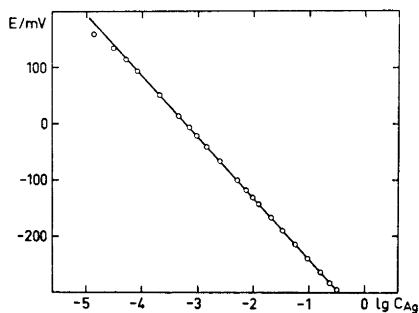


The stability constants,  $\beta_{nm}$ , are defined by

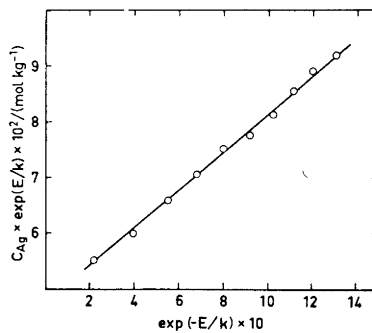
$$\beta_{nm} = [M_m L_n] / ([M]^m [L]^n) \quad (2)$$

The total concentration of central ion may be written

$$C_M = [M] + \sum_m \sum_n m [M_m L_n] \quad (3)$$



*Fig. 2.* Test of the Nernst equation. The equation of the full-drawn line is  $E/\text{mV} = -351.8 - 109.2 \log C_{Ag}$ . In the reference half-cell  $C_{Ag}^\circ = 6.02 \times 10^{-4}$  mol kg<sup>-1</sup>, yielding  $109.2 \log C_{Ag}^\circ = -351.7$ .



*Fig. 3.* Relation between  $C_{Ag} \exp(E/k)$  and  $\exp(-E/k)$  for melts saturated with (K,Na)I.

Introducing the symbols

$$\begin{aligned} X &= 1 + \sum_n \beta_{n1}[\text{L}]^n \\ Y &= \sum_n \beta_{n2}[\text{L}]^n \\ Z &= \sum_n \beta_{n3}[\text{L}]^n \\ &\text{etc.} \end{aligned}$$

eqn. (3) may be rewritten as

$$C_{\text{M}}/[\text{M}] = X + [\text{M}] 2Y + [\text{M}]^2 3Z + \dots \quad (4)$$

Since  $[\text{L}]$  is constant, the polynomials  $X, Y, Z, \dots$  take constant values. As  $C_{\text{M}}$  and  $[\text{M}]$  are known from the measurements, it is, in principle, possible to determine the order of the polynomial function of  $[\text{M}]$  in the right member of eqn. (4).

The emf,  $E$ , of cell II is

$$E = k \ln [\text{Ag}^+]_0/[\text{Ag}^+] \quad (5)$$

where  $k = 109.2 \text{ mV}/\ln 10$ .  $[\text{Ag}^+]$  and  $[\text{Ag}^+]_0$  stand for the silver ion concentration in the test melt and in the reference melt, respectively. Combination of eqns. (4) and (5) gives

$$\begin{aligned} C_{\text{Ag}} \exp(E/k) &= [\text{Ag}^+]_0 X + [\text{Ag}^+]_0^2 2Y \exp(-E/k) + \\ &+ [\text{Ag}^+]_0^3 3Z [\exp(-E/k)]^2 + \dots \end{aligned} \quad (6)$$

Table 1 gives data from a typical series of measurements. A plot of  $C_{\text{Ag}} \exp(E/k)$  versus  $\exp(-E/k)$  reveals which terms are important in the right member of eqn. (6) (see Fig. 3). It is obvious that there is a linear relationship between these quantities. Consequently the only significant terms in the right member of eqn. (6) are the  $X$  and  $Y$  terms, *i.e.* only mono- and dinuclear species are present in observable amounts. The treatment of data from measurements in unsaturated solutions has been partly based upon this fact.

From eqns. (4) and (6) it is obvious that the sum of the intercept and the slope of the straight line in Fig. 3 should be equal to the total silver ion concentration in the reference half cell,  $C_{\text{Ag}}^\circ$ . The sum of the slope and the intercept amounts to  $0.081 \text{ mol kg}^{-1}$  whereas  $C_{\text{Ag}}^\circ$  was  $0.0819 \text{ mol kg}^{-1}$ . This good agreement indicates that these measurements are self-consistent. A further discussion of the values of the intercept,  $[\text{Ag}^+]_0 X$ , and the slope,  $[\text{Ag}^+]_0^2 2Y$ , in relation to the results from the measurements in unsaturated melts will appear below.

Table 1. Potentiometric measurements in solutions, saturated with (K,Na)I. Data from a typical series.

$C_{\text{Ag}} \times 10^2/(\text{mol kg}^{-1}), E/\text{mV}, \exp(-E/k) \times 10, C_{\text{Ag}} \exp(E/k) \times 10^2/(\text{mol kg}^{-1});$
1.206, 72.1, 2.185, 5.52; 2.375, 43.9, 3.96, 5.99; 3.63, 28.3, 5.51, 6.59; 4.80, 18.4, 6.78, 7.07; 6.00, 10.7, 7.97, 7.53; 7.14, 4.0, 9.19, 7.76; 8.34, -1.1, 10.24, 8.13; 9.53, -5.1, 11.13, 8.56; 10.69, -8.7, 12.00, 8.91; 11.83, -12.6, 13.05, 9.09;

## EMF MEASUREMENTS IN UNSATURATED MELTS

The measurements have been performed with cells of type III. If the emf of the cell is  $E_1$  for  $C_L = 0$  and  $E_2$  for  $C_L > 0$ , eqn. (7) is valid for the difference  $E_M = E_1 - E_2$ .

$$E_M = 109.2 \text{ mV} \log C_M/[M] \quad (7)$$

For a system containing dinuclear and four mononuclear species eqn. (4) may be rewritten as

$$\frac{C_M/[M] - 1 - \beta_{11}[L] - \beta_{21}[L]^2}{[L]^4} = \beta_{41} + \beta_{31}[L]^{-1} + 2[M] \sum_n \beta_{n2}[L]^{n-4} \quad (8)$$

The left hand member of eqn. (8) is denoted  $f_4$ . In  $f_4$  the term  $C_M/[M]$  is known from eqn. (7) and the last term in the denominator is a small correction term in the pertinent range of  $[L]$ . A preliminary value of this term is obtained from Ref. 1. The two remaining terms of the denominator are negligible. Hence  $f_4$  is known as a function of  $[L]$ , which is obtained from the equation

$$[L] = C_L - \bar{n} C_M \quad (9)$$

where  $\bar{n} = 3$  is a good starting value in the first step of an iterative procedure to determine the stability constants from eqn. (10)

$$f_4 = \beta_{41} + \beta_{31}[L]^{-1} + 2[M] \sum_n \beta_{n2}[L]^{n-4} \quad (10)$$

More accurate values of  $\bar{n}$  can then be calculated from eqn. (11)

$$\bar{n} = \frac{\sum_n n \beta_{n1}[L]^n + [M] \sum_n n \beta_{n2}[L]^n}{1 + \sum_n \beta_{n1}[L]^n + 2[M] \sum_n \beta_{n2}[L]^n} \quad (11)$$

From eqn. (9) better values of  $[L]$  are obtained to be used in eqn. (10), *etc.*

## Calculations

The data from the measurements are given in Table 2. A plot of  $f_4$  against  $[I^-]^{-1}$  for each series of measurements, in which  $C_{Ag}$  is kept constant, gives a family of curves similar to the one in Fig. 5. For various fixed  $[I^-]$  the limiting values

$$\lim_{[Ag^+] \rightarrow 0} f_4 = f_4^\circ$$

have been determined by means of linear least squares extrapolations to  $[Ag^+] = 0$  (*cf.* eqn. (10)). The requisite values of  $[Ag^+]$  have been obtained by graphical interpolations between the measured values of  $[Ag^+]$  (from eqn. (7)) as a function of calculated  $[I^-]$  for each series.

A plot of  $f_4^\circ$  *vs.*  $[I^-]^{-1}$  yields a straight line (*cf.* Fig. 6) represented by the equation

$$f_4^\circ = \beta_{41} + \beta_{31}[L]^{-1}$$

Table 2. Potentiometric measurements in unsaturated solutions. The values of  $f_4$  and  $[I^-]$  are those calculated in the last cycle.

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$C_I/(\text{mol kg}^{-1}), E_M/\text{mV}, [I^-]/(\text{mol kg}^{-1}), f_4 \times 10^{-7}/(\text{mol kg}^{-1})^{-4};$

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$C_{Ag} = 0.916 \times 10^{-3} \text{ mol kg}^{-1}$

0.348, 670.0, 0.346, 6.95; 0.394, 686.9, 0.392, 6.28; 0.437, 701.1, 0.434, 5.77; 0.484, 715.2, 0.481, 5.25; 0.535, 729.1, 0.532, 4.83; 0.579, 739.2, 0.576, 4.40; 0.623, 749.3, 0.620, 4.12; 0.662, 757.6, 0.660, 3.86; 0.712, 768.0, 0.709, 3.65; 0.758, 776.7, 0.756, 3.43; 0.805, 785.2, 0.802, 3.26; 0.857, 794.9, 0.854, 3.15; 0.904, 802.3, 0.901, 2.986; 0.950, 809.3, 0.947, 2.855; 0.999, 816.5, 0.997, 2.728; 1.046, 823.2, 1.043, 2.630; 1.095, 829.5, 1.092, 2.509; 1.142, 835.3, 1.139, 2.408; 1.186, 841.0, 1.183, 2.343; 1.234, 846.7, 1.231, 2.263; 1.279, 852.3, 1.276, 2.214; 1.324, 857.3, 1.321, 2.152; 1.370, 862.1, 1.367, 2.081; 1.414, 866.5, 1.411, 2.015; 1.465, 871.3, 1.462, 1.942;

$C_{Ag} = 0.980 \times 10^{-3} \text{ mol kg}^{-1}$

0.339, 666.9, 0.336, 7.24; 0.396, 687.6, 0.393, 6.28; 0.463, 709.2, 0.460, 5.51; 0.500, 719.3, 0.498, 5.04; 0.553, 733.5, 0.550, 4.66; 0.616, 747.7, 0.613, 4.14; 0.667, 758.1, 0.664, 3.80; 0.724, 770.0, 0.721, 3.56; 0.780, 780.9, 0.777, 3.37; 0.837, 791.0, 0.834, 3.18; 0.891, 800.3, 0.888, 3.03; 0.943, 807.9, 0.940, 2.848; 0.991, 815.2, 0.988, 2.743; 1.059, 824.0, 1.056, 2.548; 1.133, 833.9, 1.130, 2.408; 1.197, 842.4, 1.194, 2.333; 1.251, 849.5, 1.248, 2.280; 1.310, 856.2, 1.307, 2.196; 1.371, 863.1, 1.368, 2.120; 1.426, 868.8, 1.422, 2.054;

$C_{Ag} = 3.22 \times 10^{-3} \text{ mol kg}^{-1}$

0.405, 692.7, 0.396, 6.99; 0.452, 707.0, 0.443, 6.15; 0.501, 721.0, 0.492, 5.56; 0.549, 734.0, 0.539, 5.15; 0.597, 745.5, 0.587, 4.74; 0.645, 756.2, 0.635, 4.40; 0.694, 767.1, 0.685, 4.15; 0.740, 776.3, 0.731, 3.93; 0.789, 785.6, 0.780, 3.72; 0.835, 793.7, 0.826, 3.54; 0.886, 802.1, 0.877, 3.34; 0.937, 810.2, 0.927, 3.19; 0.991, 818.0, 0.981, 3.02; 1.045, 825.9, 1.035, 2.894; 1.093, 832.4, 1.083, 2.780; 1.146, 839.0, 1.136, 2.656; 1.197, 845.3, 1.187, 2.552; 1.247, 851.3, 1.237, 2.461; 1.295, 857.0, 1.285, 2.393; 1.343, 862.4, 1.333, 2.327; 1.390, 867.2, 1.380, 2.244; 1.439, 872.2, 1.429, 2.173; 1.491, 877.0, 1.481, 2.090;

$C_{Ag} = 9.89 \times 10^{-3} \text{ mol kg}^{-1}$

0.605, 751.2, 0.577, 5.91; 0.659, 762.7, 0.630, 5.36; 0.711, 773.5, 0.682, 4.93; 0.770, 784.6, 0.741, 4.51; 0.826, 794.7, 0.797, 4.21; 0.887, 805.1, 0.857, 3.95; 0.944, 814.2, 0.914, 3.72; 1.002, 822.9, 0.972, 3.51; 1.064, 831.5, 1.034, 3.31; 1.122, 839.4, 1.092, 3.16; 1.181, 846.7, 1.151, 2.993; 1.241, 854.1, 1.211, 2.869; 1.298, 860.8, 1.267, 2.767; 1.354, 867.0, 1.323, 2.660; 1.409, 872.8, 1.378, 2.562; 1.464, 878.9, 1.434, 2.495;

$C_{Ag} = 20.08 \times 10^{-3} \text{ mol kg}^{-1}$

0.860, 807.9, 0.801, 5.61; 0.914, 816.6, 0.855, 5.21; 0.968, 824.7, 0.908, 4.86; 1.026, 832.6, 0.965, 4.52; 1.082, 840.3, 1.022, 4.24; 1.137, 846.6, 1.076, 3.95; 1.190, 852.9, 1.129, 3.73; 1.242, 858.9, 1.181, 3.55; 1.298, 864.9, 1.237, 3.35; 1.351, 871.0, 1.290, 3.23; 1.403, 876.1, 1.342, 3.03; 1.460, 882.1, 1.400, 2.959; 1.513, 887.9, 1.451, 2.899; 1.567, 894.3, 1.506, 2.873;

$C_{Ag} = 39.7 \times 10^{-3} \text{ mol kg}^{-1}$

1.087, 843.4, 0.968, 5.69; 1.138, 851.1, 1.019, 5.47; 1.192, 857.8, 1.072, 5.15; 1.247, 864.4, 1.127, 4.86; 1.303, 871.1, 1.183, 4.61; 1.356, 876.3, 1.236, 4.33; 1.414, 882.6, 1.294, 4.13; 1.467, 887.6, 1.347, 3.91; 1.525, 893.3, 1.405, 3.73; 1.578, 898.4, 1.457, 3.60; 1.633, 904.0, 1.512, 3.50;



Table 2. Continued.

$$C_{\text{Ag}} = 39.9 \times 10^{-3} \text{ mol kg}^{-1}$$

1.091, 845.0, 0.971, 5.82; 1.142, 851.1, 1.022, 5.40; 1.192, 856.8, 1.072, 5.04; 1.250, 863.5, 1.130, 4.72; 1.308, 870.1, 1.187, 4.45; 1.363, 876.0, 1.243, 4.21; 1.416, 881.4, 1.295, 4.00; 1.473, 886.9, 1.352, 3.79; 1.531, 892.8, 1.410, 3.64;

$$C_{\text{Ag}} = 79.3 \times 10^{-3} \text{ mol kg}^{-1}$$

1.541, 899.7, 1.301, 5.86; 1.596, 904.2, 1.356, 5.47; 1.652, 908.8, 1.412, 5.13; 1.706, 913.6, 1.466, 4.89; 1.760, 917.8, 1.519, 4.64;

The constants  $\beta_{31}$  and  $\beta_{41}$  have been determined from the  $f_4^\circ$ -data, employing least squares calculations.

The number of ligands in dinuclear species has been determined as follows. Introduce

$$D_4 = f_4 - \beta_{41} - \beta_{31}[\text{I}^-]^{-1}$$

Hence, from eqn. (10)

$$D_4 [\text{Ag}^+]^{-1} = 2 \sum_n \beta_{n2} [\text{I}^-]^{n-4} \quad (12)$$

$D_4 [\text{Ag}^+]^{-1}$  has been computed for each pair ( $[\text{I}^-]$ ;  $f_4$ ) in series with  $C_{\text{Ag}} \geq 3 \times 10^{-3} \text{ mol kg}^{-1}$ . In Fig. 4  $\log (D_4 [\text{Ag}^+]^{-1})$  is plotted vs.  $\log [\text{I}^-]$ . Points from

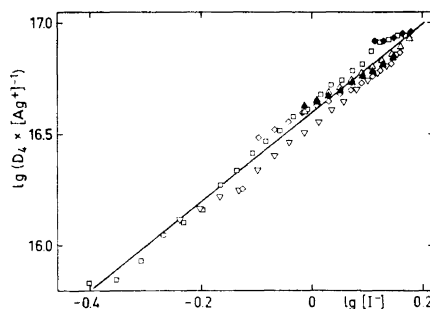


Fig. 4. A plot of  $\log (D_4 [\text{Ag}^+]^{-1})$  vs.  $\log [\text{I}^-]$ . Symbols used:  $C_{\text{Ag}} \times 10^3 / \text{mol kg}^{-1} =$  3.22 ( $\square$ ), 9.89 ( $\nabla$ ), 20.08 ( $\diamond$ ), 39.7 ( $\triangle$ ), 39.9 ( $\blacktriangle$ ), 79.3 ( $\blacklozenge$ ).

different series fall on the same straight line. (The weak tendency to systematic deviation from the line at the highest  $C_{\text{Ag}}$ -values will be discussed below.) The equation of the straight line is

$$\log (D_4 [\text{Ag}^+]^{-1}) = A + B \log [\text{I}^-]$$

with the parameter values:

$$A = 16.59 \pm 0.06$$

$$B = 1.99 \pm 0.05$$

The linearity and the fact that  $B$  assumes the integer value 2 would be the expected result, if only one dinuclear complex,  $\text{Ag}_2\text{I}_6^{4-}$  (with  $n-4=2$ ), is formed (cf. eqn. (12)). Hence,  $\beta_{62}$  may be computed from the relationship  $A = \log 2\beta_{62}$ .

Table 3. The equilibrium constants determined from emf measurements in unsaturated melts. For comparison the stability constants of Elding and Leden<sup>1</sup> are included. The errors quoted for the constants  $\beta_{n1}$  from this work are equal to three standard deviations. For  $\beta_{62}$  an estimated maximum error is given. Because of systematic errors the uncertainty of  $\beta_{41}$  is probably much higher than the error given here.

	AgI	AgI <sub>2</sub> <sup>-</sup>	AgI <sub>3</sub> <sup>2-</sup>	AgI <sub>4</sub> <sup>3-</sup>	Ag <sub>2</sub> I <sub>6</sub> <sup>4-</sup>
$\beta_{nm}/(\text{mol kg}^{-1})^{(1-n-m)}$ Ref. 1.					
Solubility data.					
$\beta_{nm}/(\text{mol kg}^{-1})^{(1-n-m)}$ This work.	$(4.2 \pm 0.3) \times 10^3$	$(3.6 \pm 0.2) \times 10^6$	$(2.9 \pm 0.3) \times 10^7$	—	—
$K_n/(\text{mol kg}^{-1})^{-1}$ $K_1$ from Ref. 1, others from this work.	$4.2 \times 10^3$	$7.4 \times 10^2$	7.3	$(2.8 \pm 0.6) \times 10^6$	$(1.9 \pm 0.7) \times 10^{16}$

Finally a refined value of  $\beta_{21}$  has been derived from eqn. (8). The computation was performed with data from series with  $C_{Ag} = 1 \times 10^{-3}$  and  $3 \times 10^{-3}$  mol kg<sup>-1</sup> in the concentration range where  $\bar{n} < 3$ .

The final values of  $\beta_{nm}$  were obtained after four iterations. Table 2 gives all experimental data and the values of  $f_4$  and  $[I^-]$ , calculated in the last cycle.

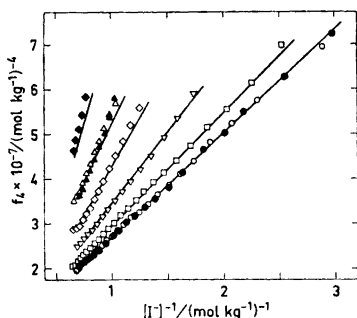


Fig. 5.  $f_4$  as a function of  $[I^-]^{-1}$ . Final values. Symbols used:  $C_{Ag} \times 10^3$ /mol kg<sup>-1</sup> = 0.916 (○), 0.980 (●), 3.22 (□), 9.89 (▽), 20.08 (◇), 39.7 (△), 39.9 (▲), 79.3 (◆). The full-drawn lines are calculated from the set of constants in Table 3.

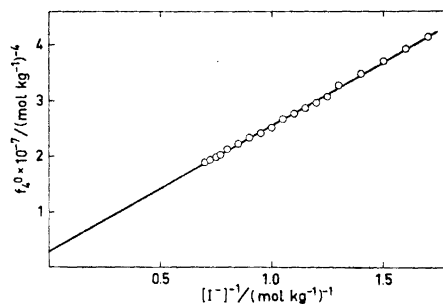


Fig. 6.  $f_4^0$  as a function of  $[I^-]^{-1}$ . The circles represent the extrapolated values.

Fig. 6 shows  $f_4^0$  as a function of  $[I^-]^{-1}$ . The final set of stability constants is given in Table 3 together with the values determined by Elding and Leden.<sup>1</sup>

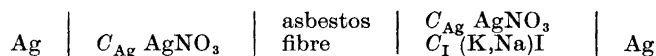
In Fig. 5  $f_4$  is plotted vs.  $[I^-]^{-1}$  for all series of measurements. The full-drawn curves have been calculated from eqns. (4) and (10) using the final set of stability constants.

#### Possible systematic errors

The results from the measurements with cells of type III may be directly compared with those from cells of type II. In principle, the experimental values of  $[Ag^+]_0 X$  and  $[Ag^+]_0^2 2Y$  at  $[I^-] = 1.577$  mol kg<sup>-1</sup> permit an estimation of one stability constant, provided the others are known. Since the values of  $\beta_{21}$  and  $\beta_{31}$  on the whole agree with those from previous solubility measurements (*vide* Table 3), the main interest will be focused to  $\beta_{41}$  and  $\beta_{62}$ . With the values of  $\beta_{21}$ ,  $\beta_{31}$ , and  $\beta_{62}$  obtained from the measurements with cells of type III, the data from cell II yield  $\beta_{41} = 1.6 \times 10^7$  (mol kg<sup>-1</sup>)<sup>-4</sup>. If, on the other hand,  $\beta_{21}$ ,  $\beta_{31}$ , and  $\beta_{41}$  are fixed, the value  $0.64 \times 10^{16}$  (mol kg<sup>-1</sup>)<sup>-7</sup> is obtained for  $\beta_{62}$ .

Even if the estimates of  $\beta_{41}$  and  $\beta_{62}$  refer to one single value of the free ligand concentration, the disagreements with the values of Table 3 are too pronounced to be completely neglected.

It is highly probable that the emf data from cells of type II are on the whole unaffected by liquid junction potentials. On the other hand, the  $E_M$ -values are in principle obtained from the cell



The rather high values of  $C_{\text{I}}$  in these cells might undoubtedly have given rise to a liquid junction potential of unknown magnitude, causing a systematic error in the  $E_{\text{M}}$ -values. Hence, the observed discrepancies in the  $\beta$ -values might be due to the junction potentials.

The magnitude of the liquid junction potential for this cell should most probably depend on  $C_{\text{I}}$  alone. A simple calculation shows that this would cause an error in  $\beta_{41}$  rather than  $\beta_{62}$ . An error in  $\beta_{62}$  alone can only be explained by assuming a liquid junction potential depending on  $C_{\text{Ag}}$  but rather independent of  $C_{\text{I}}$ . Since the latter behaviour seems rather improbable for a cell of this kind, the errors are mostly likely to appear in  $\beta_{41}$ . This might be the explanation of the disagreement between the results from the emf data of cells of type II and III.

#### DISCUSSION

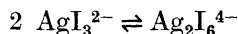
On the whole there is a good fit between the calculated curves of Fig. 5 and the experimental data. At the highest  $C_{\text{Ag}}$ , however, a small deviation is found. A somewhat better fit at these high  $C_{\text{Ag}}$ -values might be obtained by adding one or more terms to the right hand member of eqn. (10). This procedure has been tried, yielding a better, although not perfect fit to the experimental data. Furthermore, there is no unique set of additional terms, giving this small improvement, but the choice may be made rather arbitrarily within certain limits. Thus, one or more additional terms would probably be of questionable physical meaning and it seems, especially in the light of the previous discussion of systematic errors, advisable to refrain from postulating further polynuclear species. It is also possible that the small discrepancies might in part be due to increasing deviations from ideality as the concentration of big complex ions increases.

The values of  $\beta_{21}$  and  $\beta_{31}$  obtained by Elding and Leden<sup>1</sup> from solubility measurements are slightly higher than those from this work (*vide* Table 3). The main reason for this is that the stability constants from the solubility data were calculated without taking into consideration the fraction of silver present as  $\text{AgI}_4^{3-}$  and  $\text{Ag}_2\text{I}_6^{4-}$ .

In the major part of the concentration range investigated,  $\text{AgI}_3^{2-}$  is the predominating species. The existence of a fourth complex,  $\text{AgI}_4^{3-}$ , is probable although a precise value of  $\beta_{41}$  is difficult to obtain, presumably because of the unknown liquid junction potentials. From the discussion of possible systematic errors above it may be concluded that  $\beta_{41} \approx 10^7 (\text{mol kg}^{-1})^{-4}$  is a fair estimate.

The complex  $\text{Ag}_2\text{I}_6^{4-}$  is the only polynuclear species found. A possible structure of this ion would be the one of two tetrahedral  $\text{AgI}_4$ -links, sharing an edge like in solid  $[\text{Ni}(\text{en})_2][\text{AgI}_2]_2$ .<sup>26</sup>

For the dimerization reaction



the equilibrium constant  $k_{3/6} = \beta_{62}/\beta_{31}^2$  is  $(4 \pm 1) \times 10 (\text{mol kg}^{-1})^{-1}$ .

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