

## Complex Formation between Silver and Iodide Ions in Fused Potassium—Sodium Nitrate. IV. Cationic Complexes

BERTIL HOLMBERG

Division of Physical Chemistry, Lund University, Chemical Center, P.O.B. 740, S-220 07 Lund 7, Sweden

The formation of cationic complexes between silver(I) and iodide ions in fused equimolar (K,Na)NO<sub>3</sub> at 280 °C has been studied by potentiometric determination of the free ligand concentration [Ag<sup>+</sup>] and by solubility and distribution measurements in two-phase systems formed by AgI—AgNO<sub>3</sub>—(K,Na)NO<sub>3</sub>, with solid or liquid iodide-based solutions in equilibrium with alkali nitrate melts.

No polynuclear (polyiodic) species can be detected potentiometrically, and the solubility curve and distribution data are well reproduced assuming a stepwise formation of species Ag<sub>m</sub>I<sup>(m-1)+</sup> with 0 ≤ m ≤ 4, of which Ag<sub>4</sub>I<sup>3+</sup> has a remarkably high stability. The equilibrium constants, governing the distribution of solvent and solute species between the iodide phase and nitrate melt, are also estimated.

Previous investigations of the complex formation between silver(I) and iodide ions in fused alkali nitrate performed at this laboratory<sup>1-4</sup> have been concerned mainly with neutral and anionic complexes and heterogeneous equilibria between solid or liquid AgI-based solutions and alkali nitrate melts. From studies in aqueous solution the ability of silver and halide ions to form complexes Ag<sub>m</sub>X<sub>n</sub><sup>(m-n)+</sup> has become evident, and subsequent investigations in other media, including ionic melts, have also presented convincing evidence for complex cations of this kind. This topic has been briefly reviewed recently.<sup>5</sup>

For the case of iodide species the mononuclear (monoiodic) complexes Ag<sub>3</sub>I<sup>+</sup>, Ag<sub>3</sub>I<sup>2+</sup>,<sup>6-10</sup> and even Ag<sub>4</sub>I<sup>3+</sup>,<sup>7</sup> have been suggested to explain solubility data in aqueous solutions. In addition, results from UV spectroscopy<sup>11,12</sup> and self-diffusion studies<sup>13</sup> support the view that complex cations having iodide as central ion

do exist in solution. It should also be noted that a mixed complex AgHgI<sup>2+</sup> has been reported.<sup>14</sup>

It appears, however, that the information concerning cationic silver iodide complexes in fused salts is restricted to an emf study by Alvarez-Funes and coworkers,<sup>15</sup> considering Ag<sub>2</sub>I<sup>+</sup> in liquid KNO<sub>3</sub>. The present study aims at a more complete picture of the nature and thermodynamic stability of cationic silver iodide species in fused alkali nitrate. Due to the impossibility of distinguishing between mono- and polyiodic species having the same ionic charge from solubility measurements alone, we have employed both solubility and electromotive force measurements. The emf measurements have been arranged as an ordinary ligand concentration study in a composition range where the difference between the total and "free" silver(I) concentrations is large enough to be determined with an acceptable accuracy. The following cell was used:



From the measured emf the average number of silver ligands bonded to iodide,  $\bar{m}$ , may be computed. The magnitude of  $\bar{m}$  and the variation in  $\bar{m}$  with  $C_{\text{I}}$  at constant [Ag<sup>+</sup>] may then be used to indicate the presence or absence of condensed particles in measurable amounts.

As might be expected, the solubility measurements were complicated by the ability of the high temperature form of silver iodide, α-AgI, to dissolve foreign ions. In preliminary experiments it was observed that α-AgI dissolves

appreciable amounts of  $\text{AgNO}_3$  at  $280^\circ\text{C}$ . Furthermore the solid melts to a yellow-red liquid  $\text{AgI}$  phase in systems containing more than  $0.7\text{ mol kg}^{-1}$   $\text{AgNO}_3$  in the nitrate melt. This behaviour, which is analogous to what was observed in the system  $\text{AgI}-(\text{K,Na})\text{I}-(\text{K,Na})\text{NO}_3$ ,<sup>3,4</sup> made it necessary to determine the equilibrium composition of the iodide phase as well as the nitrate phase in the entire composition range under study. The evaluation of the stability constants is based on a formal thermodynamic treatment of the heterogeneous equilibria.

## EXPERIMENTAL

**Chemicals.** All chemicals were *p.a.* grade and were prepared and stored as described previously.<sup>3</sup>

**Apparatus.** The equipment used for the solubility and distribution measurements and the emf measurements have been described elsewhere.<sup>3,16,17</sup>

**Solubility and distribution measurements.** Series A: In the major range of  $\text{AgNO}_3$  concentration the solubilities were measured by a radioassay technique, using  $\text{AgI}$  labelled with  $^{131}\text{I}$ . About  $0.1\text{ g}$   $\text{AgI}$  was added to  $50.00\text{ g}$  equimolar  $(\text{K,Na})\text{NO}_3(\text{l})$  containing a known amount of  $\text{AgNO}_3$ , and the system was agitated until equilibrium was attained (as a rule within  $50\text{ h}$ , as indicated by constant solubility). Samples from the nitrate melt were withdrawn with a preheated pipette, solidified, weighed and dissolved in aqueous cyanide solution for the activity measurements.

Series B: The distribution of  $\text{AgNO}_3$ ,  $\text{KNO}_3$  and  $\text{NaNO}_3$  between the nitrate melt and the  $\text{AgI}$ -phase was separately determined in systems containing  $8.0\text{ g}$  inactive  $\text{AgI}$ ,  $50.00\text{ g}$   $(\text{K,Na})\text{NO}_3$  and various amounts of  $\text{AgNO}_3$ . The systems were equilibrated for at least  $300\text{ h}$  for solid-liquid equilibria and  $50\text{ h}$  for liquid-liquid equilibria to be established. For the systems  $\text{Ag}(\text{I,NO}_3)(\text{s})$ -nitrate melt the composition of the solid was calculated from the difference between the added and found amounts of  $\text{AgNO}_3$  in the nitrate phase. For the systems iodide melt-nitrate melt the compositions were determined by direct analysis of each phase. The phase separation technique has been described elsewhere.<sup>3</sup>

**Emf measurements.** The procedure was essentially the same as was used in a previous study of bromide complexes.<sup>5</sup> Unsaturated melts were titrated with  $\text{AgNO}_3$  to a total concentration  $C_{\text{Ag}} \approx 2.2\text{ mol kg}^{-1}$ . In some cases further additions of  $\text{AgI}$  were then made successively up to a maximum value of  $C_{\text{I}}$  of about  $0.2\text{ mol kg}^{-1}$ . Melts saturated in  $\text{AgI}$  were studied to a maximum value  $C_{\text{Ag}} \approx 1.57\text{ mol kg}^{-1}$ . In all measurements  $C^\circ_{\text{Ag}}$  was  $2.2\text{ mol kg}^{-1}$ , which is

high enough to prevent phase separation in the diffusion layer between the half-cells. In absence of iodide phase stable emf's could be read within a few minutes, whereas equilibrium times of  $2-3\text{ h}$  were required in the study of two-phase systems.

**Analyses.** Beside the radioassay method gravimetric analyses for  $\text{AgI}(\text{s})$  were used to determine solubilities greater than  $5 \times 10^{-3}\text{ mol kg}^{-1}$ . The iodide content of the liquid iodide-rich solutions was determined in the same way.

The silver content of the melts was determined by electroanalytical precipitation on a rotating platinum cathode from hot aqueous cyanide solutions. The contents of sodium and potassium ion in the liquid iodide solution were determined from atomic absorption measurements on samples dissolved in  $50\text{ mM}$  aqueous cyanide solutions.

## CALCULATIONS AND RESULTS

The following symbols will not be separately defined in the text.

*A. Quantities referring to the emf measurements.*

$E_{\text{obs}}$  = the observed electromotive force.

$\varepsilon$  = correction term, compensating for deviations from ideal Nernst behaviour.

$E_{\text{corr}} = E_{\text{obs}} + \varepsilon$

$E_0, k$  = experimental parameters, defined by eqn. (1)

*B. Quantities referring to the iodide phase, marked ' for solid and '' for liquid phase.*

$x_i$  = mol fraction of component  $i$ .

$a_i$  = activity of component  $i$ .

$f_i = a_i x_i^{-1}$

The indices 1, 2, 3, and 4 are used for  $\text{AgI}$ ,  $\text{AgNO}_3$ ,  $\text{KNO}_3$ , and  $\text{NaNO}_3$ , respectively.

*C. Quantities referring to the nitrate phase.*

All concentrations are expressed in molality units, referring to the solvent equimolar  $(\text{K,Na})\text{NO}_3$ .

$C_{\text{I}}, C_{\text{Ag}}$   
and  $C_0$  = total concentrations of iodide, silver(I) and alkali metal ion, respectively.

$[A]$  = concentration of species A.

$a(A)$  = activity of species A.

$[ ]^*, ( )^*$  etc. denote the values of the quantities in question at the  $\text{AgI}$  phase transition  $(\text{s}) \rightleftharpoons (\text{l})$ .

$\beta_m = [\text{Ag}_m \text{I}^{(m-1)}] [\text{Ag}^+]^{-m} [\text{I}^-]^{-1}$ .

$K_m = [\text{Ag}_m \text{I}^{(m-1)}] [\text{Ag}_{(m-1)} \text{I}^{(m-2)}]^{-1} [\text{Ag}^+]^{-1}$ .

$\bar{m} = (C_{\text{Ag}} - [\text{Ag}^+]) C_{\text{I}}^{-1}$ , the ligand number.

$\alpha_m = [\text{Ag}_m \text{I}^{(m-1)}] C_{\text{I}}^{-1}$ .

Table 1. Data from the potentiometric measurements.

$C_I/\text{mol kg}^{-1}$ , $C_{Ag}/\text{mol kg}^{-1}$ , $E_{\text{obs}}/\text{mV}$ , $E_{\text{corr}}/\text{mV}$ ;
Series 1
0.0148, 0.692, 48.8, 59.2; 0.0222, 0.842, 41.5, 51.0; 0.0317, 0.997, 35.3, 43.9; 0.0426, 1.155, 30.8, 38.6; 0.0555, 1.318, 26.3, 33.2; 0.0692, 1.488, 22.6, 28.8;
Series 2
0.0163, 0.720, 47.2, 57.4; 0.0234, 0.862, 40.5, 49.8; 0.0303, 0.975, 36.2, 44.9; 0.0377, 1.081, 32.5, 40.5; 0.0464, 1.207, 29.2, 36.6; 0.0578, 1.344, 25.7, 32.6; 0.0686, 1.462, 23.1, 29.3; 0.0796, 1.571, 21.3, 27.2;
Series 3
0, 0.899, 34.4, 42.6; 0, 1.099, 25.9, 32.8; 0, 1.298, 19.7, 25.1; 0, 1.497, 14.2, 18.2; 0.0699, 1.567, 20.2, 25.8; 0.0699, 1.717, 16.3, 20.9; 0.0699, 1.867, 12.3, 15.7; 0.0699, 2.017, 8.8, 11.3; 0.0699, 2.168, 5.8, 7.4; 0.0699, 2.318, 3.2, 4.0;
Series 4
0, 0.600, 51.1, 61.7; 0, 0.799, 38.9, 48.0; 0, 0.998, 29.8, 37.4; 0, 1.198, 22.4, 28.7; 0.03993, 1.238, 26.4, 33.4; 0.03993, 1.388, 21.4, 27.2; 0.03993, 1.588, 15.9, 20.4; 0.03993, 1.786, 10.9, 14.1; 0.03993, 1.986, 6.8, 8.8; 0.03993, 2.184, 3.0, 3.8; 0.0800, 2.264, 5.2, 6.5; 0.1201, 2.305, 7.3, 9.3; 0.1603, 2.345, 9.6, 12.4; 0.2007, 2.385, 11.3, 14.6;
Series 5
0, 0.611, 50.5, 61.0; 0, 0.841, 36.7, 45.5; 0, 0.966, 31.0, 38.9; 0, 1.221, 22.0, 28.0; 0.0421, 1.263, 25.9, 32.7; 0.0421, 1.414, 21.0, 26.8; 0.0421, 1.564, 16.7, 21.4; 0.0421, 1.720, 13.0, 16.7; 0.0421, 1.884, 9.2, 11.8; 0.0421, 2.241, 2.3, 2.8; 0.0893, 2.330, 4.2, 5.3; 0.1342, 2.375, 7.5, 9.6; 0.1807, 2.422, 10.2, 13.1;

*The emf measurements.* In the concentration range studied appreciable deviations from linearity in the  $E_{\text{obs}} - \lg [\text{Ag}^+]$  relationship should be expected,<sup>5</sup> and the  $E_{\text{obs}}$  values were therefore corrected by a term  $\epsilon$  to yield data ( $E_{\text{corr}}$ ;  $\lg [\text{Ag}^+]$ ) by the same procedure as described previously.<sup>5</sup> The experimental results are given in Table 1.

The parameters  $E_0$  and  $k$  were obtained from data pertaining to iodide-free systems (series 3–5) according to

$$E_{\text{corr}} = E_0 - k \lg [\text{Ag}^+] \quad (1)$$

Acta Chem. Scand. A 30 (1976) No. 10

The experimental values of  $E_0$  and  $k$  adhere closely to the theoretical  $RTF^{-1} \ln C_{\text{Ag}}^\circ = 37.4$  mV and  $RTF^{-1} \ln 10 = 109.7$  mV, respectively, which were therefore used in the calculation of  $[\text{Ag}^+]$  in series 1–2 (two-phase systems). In these runs  $C_I$  was obtained from the separate solubility measurements.

The ligand number  $\bar{m}$  has been directly computed from the concentrations of free ligand as calculated from eqn. (1). In Fig. 1  $\bar{m}$  is plotted versus  $[\text{Ag}^+]$ . On the assumption of random errors in  $E_{\text{corr}}$  of about  $\pm 0.3$  mV the experimental uncertainty in  $\bar{m}$  is estimated to fall in the range 0.1–0.3. The following important features of Fig. 1 should be noted:

1. The average ligand number is close to 4 in all investigated melts.

2. All data are collected in a rather limited range of  $C_{\text{Ag}}$  so the behaviour of  $\bar{m}$  should by no means be taken as evidence that the iodide ion is coordinatively saturated at  $\bar{m} = 4$  even if this possibility cannot be excluded.

3.  $C_I$  is at most varied by a factor 20, but no significant dependence of  $C_I$  on  $\bar{m}$  at constant  $[\text{Ag}^+]$  can be observed. This indicates that polynuclear (polyiodic) complexes  $\text{Ag}_m\text{I}_n^{(m-n)+}$  with  $m/n \neq 4$  are not present in observable amounts.

These findings have been used in support of the interpretation of the solubility and distribution data.

*The solubility and distribution measurements.*

For reasons previously discussed,<sup>5</sup> the possible effects of alkali metal ion solvation of the un-

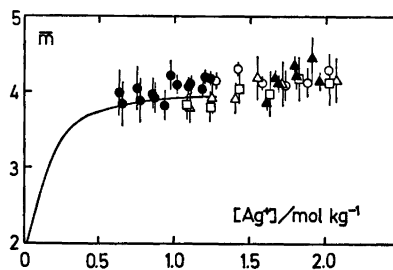


Fig. 1. Ligand numbers  $\bar{m}$ , determined from the emf measurements. Symbols: melts saturated in AgI (●);  $C_I = 0.0699$  mol  $\text{kg}^{-1}$  (○);  $C_I = 0.03993$  mol  $\text{kg}^{-1}$  (□);  $C_I = 0.0421$  mol  $\text{kg}^{-1}$  (△);  $C_I$  variable,  $0.08$  mol  $\text{kg}^{-1} \leq C_I \leq 0.20$  mol  $\text{kg}^{-1}$  (▲). The full-drawn curve is calculated from the constants of Table 7. It is drawn for the range of  $[\text{Ag}^+]$  used in the solubility measurements.

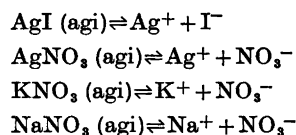
Table 2. The constitution of the iodide phase at different  $C_{Ag}$ .

Region	Range of $C_{Ag}$	Iodide phase
I	$C_{Ag} < 0.02 \text{ mol kg}^{-1}$	"Pure" $\alpha$ -AgI ( $x_2' < 0.005$ )
II	$0.02 \text{ mol kg}^{-1} \leq C_{Ag} \leq 0.66 \text{ mol kg}^{-1}$	Solid solution Ag(I,NO <sub>3</sub> )
III	$0.66 \text{ mol kg}^{-1} \leq C_{Ag}$	Liquid solution (Ag,K,Na) (I,NO <sub>3</sub> )

complexed iodide ion have been ignored in the calculations.

For convenience the total range of  $C_{Ag}$  studied will be divided into three regions, depending on the constitution of the AgI phase, *vide* Table 2. The conceptual basis for the thermodynamic treatment of the distribution equilibria encountered in regions II and III has been discussed in a recent paper.<sup>16</sup> The activity  $a_1$  and hence the product  $[Ag^+][I^-]$  is determined as follows.

In the most general case, which is met in region III, we have to consider the following heterogeneous equilibria, where the species of the right hand members are present in the nitrate melt. The symbol (agi) is used to denote a solid or liquid phase where the solvent is AgI.



The thermodynamic equilibrium conditions of relevance are

$$d \ln a_1 = d \ln ([Ag^+][I^-]) \quad (2)$$

$$d \ln a_2 = d \ln ([Ag^+]a(\text{NO}_3)) \quad (3)$$

$$d \ln a_3 = d \ln (a(\text{K})a(\text{NO}_3)) \quad (4)$$

$$d \ln a_4 = d \ln (a(\text{Na})a(\text{NO}_3)) \quad (5)$$

Furthermore, at constant  $T$  and  $P$  the Gibbs-Duhem relation yields for the iodide phase

$$\sum_{i=1}^4 x_i d \ln a_i = 0 \quad (6)$$

For the nitrate melt the Gibbs-Duhem equation may be written as<sup>16</sup>

$$\begin{aligned} &[K^+] d \ln a(\text{K}) + [Na^+] d \ln a(\text{Na}) + \\ &[NO_3^-] d \ln a(\text{NO}_3) + C_I d \ln [I^-] + \end{aligned}$$

$$C_{Ag} d \ln [Ag^+] = 0 \quad (7)$$

In order to solve eqns. (2)–(7) with respect to  $d \ln a_1$ , we make the following two assumptions:

*i.* The nitrate ion is virtually the only free anion in the nitrate melt, since practically all iodide is present as neutral or cationic complexes. Hence, the ion activity of  $\text{NO}_3^-$  may be regarded as constant, *viz.*  $d \ln a(\text{NO}_3) = 0$ .

*ii.* The ion activities of  $\text{K}^+$  and  $\text{Na}^+$  in the nitrate melt are certainly not constant as these ions are mixed with  $\text{Ag}^+$  and  $\text{Ag}_m\text{I}_n^{(m-n)+}$ . Since, however,  $[K^+] \approx [Na^+]$  in all systems, it may be reasonable to think of  $a(\text{K})$  and  $a(\text{Na})$  as being affected in the same way by the presence of other cations. The assumption to be made in the calculations is thus  $d \ln a(\text{K}) = d \ln a(\text{Na}) (= d \ln a(\text{M}))$ .

Eqns. (3)–(6) may now be combined to yield

$$\begin{aligned} d \ln a_1 &= x_1^{-1} [x_2 d \ln [Ag^+] + \\ &(x_3 + x_4) d \ln a(\text{M})] \end{aligned} \quad (8)$$

Furthermore,

$$[K^+] + [Na^+] = C_0 \quad (9)$$

The assumptions *i* and *ii* then simplify eqn. (7) to

$$\begin{aligned} C_0 d \ln a(\text{M}) + C_{Ag} d \ln [Ag^+] + \\ C_I d \ln [I^-] &= 0 \end{aligned} \quad (10)$$

Eqns. (2) and (8)–(10) finally yield the general expression for  $d \ln a_1$ , *viz.*

$$d \ln a_1 = - \left[ \frac{x_2 C_0 - (x_3 + x_4)(C_{Ag} - C_I)}{x_1 C_0 - (x_3 + x_4) C_I} \right] d \ln [Ag^+] \quad (11)$$

In a similar way an expression for  $d \ln a(\text{M})$  may be derived:

$$d \ln a(\text{M}) = - \left[ \frac{x_1 C_{Ag} - (x_3 + x_4) C_I}{x_1 C_0 - (x_3 + x_4) C_I} \right] d \ln [Ag^+] \quad (12)$$

Eqns. (11) and (12) are generally applicable irrespective of the constitution of the iodide phase. In region II eqn. (11) takes the simple form

$$d \ln a_1' = -(x_2'/x_1') d \ln [Ag^+] \quad (13)$$

since  $x_3 + x_4 = 0$ . From eqn. (12) expressions (14) and (15) for  $d \ln a(M)$  in regions II and I, respectively, are obtained:

$$d \ln a(M) = -C_0^{-1}(C_{Ag} - C_1/x_1') d \ln [Ag^+] \quad (14)$$

$$d \ln a(M) = -C_0^{-1}(C_{Ag} - C_1) d \ln [Ag^+] \quad (15)$$

The following heterogeneous equilibrium constants are now introduced in accordance with conditions *i* and *ii*:

$$K_1' = [Ag^+][I^-]/a_1' \quad (16)$$

$$K_1'' = [Ag^+][I^-]/a_1'' \quad (17)$$

$$K_2' = [Ag^+]/a_2' \quad (18)$$

$$K_2'' = [Ag^+]/a_2'' \quad (19)$$

$$K_3'' = a(M)/a_3'' \quad (20)$$

$$K_4'' = a(M)/a_4'' \quad (21)$$

Since  $a_1' = 1$  in pure  $\alpha$ -AgI, the constant  $K_1'$  is identified as the conventional solubility product which is easily determined in region I.

For the sake of clarity eqn. (11) is rewritten as

$$d \ln a_1 = G d \ln [Ag^+] \quad (22)$$

Since  $K_1'(a_1')^* = K_1''(a_1'')^*$ , the concentration product  $[Ag^+][I^-]$  will be determined as

$$([Ag^+][I^-])_j = K_1' \exp \left[ \frac{\ln [Ag^+]_j}{\ln [Ag^+]_0} \int G d \ln [Ag^+] \right] \quad (23)$$

in regions II and III, and hence the integration of eqn. (22) may be continued irrespective of the discontinuity at the phase transition (cf. Ref. 4). In eqn. (23)  $[Ag^+]_0$  refers to a system where  $G = 0$ . The index *j* denotes the values of different quantities in the same actual system.

For the solid solution we set  $\lim_{x_2' \rightarrow 0} f_2' = 1$ , and  $K_2'$  may thus be estimated from a graphical extrapolation according to eqn. (24):

$$\lim_{x_2' \rightarrow 0} (x_2'[Ag^+]^{-1}) = (K_2')^{-1} \quad (24)$$

The constant  $K_2'$  so obtained refers to a constant nitrate ion activity  $a(NO_3) = 1$ . The activities  $a_2'$  are then determined from eqn. (18).

Taking the hypothetical pure liquid AgI at 280°C as standard state with  $a_1'' = 1$ , we define a convenient activity scale for AgI in the liquid AgI phase. For  $[Ag^+]_j \geq [Ag^+]^*$

$$\exp \left[ \frac{\ln [Ag^+]_j}{\ln [Ag^+]_0} \int G d \ln [Ag^+] \right] = \lambda_1(a_1'')_j \quad (25)$$

Hence, a quantity  $\lambda_1 a_1''$ , where  $\lambda_1$  may be identified as  $K_1''/K_1'$ , will be directly obtained from the integration process, and it has been included in Table 6. The constant  $K_1''$  may be estimated according to

$$\lim_{x_1'' \rightarrow 1} [x_1''/([Ag^+][I^-])] = (K_1'')^{-1} \quad (26)$$

For the solutes in the liquid iodide phase the standard states are chosen to give  $\lim_{x_i'' \rightarrow 1} f_i = 1$  for  $i = 2, 3$ , and 4. The constant  $K_2''$  is then estimated from an expression analogous to eqn. (24).

The distribution of  $KNO_3$  and  $NaNO_3$  between the two melts has been treated as follows. By use of the general expression (12) activities  $a(M)$  were calculated by integration. For convenience an activity scale has been chosen, referring to  $a(M) = 1/2$  in pure equimolar  $(K, Na)NO_3$ . From plots of  $\lg(a(M)/x_i'' - b)$  vs.  $x_1''$  ( $i = 3, 4$ ) at different values chosen for the adjustable parameter *b*, slightly different intercepts at  $x_1'' = 1$  could be obtained, depending on *b*. From these intercepts rough estimates of  $K_3''$  and  $K_4''$  could be made. The activities  $a_i''$  ( $i = 1 - 4$ ) are finally computed from eqns. (17) and (19) - (21).

Since the only polynuclear species  $Ag_m I_n^{(m-n)+}$  that may possibly exist in the alkali nitrate melt should have a ratio  $m/n \approx 4$  in order to be in consistence with the emf measurements, they would contribute to  $C_1$  with terms representing the concentration of species having formal ionic charges  $\geq +6$ . Preliminary calculations revealed, however, that the solubility and distribution data may be well described by complexes having a maximum charge of +3. This leads to the conclusion that a stepwise formation of only monoiodic complexes  $Ag_m I^{(m-1)+}$  has to be considered, and the stability constants  $\beta_m$  have been evaluated according to

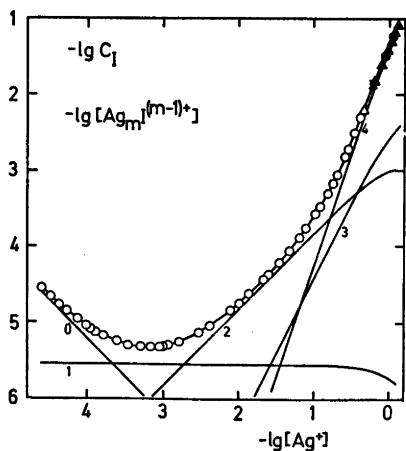


Fig. 2. The solubility curve. Symbols: Radiochemical analyses (O); gravimetric analyses ( $\Delta$ ). Filled symbols refer to liquid iodide phase. Five curves are included, which show the concentrations of the complexes  $Ag_m I^{(m-1)+}$  with  $m$  indicated on the curves. The phase transition point is marked ( $\times$ ).

$$C_I \exp \left[ \frac{\ln [Ag^+]_j}{-\int} G d \ln [Ag^+] \right] = K_1' \sum_{m=0}^4 \beta_m [Ag^+]^{(m-1)} \quad (27)$$

where  $\beta_0 = 1$ .

The  $C_I$  values used in the determination of the stability constants were measured by the radioassay technique (series A) over the whole composition range under study and determined gravimetrically in series B in region III and for  $C_{Ag} = 0.478 \text{ mol kg}^{-1}$ . Hence, in region II the

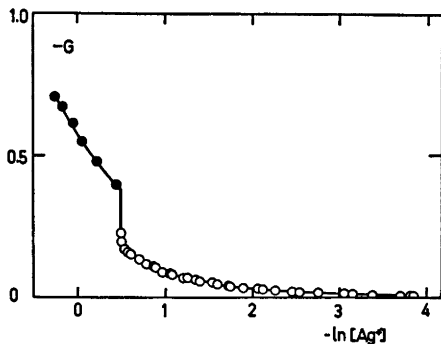


Fig. 3. A plot of  $G$  vs.  $\ln [Ag^+]$ . The integration is performed along the smooth curve. Symbols: Data from region II (O); region III ( $\bullet$ ).

requisite values of  $x_1'$  to be used in the calculation of the product  $[Ag^+][I^-]$  were obtained by interpolation between the experimentally determined ones from series B. In region III the experimental data from series B were used directly in the integration according to eqn. (23). In the further calculations on the complex formation in region III the data from series A were incorporated and the corresponding values of  $[Ag^+][I^-]$  were obtained by interpolation between those calculated from series B.

The solubility curve,  $\lg C_I$  vs.  $\lg [Ag^+]$ , is given in Fig. 2, where the full-drawn curve is calculated from eqn. (27) by use of the final set of equilibrium constants and the experimentally determined  $x_i$  values.

The concentration of free silver ion,  $[Ag^+]$ , has been calculated iteratively by use of eqns. (28)–(30):

$$[Ag^+] = C_{Ag} - \bar{m} C_I \quad (28)$$

$$\bar{m} \approx 1 + d \lg C_I / d \lg C_{Ag} \quad (29)$$

$$\bar{m} = \left( \sum_{m=1}^4 m \beta_m [Ag^+]^m \right) / \sum_{m=0}^4 \beta_m [Ag^+]^m \quad (30)$$

In the first step approximate values of  $\bar{m}$  were derived from eqn. (29). The concentrations  $[Ag^+]$  so obtained from eqn. (28) were used in eqn. (27) yielding a provisional set of constants  $\beta_m$  and  $K_1'$ . Better values of  $\bar{m}$  and  $[Ag^+]$  were then computed from eqns. (30) and (28) etc. until all variables remained unaltered.

Fig. 3 displays a graph of  $G$  versus the final values of  $\ln [Ag^+]$ . The integration was carried out along the smooth curve.

Tables 3–6 give the experimental and calculated data from all solubility and distribution

Table 3. Solubility data pertinent to region I. All data from series A.

$$C_{Ag} \times 10^5 / \text{mol kg}^{-1}, C_I \times 10^5 / \text{mol kg}^{-1}, [Ag^+] \times 10^5 / \text{mol kg}^{-1};$$

2.789,	2.789,	2.48;	3.564,	2.196,	3.26;	4.56,
1.731,	4.26;	5.72,	1.440,	5.41;	7.77,	1.143,
7.45;	10.25,	0.926,	9.93;	11.45,	0.852,	11.14;
13.42,	0.765,	13.11;	16.82,	0.693,	16.48;	24.50,
0.580,	24.14;	34.4,	0.516,	34.0;	50.4,	0.484,
49.9;	69.0,	0.488,	68.5;	90.5,	0.492,	89.9;
101.0,	0.503,	100.4;	116.8,	0.519,	116.2;	161.4,
0.563,	160.6;	297.2,	0.756,	296.0;	413,	0.925,
411;	784,	1.487,	782;	1018,	1.850,	1014;
1371,	2.409,	1367;				

Table 4. Solubility and distribution data pertinent to region II. Values in italics are interpolated (further details in the text).

Series	$C_{Ag} \times 10^3$ mol kg <sup>-1</sup>	$C_I \times 10^3$ mol kg <sup>-1</sup>	$x_1'$	$a_1'$	$f_1'$	$a_2'$	$f_2'$	$[Ag^+] \times 10^3$ mol kg <sup>-1</sup>	$[Ag^+][I^-] \times 10^{10}$ (mol kg <sup>-1</sup> ) <sup>2</sup>
A	21.35	3.69	<i>0.995</i>	0.999				21.28	6.15
B	22.09	<i>4</i>	<i>0.994</i>	0.999	1.00	0.006	1.0	22.03	6.15
A	24.89	4.30	<i>0.994</i>	0.999				24.80	6.14
A	34.30	6.11	<i>0.992</i>	0.996				34.20	6.14
B	43.1	<i>8</i>	<i>0.989</i>	0.994	1.00	0.013	1.2	42.9	6.12
A	47.3	8.86	<i>0.988</i>	0.993				47.1	6.12
A	63.7	13.01	<i>0.984</i>	0.989				63.4	6.09
A	78.8	17.46	<i>0.981</i>	0.985				78.4	6.07
B	86.0	<i>21</i>	<i>0.980</i>	0.984	1.00	0.025	1.2	85.5	6.06
A	104.2	26.78	<i>0.975</i>	0.979				103.5	6.03
A	120.2	33.5	<i>0.971</i>	0.975				119.3	6.01
B	128.1	<i>38</i>	<i>0.968</i>	0.974	1.01	0.037	1.16	126.9	6.00
A	151.1	50.2	<i>0.966</i>	0.968				149.6	5.96
B	176.1	<i>67</i>	<i>0.963</i>	0.963	1.00	0.051	1.38	173.9	5.93
A	178.6	69.0	<i>0.960</i>	0.962				176.5	5.92
A	204.3	89.2	<i>0.954</i>	0.956				201.4	5.89
B	218.0	<i>104</i>	<i>0.948</i>	0.953	1.00	0.063	1.21	214.6	5.87
B	251.2	<i>139</i>	<i>0.945</i>	0.946	1.00	0.072	1.31	246.3	5.83
A	265.2	154.7	<i>0.940</i>	0.943				259.9	5.81
A	289.8	190.9	<i>0.935</i>	0.937				283.2	5.77
B	304	<i>218</i>	<i>0.937</i>	0.935	1.00	0.087	1.38	296.4	5.76
B	348	<i>305</i>	<i>0.926</i>	0.926	1.00	0.099	1.34	337	5.70
A	356	309	<i>0.920</i>	0.924				345	5.69
B	395	<i>420</i>	<i>0.919</i>	0.916	1.00	0.112	1.38	380	5.64
A	426	499	<i>0.906</i>	0.910				408	5.60
B	433	<i>480</i>	<i>0.902</i>	0.908	1.01	0.122	1.24	415	5.59
B	478	<i>629</i>	<i>0.895</i>	0.899	1.00	0.134	1.28	455	5.54
B	525	<i>870</i>	<i>0.883</i>	0.890	1.01	0.145	1.24	493	5.48
B	583	<i>1090</i>	<i>0.868</i>	0.878	1.01	0.159	1.20	542	5.41
B	605	<i>1180</i>	<i>0.864</i>	0.874	1.01	0.165	1.21	560	5.38
B	631	<i>1290</i>	<i>0.857</i>	0.868	1.01	0.171	1.20	582	5.35
B	654	<i>1390</i>	<i>0.837</i>	0.863	1.03	0.177	1.08	601	5.32
B	658	<i>1410</i>	<i>0.815</i>	0.862	1.06	0.178	0.96	605	5.31
B	663		<i>0.81<sup>a</sup></i>						

<sup>a</sup> Extrapolated.Table 5. Data on the distribution of KNO<sub>3</sub> and NaNO<sub>3</sub> between the two melts (region III). All data from series B.

$C_{Ag}$ mol kg <sup>-1</sup>	$a(M)$	$x_3'' \times 10^4$	$x_4'' \times 10^4$	$a_3'' \times 10^4$	$a_4'' \times 10^4$	$f_3''$	$f_4''$
0.663	0.472	33 <sup>a</sup>	16 <sup>a</sup>				
0.693	0.470	36	17	12	5	0.3	0.3
0.890	0.463	61	31	12	5	0.20	0.16
1.083	0.457	89	43	11	5	0.12	0.12
1.228	0.452	109	55	11	4	0.10	0.07
1.439	0.445	143	70	11	4	0.08	0.06
1.591	0.441	173	90	11	4	0.06	0.04

<sup>a</sup> Extrapolated.

Table 6. Data on the distribution of AgI and AgNO<sub>3</sub> between the two melts (region III). Interpolated values are printed in italics.

Series	$C_{Ag}$ mol kg <sup>-1</sup>	$C_I$ mol kg <sup>-1</sup>	$x_1''$	$x_2''$	$\lambda_1 a_1''$	$a_1''$	$a_2''$	$f_1''$	$f_2''$	$[Ag^+]$ mol kg <sup>-1</sup>	$[Ag^+][I^-] \times 10^{10}$ (mol kg <sup>-1</sup> ) <sup>2</sup>
B	0.663		0.721 <sup>a</sup>	0.274 <sup>a</sup>							
B	0.693	0.01475	0.714	0.281	0.846	0.43	0.46	0.60	1.6	0.637	5.21
B	0.890	0.02526	0.671	0.320	0.769	0.39	0.57	0.58	1.8	0.792	4.74
A	0.974	0.0323	<i>0.654</i>	<i>0.335</i>	<i>0.740</i>	<i>0.38</i>				0.881	<i>4.56</i>
B	1.083	0.0377	0.637	0.349	0.706	0.36	0.67	0.56	1.9	0.936	4.35
B	1.228	0.0483	0.611	0.372	0.665	0.34	0.75	0.56	2.0	1.039	4.10
A	1.291	0.0580	<i>0.604</i>	<i>0.377</i>	<i>0.647</i>	<i>0.33</i>				1.121	<i>3.98</i>
B	1.439	0.0660	0.587	0.392	0.613	0.31	0.85	0.53	2.2	1.180	3.78
B	1.591	0.0815	0.573	0.401	0.583	0.30	0.92	0.52	2.3	1.271	3.59

<sup>a</sup> Extrapolated.Table 7. Over-all and stepwise stability constants for complexes Ag<sub>m</sub>I<sup>(m-1)+</sup> in (K,Na)NO<sub>3</sub>(l) from solubility measurements at 280 °C. The errors quoted are three standard deviations from the least-squares calculations.

Quantity	$m = 1$	$m = 2$	$m = 3$	$m = 4$
$\beta_m / (\text{mol kg}^{-1})^{-m}$	$(4.7 \pm 0.1) \times 10^3$	$(2.43 \pm 0.06) \times 10^6$	$(6.3 \pm 1.1) \times 10^6$	$(9.7 \pm 0.3) \times 10^6$
$K_m / (\text{mol kg}^{-1})^{-1}$	$4.7 \times 10^3$	$5.2 \times 10^2$	2.6	15
$K_m / K_{(m+1)}$	9.1	200	0.17	—

experiments. The composition of the solid iodide phase at the melting point was obtained by extrapolation of  $x_2'$  to  $C_{Ag} = 0.66 \text{ mol kg}^{-1}$ . For the liquid iodide phase the limiting values of  $x_i''$  were obtained by extrapolations of  $x_i''/x_1''$  versus  $\ln [Ag^+]$  to yield the limiting quotients  $(x_i''/x_1'')^*$  at  $[Ag^+] = [Ag^+]^*$  for  $i = 2, 3, 4$ .  $(x_1'')^*$  is obtained as  $1 - \sum_{i=2}^4 (x_i'')^*$ . The limiting values, which are included in Tables 4–6, define the “gap” over which the integration has to be continued at the phase transition point.

The conventional solubility product  $K_1'$  and  $\beta_1$  were obtained by standard methods<sup>18</sup> from data pertaining to region I. Least-squares calculations yield  $K_1' = (6.16 \pm 0.12) \times 10^{-10} (\text{mol kg}^{-1})^2$  (the errors are expressed as three standard deviations). This value has been used in the further calculations in regions II and III.

All stability constants are given in Table 7 and the primarily estimated heterogeneous constants are collected in Table 8, where the anion exchange constants  $K_{12}'$  and  $K_{12}''$  and

the cation exchange constants  $K_{23}''$  and  $K_{24}''$  are also included.

## DISCUSSION

*The iodide phase and the heterogeneous equilibria.* Considering the solid iodide phase, the results from this and previous<sup>3,4,16</sup> investigations clearly illustrate the necessity for careful investigation of the composition of the solid in solubility studies on complex formation at elevated temperatures.

The ideal Temkin behaviour,<sup>19</sup> as indicated by the experimentally verified relation  $a_1' = x_1'$  for  $0.86 \leq x_1' \leq 1$ , suggests that the solid phase Ag(I,NO<sub>3</sub>) may be regarded as a substitutional solution with the anions mixing at random on the bodycentered cubic iodide sublattice, making the partial molar configurational entropy of AgI take the value  $-R \ln x_1'$ . Ideal behaviour should then be displayed if the enthalpy of mixing were negligible. In particular, the partial substitution of iodide ions for nitrate



Table 8. The estimated heterogeneous equilibrium constants. The solid and liquid AgI solutions are designated agis and agil, respectively.

Equilibrium reaction	Equilibrium constant
$\text{AgI}(\text{agis}) \rightleftharpoons \text{Ag}^+ + \text{I}^-$	$K_1'$ $(6.2 \pm 0.1) \times 10^{-10}$ (mol kg <sup>-1</sup> ) <sup>2</sup>
$\text{AgNO}_3(\text{agis}) \rightleftharpoons \text{Ag}^+ + \text{NO}_3^-$	$K_2'$ $(3.4 \pm 0.5)$ mol kg <sup>-1</sup>
$\text{AgI}(\text{agil}) \rightleftharpoons \text{Ag}^+ + \text{I}^-$	$K_1''$ $(12 \pm 3) \times 10^{-10}$ (mol kg <sup>-1</sup> ) <sup>2</sup>
$\text{AgNO}_3(\text{agil}) \rightleftharpoons \text{Ag}^+ + \text{NO}_3^-$	$K_2''$ $(1.4 \pm 0.2)$ mol kg <sup>-1</sup>
$\text{KNO}_3(\text{agil}) \rightleftharpoons \text{K}^+ + \text{NO}_3^-$	$K_3''$ $(4 \pm 2) \times 10^2$
$\text{NaNO}_3(\text{agil}) \rightleftharpoons \text{Na}^+ + \text{NO}_3^-$	$K_4''$ $(10 \pm 4) \times 10^2$
$\text{AgI}(\text{agis}) + \text{NO}_3^- \rightleftharpoons \text{AgNO}_3(\text{agis}) + \text{I}^-$	$K_{12}$ $1.8 \times 10^{-10}$ mol kg <sup>-1</sup>
$\text{AgI}(\text{agil}) + \text{NO}_3^- \rightleftharpoons \text{AgNO}_3(\text{agil}) + \text{I}^-$	$K_{12}''$ $8.6 \times 10^{-10}$ mol kg <sup>-1</sup>
$\text{AgNO}_3(\text{agil}) + \text{K}^+ \rightleftharpoons \text{KNO}_3(\text{agil}) + \text{Ag}^+$	$K_{23}$ $3 \times 10^{-3}$ mol kg <sup>-1</sup>
$\text{AgNO}_3(\text{agil}) + \text{Na}^+ \rightleftharpoons \text{NaNO}_3(\text{agil}) + \text{Ag}^+$	$K_{24}$ $1 \times 10^{-3}$ mol kg <sup>-1</sup>
$\text{KNO}_3(\text{agil}) + \text{Na}^+ \rightleftharpoons \text{NaNO}_3(\text{agil}) + \text{K}^+$	$K_{34}$ $4 \times 10^{-1}$

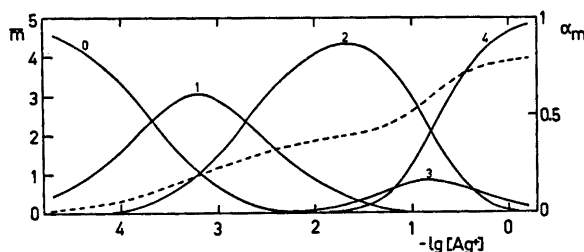
Fig. 4. Ligand numbers  $\bar{m}$ , calculated according to eqn. (30) (dashed curve), and the distribution of iodide on different species  $\text{Ag}_m\text{I}^{(m-1)+}$  in the nitrate melt ( $m$  is indicated on the distribution curves).

Table 9. Stepwise stability constants and quotients in different media.

Medium	Ref.	Quantity	$m=1$	$m=2$	$m=3$	$m=4$
$\text{KNO}_3(\text{l}), 402^\circ\text{C}$	15	$K_m/(\text{mol kg}^{-1})^{-1}$	$5.5 \times 10^2$	$3.6 \times 10^2$	—	—
$\text{H}_2\text{O}, 25^\circ\text{C}, I=4 \text{ M} (\text{NaClO}_4)$	7	$K_m/\text{M}^{-1}$	$(1.3 \times 10^8)$	$(1.7 \times 10^2)$	$7.1 \times 10^2$	5.2
$\text{H}_2\text{O}, 20^\circ\text{C}, I=0$	9	$K_m/\text{M}^{-1}$	$3.8 \times 10^6$	$2.6 \times 10^4$	$4.2 \times 10^2$	—
$\text{KNO}_3(\text{l}), 402^\circ\text{C}$	15	$K_m/K^{(m+1)}$	1.5	—	—	—
$\text{H}_2\text{O}, 25^\circ\text{C}, I=4 \text{ M} (\text{NaClO}_4)$	7	$K_m/K^{(m+1)}$	$(10^6)$	(2)	140	—
$\text{H}_2\text{O}, 20^\circ\text{C}, I=0$	9	$K_m/K^{(m+1)}$	140	63	—	—

ions must not change the accessibility of structurally different cation sites, *i.e.* no restrictions must be imposed on the mobility of  $\text{Ag}^+$  ions over the cation sublattice. The structural conditions for random anion mixing are, on the whole, advantageous. In the Stroock model<sup>20</sup> of  $\alpha\text{-AgI}$  the closest iodide-iodide distance is 4.36 Å. The nitrate ion, on the other hand, may be roughly approximated with a disc, having

an effective diameter of 4.6 Å and a thickness of 2.2 Å.<sup>21</sup> Hence, judging from the dimensions of the anions, the nitrate ion might fit sufficiently well into the structure with only a minor perturbation of the anion sublattice.

The liquid iodide phase displays a pronounced non-ideal behaviour, similar to that of  $(\text{Ag},\text{K})\text{I}$  melts.<sup>4</sup> It should be noted that — in contrast to what is often found for other silver

halide based melts<sup>23</sup> – the thermodynamic data pertaining to the composition range investigated cannot be rationalized in terms of simple regular solution parameters.

Except for  $K_1'$ , the relatively large uncertainties in the distribution constants of Table 8 are due to the wide limits of error which are subjectively estimated from the non-linear extrapolations. One relevant comparison of the results with previous findings can be made. The value of  $K_1''$  obtained in this study,  $(12 \pm 3) \times 10^{-10}$  (mol kg<sup>-1</sup>)<sup>3</sup>, agrees with the recently estimated value<sup>4</sup>  $(12.5 \pm 0.8) \times 10^{-10}$  (mol kg<sup>-1</sup>)<sup>2</sup>, derived from data on (Ag,K)I melts with a similar extrapolation technique.

*The complex formation equilibria in the nitrate melt.* The complex formation proceeds rather similarly to that in the AgBr–AgNO<sub>3</sub>–(K,Na)NO<sub>3</sub> system,<sup>5</sup> and the virtual absence of polyiodic species is rather interesting in view of the well-known ability of silver(I) to coordinate several halide ions in nitrate melts having halide in excess over silver(I). King and coworkers<sup>12</sup> concluded, from light absorption measurements, that polyiodic cationic Ag–I-complexes may exist in aqueous solutions, but the effects observed were very much smaller than the corresponding ones for anionic complexes. Berne and Weill<sup>13</sup> later found no evidence for polynuclear complexes on the cationic side of the silver-iodide system, from self-diffusion measurements on aqueous solutions, whereas clear evidence for polynuclearity on the anionic side was given. The results from this study and from Refs. 3 and 4 are in obvious agreement with these observations; the tendency of condensation in the silver iodide system is much smaller (if any) on the cationic side than on the anionic side in nitrate melts as well.

Fig. 4 gives a survey of the complex formation in the range of free ligand concentrations studied. For  $[Ag^+] < 0.01$  mol kg<sup>-1</sup> the only species of importance besides Ag<sup>+</sup> are I<sup>-</sup>, AgI and Ag<sub>2</sub>I<sup>+</sup>. The solubility product  $K_1'$  and the stability constant  $\beta_1$  for AgI are in good agreement with the values obtained by Elding and Leden<sup>1</sup> from solubility measurements in systems AgI–(K,Na)I–(K,Na)NO<sub>3</sub>. The emf data of Alvarez-Funes *et al.*<sup>15</sup> on the formation of AgI and Ag<sub>2</sub>I<sup>+</sup> in liquid KNO<sub>3</sub> at 402 °C seem to be the only available comparison material on cationic silver iodide complexes in fused nitrate

medium (Table 9). Their values of  $K_1$  and  $K_2$  are considerably smaller than those from the present study. This is largely due to the difference in temperature, but may also be attributed in part to the difference in solvent composition in accordance with the general trend for iodide complexes.<sup>23,24</sup>

The second complex, Ag<sub>3</sub>I<sup>+</sup>, exhibits a remarkable stability relative to AgI and Ag<sub>2</sub>I<sup>2+</sup>. This is evident from the quotients between the successive formation constants of Table 7 and from the flattening out of the  $\bar{m}$  curve at  $\bar{m} = 2$  (Fig. 4). A similar, although not so pronounced effect was found in the corresponding bromide system.<sup>5</sup>

From the solubility study of Lieser<sup>9</sup> (*vide* Table 9) it becomes evident that there is no such stabilization of Ag<sub>2</sub>I<sup>+</sup> in aqueous solution (Leden's solubility data have been discussed in Ref. 4. Anderson and coworkers<sup>25</sup> recently suggested a value of  $K_2$  in water (25°C) which seems to be in conflict with most experience in this field).

From Fig. 4 it is seen that Ag<sub>3</sub>I<sup>2+</sup> contributes at most with about 17 % to  $C_1$  (which is also reflected in the large uncertainty in the value of  $\beta_3$ ), whereas more than 90 % of the iodide in the nitrate melt is present as Ag<sub>4</sub>I<sup>3+</sup> at  $[Ag^+] = 1$  mol kg<sup>-1</sup>. The fourth complex is undoubtedly strong, but it is an open question whether or not the iodide is coordinatively saturated at  $\bar{m} = 4$  in the fused nitrate medium. A close inspection of Fig. 1 reveals that  $\bar{m}$  actually seems to exceed 4 in the range  $1 \text{ mol kg}^{-1} < [Ag^+] < 2 \text{ mol kg}^{-1}$ . A value of, *e.g.*,  $K_5 = 10^{-1} \text{ mol}^{-1} \text{ kg}$  would give a better fit to the emf measurements than  $K_5 = 0$ . It cannot be excluded, however, that systematic errors at these high silver ion concentrations are responsible for the observed increase of  $\bar{m}$  above 4, and it is also to be noted that the differences  $\bar{m} - 4$  are in general not larger than the estimated random errors in  $\bar{m}$ . Therefore we have abstained from introducing a complex Ag<sub>5</sub>I<sup>4+</sup> (or Ag<sub>6</sub>I<sup>5+</sup>) in our model, even if this would give a better formal description of the emf measurements without violating significantly our model used to describe the solubility data.

It is evident from studies of solution equilibria involving anionic complexes AgX<sub>*n*</sub><sup>(*n*-1)-</sup> that Ag<sup>+</sup> coordinates at most four halide ions. This

is well reflected in the structure of crystalline solids of different general formulae, such as  $M_xAg_yX_z$  ( $y < z$ ). The halide ions always seem to be arranged in a more or less distorted tetrahedron around Ag.<sup>26-41</sup>

In the case of cationic complexes there is no similar univocal support from structure determinations to be found when discussing the coordination number. In  $Ag_3I(NO_3)_2$ <sup>42</sup> and  $Ag_2INO_3$ <sup>43</sup> every iodine atom is surrounded by six nearest silver atoms, but preliminary results from our structure determinations of  $Ag_2BrNO_3$  and  $Ag_2IF \cdot H_2O$ <sup>44</sup> indicate that Br and I have five and four Ag, respectively, as nearest cation neighbours in these compounds. Further structural studies of similar compounds are in progress.

*Acknowledgements.* I express my sincere gratitude to Professor Ido Leden for his very stimulating support of this work. I also thank Dr. Peter Sellers for revision of the English text.

#### REFERENCES

- Elding, I. and Leden, I. *Acta Chem. Scand.* 23 (1969) 2430.
- Holmberg, B. *Acta Chem. Scand.* 27 (1973) 875.
- Holmberg, B. *Acta Chem. Scand.* 27 (1973) 3550.
- Holmberg, B. *Acta Chem. Scand.* 27 (1973) 3657.
- Holmberg, B. *Acta Chem. Scand. A* 30 (1976) 680.
- Kratohvil, J., Tezák, B. and Vouk, V. B. *Arch. Kem.* 26 (1954) 191.
- Leden, I. and Parck, C. *Acta Chem. Scand.* 10 (1956) 535.
- Lieser, K. H. *Z. Anorg. Allg. Chem.* 292 (1957) 114.
- Lieser, K. H. *Z. Anorg. Allg. Chem.* 304 (1960) 296.
- Lieser, K. H. *Z. Anorg. Allg. Chem.* 305 (1960) 133.
- Fromherz, H. and Menschick, W. *Z. Phys. Chem. Abt. B* 3 (1929) 1.
- King, E. L., Krall, H. J. and Pandow, M. L. *J. Am. Chem. Soc.* 74 (1952) 3492.
- Berne, E. and Weill, M. J. *J. Phys. Chem.* 64 (1960) 258.
- Yakhkind, N. D. and Gyunner, E. A. *Zh. Neorg. Khim.* 13 (1968) 1005.
- Alvarez-Funes, A., Braunstein, J. and Blander, M. J. *J. Am. Chem. Soc.* 84 (1962) 1538.
- Holmberg, B. *Acta Chem. Scand. A* 30 (1976) 641.
- Holmberg, B. *Acta Chem. Scand. A* 28 (1974) 284.
- Johansson, L. *Coord. Chem. Rev.* 3 (1968) 293.
- Temkin, M. *Acta Physicochim. URSS* 20 (1945) 411.
- Stroock, L. W. *Z. Phys. Chem. (Leipzig)* 25 (1934) 441.
- Janz, G. J. and James, D. W. *Electrochim. Acta* 7 (1962) 427.
- Lumsden, J. *Thermodynamics of Molten Salt Mixtures*, Academic, London 1966.
- Braunstein, J. and Hagman, R. E. *J. Phys. Chem.* 67 (1963) 2881.
- Hsu, Y.-T., Escue, R. B. and Tidwell, T. H. *J. Electroanal. Chem.* 15 (1967) 245.
- Andersson, K. P., Butler, E. A. and Woolley, E. M. *J. Phys. Chem.* 78 (1974) 2244.
- Brink, C. and MacGillavry, C. H. *Acta Crystallogr.* 2 (1949) 158.
- Brink, C. and Kroese, H. A. S. *Acta Crystallogr.* 5 (1952) 433.
- Brink, C., Binnendijk, N. F. and van de Linde, J. *Acta Crystallogr.* 7 (1954) 176.
- Hahn, H., Frank, G. and Klingler, W. *Z. Anorg. Allg. Chem.* 279 (1955) 271.
- Meyer, H.-J. *Acta Crystallogr.* 16 (1963) 788.
- Geller, S. *Science* 157 (1967) 310.
- Stomberg, R. *Acta Chem. Scand.* 23 (1969) 3498.
- Geller, S. and Lind, M. D. *J. Chem. Phys.* 52 (1970) 5854.
- Gilmore, C. J., Tucker, P. A. and Woodward, P. J. *J. Chem. Soc. A* (1971) 1337.
- Geller, S. *Science* 176 (1972) 1016.
- Geller, S., Skarstad, P. M. and Wilber, S. A. *J. Electrochem. Soc.* 122 (1975) 332.
- Coetzer, J. *Acta Crystallogr. B* 31 (1975) 622, 2115.
- Coetzer, J. and Thackeray, M. M. *Acta Crystallogr. B* 31 (1975) 2113.
- Thackeray, M. M. and Coetzer, J. *Acta Crystallogr. B* 31 (1975) 2339, 2341.
- Coetzer, J., Kruger, G. J. and Thackeray, M. M. *Acta Crystallogr. B* 32 (1976) 1248.
- Thackeray, M. M. and Coetzer, J. *Acta Crystallogr. B* 32 (1976) 2197.
- Birnstock, R. and Britton, D. Z. *Kristallogr.* 132 (1970) 87.
- Persson, K. *Private communication.*
- Holmberg, B. and Persson, K. *Acta Crystallogr. A* 31 (1975) S 65.

Received April 23, 1976.