Complex Formation between Silver Ions and Bromide Ions in Alkali Nitrate Melts. A Potentiometric Study

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A potentiometric determination in unsaturated solutions of the reaction between silver and bromide ions in a fused equimolar mixture of KNO_3-$NaNO_3$ as solvent has been performed at 280°C. The deviations from ideal behaviour were ascribed to complex formation, and the over-all complexity constants $\beta_{n,m}$ were computed. The results have been interpreted by assuming that the mononuclear species $AgBr$, $AgBr_2^-$, $AgBr_3^{2-}$ and the dinuclear species $Ag_2Br_6^{4-}$ were formed. The following results were obtained: $\beta_{1,1} = 2.70 \times 10^2$ (m^{-1}); $\beta_{2,1} = 2.4 \times 10^4$ (m^{-2}); $\beta_{3,1} = 5.9 \times 10^4$ (m^{-3}) and $\beta_{1,1} = 1.2 \times 10^{10}$ (m^{-7}). However, the existence of the dinuclear species must be considered as somewhat uncertain.

The solubility product $K_{s,0}$ of silver bromide was also determined from e.m.f. measurements in saturated solutions.

In recent years a great number of papers have been published concerning the behaviour of metal ions in fused salt media. Surveys with many references have been written for exampel by Blomgren and Van Artsdalen,[1] Blander [2a,2b] and Sundheim.[2c]

One of the methods of studying the chemistry in salt melts is e.m.f. measurements of galvanic cells, which provide a direct method of obtaining thermodynamic data. The e.m.f. measurements have sometimes been interpreted by assuming complex formation.

In this paper a potentiometric determination of silver bromide complexes is described and the results are compared with the determinations made by previous authors. Our measurements can very well be described by assuming complex formation. In a following paper [3] the solubility of solid silver bromide in fused alkali nitrates containing different amounts of alkali bromide will be reported.* The changes in solubility with increasing amounts of bromide ions is interpreted as complex formation.

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* A preliminary report [4] was given at the XIXth IUPAC meeting in London in July 1963.

Since Flengas and Rideal [5] in 1956 reported that a silver-silver nitrate electrode behaves ideally, the reactions between silver ions and halide ions in fused alkali nitrate melts have been studied with electrometric methods by several chemists.[6–12]

EQUATIONS FOR CALCULATION OF THE COMPLEXITY CONSTANTS

The calculations have been performed according to methods elaborated by Bjerrum,[13] Leden,[14] and Fronæus.[15] In this paper only definitions of symbols and a short summary of the used equations are given.

The experimental method applied was determination of the free central ion concentration by potentiometric measurements in unsaturated melts. The solubility product of silver bromide was also determined from potentiometric measurements in saturated melts.

Complex formation between the metal ion M and the ligand A can be completely described by the equilibria

$$mM + nA \rightleftharpoons M_mA_n \tag{1}$$

Denoting the over-all complexity (concentration) constant of the above reaction $\beta_{n,m}$ the law of mass action gives

$$\beta_{n,m} = [M_mA_n]/[M]^m[A]^n \tag{2}$$

A. Mononuclear complexes. For a mononuclear system ($m = 1$) we have the following expression for the total concentrations C_M and C_A of the central metal ions and the ligand

$$C_M = [M] + \sum_{n=1} [MA_n] = [M]\sum_{n=0} \beta_{n,1} [A]^n \tag{3}$$

$$C_A = [A] + \sum_{n=1} n[MA_n] = [A] + [M]\sum_{n=1} n\beta_{n,1} [A]^n \tag{4}$$

The ligand number $\bar{n}$ is defined as

$$\bar{n} = (C_A - [A])/C_M \tag{5}$$

and thus for a mononuclear system we obtain

$$\bar{n} = \sum_{n=1} n\beta_{n,1} [A]^n / \sum_{n=0} \beta_{n,1} [A]^n \tag{6}$$

From eqn. (6) it follows that in a mononuclear system $\bar{n}$ is a function only of [A].

With the notation of Leden (Ref.[14]) we write

$$F_0([A]) \equiv C_M/[M] \tag{7}$$

Also $F_0([A])$ is a function only of [A], since eqns. (3) and (4) give

$$F_0([A]) = \sum_{n=0} \beta_{n,1} [A]^n \tag{8}$$

As [M] is known from measurements $F_0([A])$ can be calculated from eqn. (7) for every solution in a titration series. We can obtain the coefficients $\beta_{n,1}$ graphically, if we only know [A], and [A] is determined in a way that is described below.

We rewrite eqn. (8) and introduce the functions $F_1([A])$ and $F_2([A])$

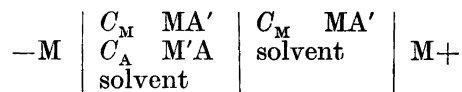$$F_1([A]) \equiv (C_M - [M])/([M][A]) = (F_0([A]) - 1)/[A] = \sum_{n=1} \beta_{n,1}[A]^{n-1} \qquad (9)$$

$$F_2([A]) \equiv (F_1([A]) - \beta_{1,1})/[A] = \sum_{n=2} \beta_{n,1}[A]^{n-2} \qquad (10)$$

From eqn. (9) $\beta_{1,1}$ may be obtained as origo ordinate and $\beta_{2,1}$ as the slope if $F_1([A])$ is graphically extrapolated to $[A] = 0$. We can compute $\beta_{2,1}$ and $\beta_{3,1}$ in a similar way from eqn. (10), and so on, for $\beta_{n,1}$ with $n \geq 3$.

In the following the functions $F_1([A])$, $F_2([A])$ etc. are written F_1, F_2 etc. We measure the e.m.f. of the following cell

$$-M \left| \begin{array}{c} C_M \quad MA' \\ C_A \quad M'A \\ \text{solvent} \end{array} \right| \begin{array}{c} C_M \quad MA' \\ \text{solvent} \end{array} \left| M+ \right.$$

where MA' is the salt containing our complexforming metal ion and M'A is the salt containing the ligand of the complex formation. The activity is assumed to be equal to the stoichiometric concentration, and the e.m.f. of the cell is denoted E

$$E = (RT/\nu F) \ln C_M/[M] \qquad (11)$$

From eqn. (5) we find

$$[A] = C_A - \bar{n} C_M \qquad (12)$$

but we ought to know $\bar{n}$ to be able to deduce $[A]$ from the known quantities of C_M and C_A.

A sufficiently accurate value of $\bar{n}$ can be deduced from Bodländer's formula approximated to (cf. Ref.[14], p. 13)

$$\Delta E / \Delta \ln C_A \simeq RT\bar{n}/\nu F \qquad (13)$$

where ΔE and $\Delta \ln C_A$ are the differences between two consecutive values of E and C_A in a titration series.

With these values of $\bar{n}$ we can obtain $[A]$ from eqn (12) and determine approximate values of the constants $\beta_{n,1}$. A more accurate value of $\bar{n}$ and $[A]$ can then be found by the aid of eqn. (6) and so forth from eqns. (12) and (6).

The method described above is only valid when no polynuclear complexes are present in the solutions. But for small values of C_M the eventual polynuclear species can be omitted.

B. *Dinuclear complexes.* If only mono- and dinuclear species are assumed to exist in the solution, eqn. (3) is changed to

$$C_M = [M] \left[\sum_{n=0} \beta_{n,1} [A]^n + 2[M] \sum_{n=1} \beta_{n,2} [A]^n \right] \qquad (14)$$

The fraction $(C_M - [M])/([M][A])$ corresponding to our earlier F_1 is no more independent of $[M]$ and thus not of C_M either. The same dependency on $[M]$ and $[A]$ is also found for F_2 and so on.

In order to point out this dependency we write $F_1{}^{C_M}$ and $F_2{}^{C_M}$ and obtain

$$F_1{}^{C_M} \equiv (C_M - [M])/([M][A]) = \sum_{n=1} \beta_{n,1} [A]^{n-1} + 2[M] \sum_{n=1} \beta_{n,2}[A]^{n-1} \qquad (15)$$

and

$$F_2{}^{C_M} \equiv (F_1{}^{C_M} - \beta_{1,1})/[A] = \sum_{n=2} \beta_{n,1}[A]^{n-2} + 2[M] \sum_{n=1} \beta_{n,2}[A]^{n-2} \qquad (16)$$

For decreasing C_M the $F_1{}^{C_M}$ curves approach the limit curve $F_1{}^0$ as well as the $F_2{}^{C_M}$ ones approach the limit curve $F_2{}^0$.

$$F_1{}^0 = \sum_{n=1} \beta_{n,1} [A]^{n-1} \qquad (17)$$

$$F_2{}^0 = \sum_{n=2} \beta_{n,1} [A]^{n-2} \qquad (18)$$

From eqns. (17) and (18) the constants $\beta_{n,1}$ can be deduced as described earlier.

For every titration series we now introduce the functions D_1 and D_2 and obtain

$$D_1 \equiv (F_1{}^{C_M} - F_1{}^0)/2[M] = \sum_{n=1} \beta_{n,2}[A]^{n-1} \qquad (19)$$

$$D_2 \equiv (F_2{}^{C_M} - F_2{}^0)/2[M] = \sum_{n=1} \beta_{n,2}[A]^{n-2} \qquad (20)$$

from which the complexity constants of the dinuclear species can be calculated.

C. Polynuclear complexes. For polynuclear complexes we can deduce the equations

$$C_M = \sum_{n=0} \beta_{n,1}[M][A]^n + \sum_{m=2} \sum_{n=1} m\beta_{n,m} [M]^m [A]^n \qquad (21)$$

$$F_1{}^{C_M} = \sum_{n=1} \beta_{n,1} [A]^{n-1} + \sum_{m=2} \sum_{n=1} m\beta_{n,m} [M]^{m-1} [A]^{n-1} \qquad (22)$$

$$F_2{}^{C_M} = \sum_{n=2} \beta_{n,1}[A]^{n-2} + \sum_{m=2} \sum_{n=1} m\beta_{n,m} [M]^{m-1} [A]^{n-2} \qquad (23)$$

$$\bar{n} = \frac{\sum\limits_{m=1} \sum\limits_{n=1} n\beta_{n,m} [M]^{m-1} [A]^n}{\sum\limits_{n=0} \beta_{n,1} [A]^n + \sum\limits_{m=2} \sum\limits_{n=1} m\beta_{n,m} [M]^{m-1} [A]^n} \qquad (24)$$

The possibility to obtain reliable values of the complexity constants with the deduced equations depends on the accuracy of the experimental data. A great number of measurements are necessary to calculate complexity constants of polynuclear complexes.

EXPERIMENTAL

Chemicals used. Silver nitrate, sodium bromide and *potassium bromide* were "Baker Analyzed" REAGENT. *Potassium nitrate* and *sodium nitrate* were of Merck's p.a. quality. The used *silver wire* was of spec. pure silver, JM 50 from Johnson, Matthey and Co., London. The potassium nitrate, sodium nitrate and potassium bromide were dried for several days at 120°C, whereas sodium bromide was dried for weeks at 220°C.

Apparatus. A high-temperature thermostat was constructed. As heating bath a melt of an equimolar mixture of sodium-potassium nitrate was used. The temperature was measured with a mercury thermometer that had been calibrated against the freezing points of Sn, Bi and Cd. It was possible to maintain the temperature within less than 1°C of the desired value.

The cell containing the solutions for the e.m.f. measurements is shown in Fig. 1.

Indicator electrode. Spectrographically pure silver wire (1 mm diameter) was spot-welded to a platina wire sealed into the end of a soft glasstube.

Reference electrode. The reference electrode was immersed in the solution to be tested. It was made from a 215 × 12 mm Pyrex glasstube and a very fine asbestos fibre (diameter ≈ 0.05 mm) was sealed through the bottom of the tube to give electrolytic contact with the test solution. No contamination of the test solution due to diffusion occurred, if the asbestos fibre was fine enough. A 0.01000 m solution of silver nitrate in potassium-sodium nitrate served as electrolyte in the reference half-cell. The metallic silver electrode in the reference was the same as the indicator electrode. The reference half-cells were stable within 0.2 mV during 24 h.

For the measurements a Students' Potentiometer from Leeds and Northrup was used in connection with a Cambridge Light Spot Galvanometer as zeroinstrument. In some
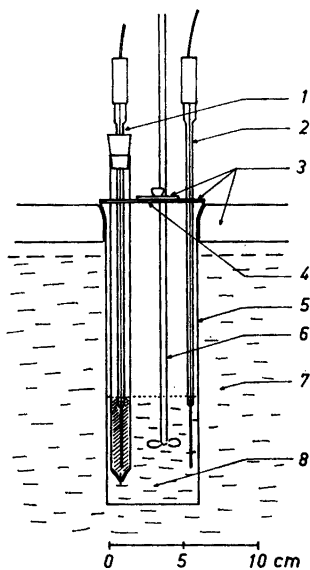
Fig. 1. Details of an apparatus for potentiometric investigation of salt melts. 1, Reference electrode. 2, Indicator electrode. 3, Asbestos covers. 4, Feeding aperture. 5, Pyrex beaker, 20 cm high, 5.5 cm inner diameter. 6, Motor driven glass stirrer. 7, A fused heating bath. 8, A melt to be investigated (300 g).
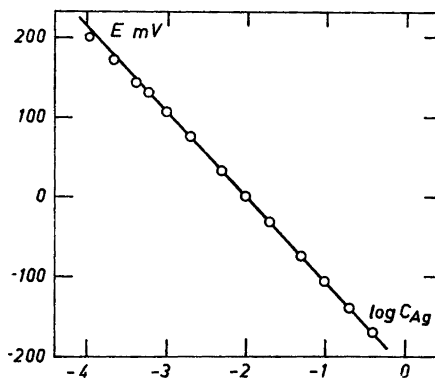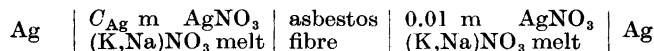

Fig. 2. A test of the validity of Nernst's equation for silver-silver nitrate electrodes in a molten equimolar mixture of potassium and sodium nitrate.

of the measurements a valve potentiometer, PHM4c from Radiometer, Copenhagen, was used. With both apparatus the e.m.f. was measured within 0.2 mV and could be reproduced within 0.5 mV. The uncertainty of the E-values is estimated to ± 0.3 mV.

The silver indicator electrode functioned very well and the e.m.f.'s could be obtained about 10 min (with a few exceptions) after addition of silver nitrate or potassium-sodium bromide to the test solution. The e.m.f.'s were stable for hours.

Measurements. As a check of the applicability of Nernst's equation to the silver-silver nitrate electrode in nitrate melts the e.m.f. of the following cell was measured at 280°C.
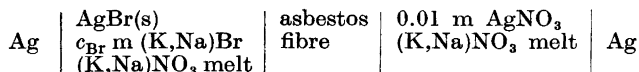
$$\text{Ag} \quad \begin{array}{|c|} C_{\text{Ag}} \text{ m} \quad \text{AgNO}_3 \\ \text{(K,Na)NO}_3 \text{ melt} \end{array} \begin{array}{|c|} \text{asbestos} \\ \text{fibre} \end{array} \begin{array}{|c|} 0.01 \text{ m} \quad \text{AgNO}_3 \\ \text{(K,Na)NO}_3 \text{ melt} \end{array} \quad \text{Ag}$$

If it holds, as has been shown by Flengas and Rideal (Ref.[5]). that the activity coefficient $f\pm$ of $AgNO_3$ is equal to 1, we can write the e.m.f. of the cell

$$E = E' - (RT/F)\ln 10 \times \log C_{\text{Ag}}$$

In Fig. 2 log C_{Ag} is plotted against E (mV). The theoretical value of (RT/F) ln 10 is 109.7 mV at 280°C. Fig. 2 gives 108.1 mV. The small deviation from the theoretical value probably depends on cooling of the electrodes from outside. When electrodes were made of silver wire without protecting glass tube the Nernst's slope was obtained as $\sim$ 106 mV. The figure indicates that a solution of silver nitrate in molten potassium-sodium nitrate probably is ideal within experimental errors for the concentration range $6 \times 10^{-4} \leq C_{\text{Ag}} \leq 0.2$ (m).

Measurements in saturated solutions were performed for the determination of the solubility product $K_{\text{s},0}$ of silver bromide. The e.m.f. of the following cell was measured, $0 \leq c_{\text{Br}} \leq 2.0$ (m) where c_{Br} is the amount of bromide added to the melt as (K,Na)Br.

$$\text{Ag} \quad \begin{array}{|c|} \text{AgBr(s)} \\ c_{\text{Br}} \text{ m (K,Na)Br} \\ \text{(K,Na)NO}_3 \text{ melt} \end{array} \begin{array}{|c|} \text{asbestos} \\ \text{fibre} \end{array} \begin{array}{|c|} 0.01 \text{ m AgNO}_3 \\ \text{(K,Na)NO}_3 \text{ melt} \end{array} \quad \text{Ag}$$

Solid silver bromide was first stirred in a solution of pure solvent. Equilibrium was reached after *ca.* 6 h when the e.m.f. was measured. Then (K,Na)Br was added to the melt. Stable e.m.f.'s were obtained after a few minutes until $c_{\text{Br}} \sim 0.5$ (m) when the equilibria were reached rather slowly (about 2 h).

The results of the measurements are given in Table 1 where [Br⁻] is calculated from the distribution of silver bromide complexes in these solutions calculated from the solubility measurements reported in Ref.[3]

Table 1. Determination of the solubility produkt $K_{\text{s},0}$ of silver bromide at increasing concentration of free bromide ions. S_{AgBr} is the solubility of silver bromide. In the reference electrode was $C_{\text{Ag}} = 10.00 \times 10^{-3}$ (m).
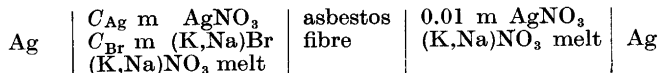Run 2.

c_{Br} m	$\bar{n}$	$S_{\text{AgBr}} \times 10^4$ m	[Br⁻] m	E mV	[Ag⁺] m	$K_{\text{s},0} \times 10^7$ m²
0			5.49×10^{-4}	136.3	5.49×10^{-4}	3.01
1.090×10^{-3}	0.33	2.99	1.29×10^{-3}	176.8	2.32×10^{-4}	2.99
2.103×10^{-3}	0.51	2.16	2.21×10^{-3}	201.9	1.36×10^{-4}	3.01
5.418×10^{-3}	0.94	1.68	5.43×10^{-3}	244.0	5.53×10^{-5}	3.00
1.044×10^{-2}	1.28	1.82	1.04×10^{-2}	274.7	2.88×10^{-5}	3.00
2.039×10^{-2}	1.60	2.41	2.02×10^{-2}	306.0	1.48×10^{-5}	2.99
5.034×10^{-2}	1.92	4.86	4.99×10^{-2}	348.3	6.00×10^{-6}	2.99
0.1003	2.12	9.82	9.92×10^{-2}	380.8	3.00×10^{-6}	2.98
0.2003	2.32	22.8	0.197	413.0	1.51×10^{-6}	2.97
0.5005	2.58	86.1	0.487	455.8	6.08×10^{-7}	2.96
1.000	2.76	282	0.954	486.6	3.15×10^{-7}	3.01
1.500	2.84	630	1.38	502.1	2.27×10^{-7}	(3.13)
2.000	2.89	1148	1.78	512.0	1.84×10^{-7}	(3.28)

Mean   2.99 ± 0.04

From the measurements $K_{s,0} = (3.00 \pm 0.10) \times 10^{-7}$ (m²) was obtained. The measurements were easy to reproduce.

The measurements in unsaturated solutions were carried out as potentiometric titrations. When $C_{Ag} \leq 3.00 \times 10^{-3}$ (m), bromide was added to melts with constant C_{Ag}. When $C_{Ag} \geq 10.00 \times 10^{-3}$ (m), silver nitrate was added to melts with constant C_{Br} since the e.m.f.'s drifted for hours when alkali bromide was added to melts with $C_{Ag} \geq 0.01$ (m). Measurements were made for $C_{Ag} = (0.3007, 1.001, 3.00, 10.00, 20.0, 50.0$ and $80.0) \times 10^{-3}$ (m). In all measurements [Ag⁺] was determined by the aid of a silver electrode. E.m.f. of the following cell was measured

$$\text{Ag} \left| \begin{array}{c} C_{Ag}\text{ m } \text{AgNO}_3 \\ C_{Br}\text{ m } (\text{K,Na})\text{Br} \\ (\text{K,Na})\text{NO}_3 \text{ melt} \end{array} \right| \begin{array}{c} \text{asbestos} \\ \text{fibre} \end{array} \left| \begin{array}{c} 0.01 \text{ m } \text{AgNO}_3 \\ (\text{K,Na})\text{NO}_3 \text{ melt} \end{array} \right| \text{Ag}$$

The E-values tabulated in Tables 2 and 3 are equal to $E_{II} - E_I$, where E_I is the measured e.m.f. when no bromide is added to the half-cell to be investigated, and E_{II} is the measured e.m.f. when the half-cell contains the actual amount of bromide. When [Ag⁺] was calculated the experimentally found value of $(RT/F)\ln 10 = 108.1$ (mV) was used.

Corrections for junction potentials were not made as the ionic mobilities were unknown and it was assumed that essentially all the current was carried by the solvent.

COMPUTION OF THE COMPLEXITY CONSTANTS

For the measurements where $C_{Ag} = 3.007 \times 10^{-4}$ and 10.01×10^{-4} (m) eqn. (9) was utilized, $F_1 = (C_{Ag} - [\text{Ag}^+])/([\text{Ag}^+][\text{Br}^-])$. A sufficiently accurate value of [Br] was obtained from the expression $[\text{Br}^-] = C_{Br} - (C_{Ag} - [\text{Ag}^+])$, i.e. it was assumed that the only complex present was AgBr.
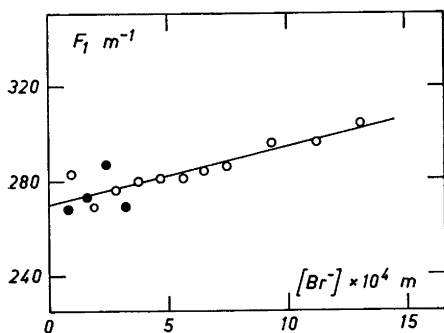

Fig. 3. $F_1 = (C_{Ag} - [\text{Ag}^+])/([\text{Ag}^+][\text{Br}^-])$ as a function of [Br⁻] for the determination of $\beta_{1,1}$ and a preliminary value of $\beta_{2,1}$. $10^4 \times C_{Ag} = 3.007$ (O) and 10.01 (●) (m).
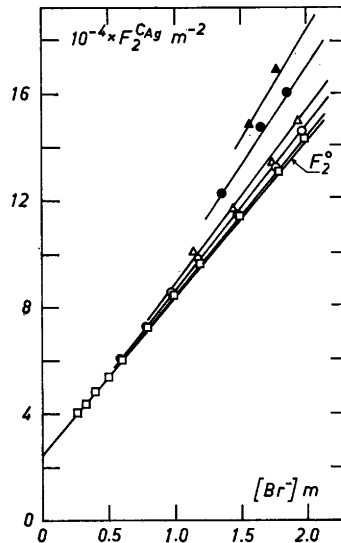

Fig. 4. $F_2{}^{C_{Ag}} = (F_1{}^{C_{Ag}} - \beta_{1,1})/[\text{Br}^-]$ as a function of [Br⁻]. $10^3 \times C_{Ag} = 3$ (□), 10 (O), 20 (△), 50 (●), and 80 (▲) (m.) The full-drawn curves are calculated from the final values of $\beta_{n.m}$ by the aid of eqns. (14) and (16).

The results of these measurements are found in Table 2. In Fig. 3 F_1 is drawn as a function of [Br⁻] and it is seen that F_1 is independent of C_{Ag} for the actual silver concentrations. The following values were obtained from Fig. 3: $\beta_{1,1} = 270 \pm 5$ (m⁻¹) and $\beta_{2,1} = (2.4 \pm 0.3) \times 10^4$ (m⁻²).

The determination of [Br⁻] in the titration series where $C_{Ag} \geq 0.003$ was more laborious. When $C_{Ag} = 0.003$ (m), eqn. (13) could be used to obtain a sufficient accurate value of $\bar{n}$ and then [Br⁻] was calculated from eqn. (12). Knowing [Br⁻] the function $F_2^{0.003} = (F_1^{0.003} - \beta_{1,1})/[Br^-]$ could be calculated. From Fig. 4. it is seen that this function is linear and can be used to obtain values of $\beta_{2,1}$ and $\beta_{3,1}$.

When $F_2^{C_{Ag}}$ was calculated for the other silver concentrations, it was found that the experimental points belonging to the series with $C_{Ag} \geq 0.010$ (m) lay above the straight line $\beta_{2,1} + \beta_{3,1}$ [Br⁻] calculated from the series with $C_{Ag} = 0.003$ (m) in Fig. 4. This can be accounted for by assuming that polynuclear complexes were present, provided that the activity factors were constant. The results of the measurements are collected in Table 3.

An effort was made to find out what kind of polynuclear complexes could be used to describe the results. We found that the presence of a dinuclear complex with six ligands, $Ag_2Br_6^{4-}$, was consistent with the measurements.

In order to obtain more accurate values of the constants $\beta_{2,1}$, $\beta_{3,1}$, and $\beta_{6,2}$ we calculated $\bar{n}$ from eqn. (24) using $m = 2$. It was then possible to calculate more accurate values of [Br⁻] from eqn. (12), and using these values, refined values of the complexity constants were calculated.

Table 2. Potentiometric measurements used to calculate F_1 for the determination of the complexity constants $\beta_{1,1}$ and $\beta_{2,1}$.

$C_{Ag} \times 10^4$ m	$C_{Br} \times 10^4$ m	E mV	$[Ag^+] \times 10^4$ m	$[Br^-] \times 10^4$ m	$F_1 \times 10^{-2}$ m⁻¹
10.01	0	0			●
	1.013	1.0	9.80	0.802	2.67
	2.013	2.0	9.59	1.596	2.73
	3.017	3.1	9.37	2.377	2.87
	4.016	3.9	9.21	3.22	2.70
3.007	0	0			○
	0.992	1.2	2.931	0.916	2.83
	2.017	2.3	2.863	1.873	2.69
	3.022	3.5	2.791	2.806	2.76
	4.042	4.7	2.721	3.76	2.80
	5.030	5.8	2.658	4.68	2.81
	6.045	6.9	2.596	5.63	2.81
	7.012	8.0	2.536	6.54	2.84
	8.021	9.1	2.477	7.49	2.86
	10.03	11.5	2.354	9.38	2.96
	12.01	13.5	2.255	11.27	2.96
	14.01	15.8	2.148	13.15	3.04

The following values of the over-all complexity constants were obtained. The limits of error refer to the maximum random errors.

$\beta_{1,1} = (2.70 \pm 0.05) \times 10^2$ (m^{-1})
$\beta_{2,1} = (2.4 \pm 0.1) \times 10^4$ (m^{-2})
$\beta_{3,1} = (5.9 \pm 0.7) \times 10^4$ (m^{-3})
$\beta_{6,2} = (1.2 \pm 0.6) \times 10^{10}$ (m^{-7})

DISCUSSION

The fact that the ligand number $\bar{n}$, calculated with eqn. (13) for $C_{Ag} = 3.00 \times 10^{-3}$ (m), attains a highest value of ~ 2.9 might indicate that no complexes with four ligands are present. The values of $\bar{n}$ from eqn. (13) are not quite accurate as dinuclear complexes seem to be present. However, these $\bar{n}$-values give values of [Br⁻], calculated from eqn. (12), that agree within 2 % with the values computed by using the final complexity constants. The complex formation curve for $C_{Ag} = 3.00 \times 10^{-3}$ (m) is shown in Fig. 5.
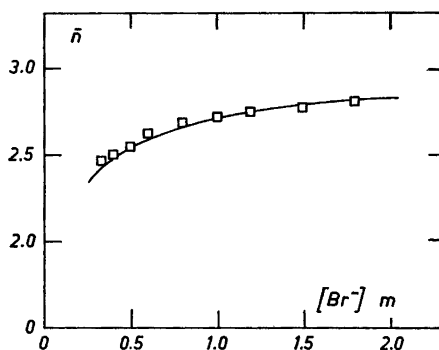

Fig. 5. The ligand number $\bar{n}$ as a function of [Br⁻] for $C_{Ag} = 0.003$ (m). The ordinates of the symbols are obtained from eqn. (13) and the full-drawn curve is calculated from eqn. (24), $m = 2$.

We can get an idea of how much the activity factors vary from the potentiometric determination of the solubility product $K_{s,0}$ as a function of [Br⁻]. As can be seen from Table 1, $K_{s,0}$ is constant over the rather large concentration range [Br⁻] $= 5 \times 10^{-4} - 1.0$ (m) but for higher values of [Br⁻] the solubility product increases. This may indicate that the solutions do not behave ideally for [Br⁻] >1 (m). If the concentrations had been expressed in mole fractions instead of molality, discrepancy from ideal behaviour should have turned up at lower bromide concentrations (around 0.2 or 0.3 (m)).

From measurements in aqueous solutions [16] it has been verified that the co-ordination number of Ag⁺ is four in its bromide complexes. Several authors have found, however, that the complex formation of mononuclear complexes in melts "stops" at MA₃. In this paper it is also shown that mononuclear species with four ligands would probably not be formed, unless they are formed at still higher bromide ion concentration or in solutions with the salt, containing the ligand ion, used as solvent.

Table 3. Potentiometric measurements to calculate $F_2{}^{C_{Ag}}$. The figures within brackets refer to the equation used in the calculation.

$C_{Ag} \times 10^3$ m	C_{Br} m	$\bar{n}$ (24)	$\bar{n}$ (13)	[Br⁻] m (12)	E mV	[Ag⁺] × 10⁸ m	$F_2{}^{C_{Ag}} \times 10^{-4}$ m⁻² (16)
3.00	0			0	0		□
	0.270	2.36		0.263	373.5	105.2	4.02
	0.330	2.42	2.47	0.323	396.2	64.9	4.35
	0.400	2.47	2.51	0.393	419.1	39.8	4.81
	0.500	2.54	2.55	0.492	445.2	22.85	5.37
	0.600	2.59	2.63	0.592	467.5	14.20	5.98
	0.800	2.66	2.69	0.792	503.5	6.60	7.22
	1.000	2.70	2.72	0.992	531.9	3.60	8.43
	1.200	2.74	2.75	1.192	555.2	2.193	9.61
	1.500	2.79	2.77	1.492	584.3	1.180	11.40
	1.800	2.81	2.81	1.792	608.0	0.712	13.10
	2.000	2.83		1.991	662.1	0.528	14.33
10.00	0			0	0		○
	0.600	2.58		0.574	465.1	49.8	6.04
	0.800	2.66		0.773	501.5	22.95	7.26
	1.000	2.71		0.973	530.6	12.35	8.53
	1.200	2.75		1.172	554.8	7.38	9.83
	1.500	2.79		1.472	583.4	4.01	11.49
	1.800	2.82		1.772	607.5	2.400	13.25
	2.000	2.83		1.972	622.2	1.755	14.64
20.0	0			0	0		△
	1.200	2.75		1.145	553.6	15.13	10.06
	1.500	2.79		1.444	582.4	8.19	11.69
	1.800	2.82		1.744	606.6	4.89	13.43
	2.000	2.84		1.943	621.9	3.53	14.99
50.0	0			0	0		●
	1.500	2.80		1.360	579.1	21.97	12.29
	1.800	2.83		1.659	606.4	12.29	14.77
	2.000	2.85		1.858	621.0	9.00	16.07
80.0	0			0	0		▲
	1.800	2.84		1.573	601.7	21.73	14.86
	2.000	2.85		1.772	619.0	15.03	16.93

In aqueous solutions complex formation between Ag^+ and NO_3^- has been found [17] and the stability constant K_1 of the species $AgNO_3$ is of the order 0.5—0.8 M^{-1}. Due to similar behaviour of Ag^+ in fused alkali nitrates and in aqueous solutions we might expect some degree of association between silver ions and nitrate ions in fused nitrates. From the measurements no conclusion can be drawn about such species since the great concentration of nitrate ions was not changed very much. Therefore, Ag_mBr_n is only an abbreviation of $K_xNa_y(NO_3)_zAg_mBr_n$ where x,y, and z are unknown numbers.

The existence of the species $AgBr$, $AgBr_2^-$ and $AgBr_3^{2-}$ has been shown both by solubility and by potentiometric measurements. Both methods gave

Table 4. Complexity constants $\beta_{n,m}$ and step-wise stability constants K_n calculated from the complexity constants obtained by different investigators and with different methods. All constants are valid in an approximate equimolar mixture of KNO_3 — $NaNO_3$ as solvent and at 280°C.

Reference and method	KNO_3-$NaNO_3$ mole %	$\beta_{1,1}$ m^{-1}	$\beta_{2,1}$ m^{-2}	$\beta_{3,1}$ m^{-3}	$\beta_{1,2}$ m^{-2}	$\beta_{6,2}$ m^{-7}	K_1 m^{-1}	K_2 m^{-1}	K_3 m^{-1}
This work e.m.f.	50—50	270	2.4×10^4	5.9×10^4		1.2×10^{10}	270	89	2.5
Ref.[3] solubility	50—50	267[a]	2.3×10^4	6.7×10^4		2.2×10^{10}	267	88	2.9
Ref.[6] e.m.f.	47—53	208	4.5×10^4				208	216	
Refs.[7,8] e.m.f.	50—50[b]	203	2.0×10^4		2.3×10^4		203	97	

[a] The values of $\beta_{n,m}$ from Ref.[3] are calculated using $K_{s,0} = 3.00 \times 10^{-7}$ (m^2).

[b] The figures given in Refs.[7,8] are interpolated to be valid for a 50—50 mole % mixture.

complexity constants that are in good agreement as can be seen from Table 4. From the over-all complexity constants $\beta_{n,m}$ the step-wise stability constants K_n for mononuclear species

$$K = [MA_n]/([MA_{n-1}][A]) = \beta_{n,1}/\beta_{n-1,1}$$

have been calculated and given in Table 4. In that table some values of complexity constants obtained by other authors are also collected.

The existence of dinuclear complexes $Ag_2Br_n{}^{2-n}$ is not convincingly proved though there is some experimental evidence of them. Blander *et al.*[7,8] report the complex species Ag_2Br^+ at low bromide concentration and our measurements indicate the presence of $Ag_2Br_6{}^{4-}$ in solutions with high bromide concentration. Our measurements cannot be decribed by assuming ideal solutions in which the complexes $AgBr$, $AgBr_2{}^-$, and $AgBr_3{}^{2-}$ are the only species formed. As the ligand number $\bar{n}$ never exceeds ~ 2.9 (Fig. 5) it seems probable that no mononuclear complexes with four or more ligands are present in the solutions. Therefore, it is necessary to assume dinuclear complexes to describe the experimental results. The only dinuclear complexes that can be used for this description are $Ag_2Br_5{}^{3-}$ and $Ag_2Br_6{}^{4-}$. The measurements are very well described by assuming the presence of the species $Ag_2Br_6{}^{4-}$, but it should be kept in mind that the ideality of the solutions at the highest bromide concentrations might be questioned. From Table 5 we can see that the agreement between the values of the complexity constant obtained from solubility and potentiometric measurements are good except in the case of $\beta_{6,2}$.

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