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Cationic Silver Bromide Complexes in Alkali Nitrate Melts

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Potentiometric measurements of the free ligand concentration [Ag^+] and solubility measurements have been used to investigate the formation of cationic complexes between silver(I) and bromide ions in fused equimolar $(K,Na)NO_3$ at 280 °C. No polynuclear (polybromic) species can be detected potentiometrically. The distribution of AgBr and $AgNO_3$ between solid solutions $Ag(Br,NO_3)$ and the nitrate melt indicates a stepwise formation of complexes $Ag_mBr^{(m-1)+}$ with $m = 2$, 3, and 4. The corresponding stability constants have been evaluated from the solubility data.

The formation and thermodynamic stability of neutral and anionic silver bromide complexes in alkali nitrate melts have been studied previously at this laboratory.[1-3] From studies in aqueous solution – mostly by solubility measurements[4-8] – the ability of silver and bromide ions to form cationic complexes $Ag_mBr^{(m-1)+}$ has become evident. Analogous chloride and iodide complexes with ion charges +1, +2, and +3 have also been suggested in aqueous solution[5-7,9-12] and strong evidence for similar ions in polar organic solvents has emerged as well.[13-15]

Solid compounds of the general formulae $Ag_mXA_{(m-1)}$ ($X = Cl$, Br or I and $A = NO_3$, ClO_4, or F) have been prepared from aqueous solutions[7,16-21] and from anhydrous melts.[22-26]

In some binary melts $AgX-AgNO_3$ the existence of cationic silver halide species has been suggested.[26-28] In ternary systems so-called "dinuclear" species Ag_2X^+ have been proposed as an interpretation of emf data obtained in fused alkali or alkaline earth metal nitrates. Thus, evidence for Ag_2Cl^+ and Ag_2Br^+ has been found in a number of nitrate media,[29-35] and Guion[36] explained the results from similar emf measurements in molten eutectic $(K,Li)_2SO_4$ by assuming the presence of Ag_2Br^+. The emf method that was solely used in these investigations[29-36] is, however, not very convenient for studying relatively weak cationic complexes, since – in general – the measured concentration of free ligand, [Ag^+], does not differ very much from the total ligand concentration C_{Ag}. Furthermore, the fraction of halide ion present as Ag_2X^+ has often been small, making an accurate evaluation of the corresponding stability constant impossible.[37,38]

A more convenient method is to study the solubility of a silver halide in melts containing various amounts of, *e.g.*, $AgNO_3$. Seward and Field[39] used this method to indicate the presence of Ag_2Cl^+ in fused $NaNO_3$ and Sinistri and Pezzati[40] have made a more extensive study of silver chloride and bromide complexation in equimolar $(K,Na)NO_3$ employing the solubility method. They found evidence for complex ions with net charges +1 and +2 and determined the stability constants for the proposed species Ag_2X^+ and Ag_3X^{2+}.

This study of systems $AgBr-AgNO_3-(K,Na)NO_3$ has been undertaken in order to complete the picture of the silver bromide complexation in nitrate melts and to compare the results with those from aqueous media with respect to relative stability of different species and to the maximum number of silver(I) ligands attached to a bromide central ion.

The study is restricted to the range 0.2 mol $kg^{-1} < C_{Ag} < 2$ mol kg^{-1}, which is of primary interest as far as only positively charged complexes are concerned. In contrast to what has been found for dissolution of alkali halides in solid AgI[41] and AgBr,[3] it appeared that the solubility of $AgNO_3$ in solid AgBr was rather small. Nevertheless it was analytically significant and the composition of both phases have been determined. The activity of AgBr in the solid is computed as described recently.[3]

In the region $0.8\ \text{mol kg}^{-1} < C_{Ag} \leq 2.4\ \text{mol kg}^{-1}$ the free ligand concentration $[Ag^+]$ has been directly determined from emf measurements.

From the emf data the average ligand number $\bar{m}$ can be calculated with an accuracy good enough to provide a semi-quantitative picture of the complex formation at high ligand concentrations, which assists the interpretation of the solubility data.

EXPERIMENTAL

Chemicals. All chemicals were *p.a.* grade and prepared and stored as described previously.[3,41]

Apparatus. The equipment used for the solubility and emf measurements has been described in Ref. 3 and Refs. 42 and 43, respectively.

Procedure. Solubility measurements: Systems containing 75.00 g equimolar $(K,Na)NO_3$, 12 g AgBr and various amounts of $AgNO_3$ were agitated for at least 50 h until equilibrium was attained (as concluded from constant solubility). Samples were withdrawn from the nitrate phase and analysed for silver and bromide.

Emf measurements: Two general types of cells were used; *cf.* Scheme 1.

In the study of unsaturated melts the electrode function was checked by measuring emfs after adding successive portions of $AgNO_3$ to the left hand compartment of cell II, keeping $C_{Br} = 0$. Silver bromide was then dissolved in the melt, and the titration with $AgNO_3$ was continued to $C_{Ag} \approx 2.4$ mol kg^{-1}.

The measurements on cell I were started with a two-phase system, $Ag(Br,NO_3)(s)$ – nitrate melt, and C_{Ag} was varied by additions of $AgNO_3$ in the range $0.8\ \text{mol kg}^{-1} \leq C_{Ag} \leq 2.2\ \text{mol kg}^{-1}$. In all measurements C^0_{Ag} was kept as high as 2.2 mol kg^{-1} in order to minimize the effects of AgBr-precipitation in the diffusion layer between the half-cells. Stable emf readings were obtained within a few minutes in the study of unsaturated melts, whereas equilibrium times of 2 – 3 h were required when solid-liquid equilibria had to be established.

Analyses. The solubilities were determined by gravimetric analyses for bromide as AgBr. Silver was determined by electroanalytical precipitation of Ag on a rotating platinum cathode from hot aqueous cyanide solutions. The composition of the solid solution was calculated from the difference between added and found amounts of silver nitrate in the melt.

NOTATIONS

A. Quantities referring to the emf measurements.

E_{obs} = the observed electromotive force of cells I and II.

ε = correction term, compensating for deviations from ideal Nernst behaviour.

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

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

B. Quantities referring to the solubility measurements.

For the solid phase:

x_i = mol fraction of component i ($i = 1$ for AgBr and 2 for $AgNO_3$).

a_i = activity of component i.

$f_i = a_i x_i^{-1}$.

For the nitrate melt (all concentrations are expressed in molality units mol kg^{-1}, referring to equimolar $(K,Na)NO_3$ as solvent):

C_{Ag}, C_{Br} = total concentration of silver(I) and bromide, respectively.

[A] = concentration of species A.

I:	Ag $Ag(Br,NO_3)(s)$	C'_{Ag} $AgNO_3$ C_{Br} AgBr (saturated) $(K,Na)NO_3$	asbestos fibre	C°_{Ag} $AgNO_3$ $(K,Na)NO_3$	Ag
II:	Ag	C'_{Ag} $AgNO_3$ C_{Br} AgBr (unsaturated) $(K,Na)NO_3$	asbestos fibre	$C^{\circ}_{Ag}AgNO_3$ $(K,Na)NO_3$	Ag

Scheme 1.

$a(\mathrm{NO_3})$ = the nitrate ion activity.
β_m = $[\mathrm{Ag}_m\mathrm{Br}^{(m-1)+}][\mathrm{Ag}^+]^{-m}[\mathrm{Br}^-]^{-1}$.
K_m = $[\mathrm{Ag}_m\mathrm{Br}^{(m-1)+}][\mathrm{Ag}_{(m-1)}\mathrm{Br}^{(m-2)+}]^{-1}\cdot[\mathrm{Ag}^+]^{-1}$.
$\bar{m}$ = $(C_{\mathrm{Ag}}-[\mathrm{Ag}^+])C_{\mathrm{Br}}^{-1}$.
M = maximum value of m.

CALCULATIONS AND RESULTS

Electromotive force measurements. In order to minimize the uncertainties in $\bar{m}$ which are due to random errors in E_{obs} the measurements had to be restricted to melts with rather large total concentrations of silver and bromide. In the studied composition range, however, another complication arises, *viz.* that the ideal linear relationship between E_{obs} and log $[\mathrm{Ag}^+]$ ceases to be valid when log $[\mathrm{Ag}^+] \gtrsim 0$.[43] However, E_{obs} is still well reproducible. If we make the reasonable assumption that the presence of bromide in the melts does not affect the deviations from linearity as compared to halide-free systems, we may use the emf data collected in such melts [43] in the calculation of a correction term ε to be added to E_{obs}, yielding data (E_{corr}; log $[\mathrm{Ag}^+]$) which should be rationalized as

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

The correction, which accounts mainly for liquid junction potentials and possible deviations from thermodynamic ideality, was tested in the bromide-free systems in series 3 – 5 (Table 1). The resulting parameter values (E_0/mV; k/mV), which were used in the calculations pertaining to bromide containing melts in each series, (37.6; 109.8), (37.4; 109.4), and (37.4; 109.8), respectively. These values of E_0 and k are in excellent agreement with the theoretical Nernst equation parameters RTF^{-1} ln C°_{Ag} = 37.4 mV and RTF^{-1} ln 10 = 109.7 mV, and hence $[\mathrm{Ag}^+]$ has been calculated from

$$E_{\mathrm{corr}} = (RT/F)\ \ln\ (C^\circ_{\mathrm{Ag}}/[\mathrm{Ag}^+])$$

in series 1 and 2 (systems $\mathrm{Ag(Br,NO_3)(s)}$ – nitrate melt). All experimental emf data are collected in Table 1.

In series 1 and 2 the ligand numbers were calculated by use of C_{Br} from the separate solubility data. In Fig. 1 the ligand numbers $\bar{m}$ are plotted *vs.* $[\mathrm{Ag}^+]$. The uncertainties in the $\bar{m}$-values are of an order of magnitude of

Table 1. Data from the electromotive force measurements.

C_{Br}/mol kg^{-1}, C_{Ag}/mol kg^{-1}, E_{obs}/mV, E_{corr}/mV;

Series 1, cell type I

0.0162, 0.912, *36.1*, *44.8*; 0.0246, 1.108, *29.0*, *36.5*; 0.0364, 1.325, *22.5*, *28.7*; 0.0470, 1.491, *18.8*, *24.0*; 0.0631, 1.717, *14.3*, *18.4*; 0.0804, 1.927, *10.8*, *13.8*; 0.0977, 2.119; *8.2*, *10.5*;

Series 2, cell type I

0.0128, 0.817, *40.5*, *49.8*; 0.0198, 1.003, *32.6*, *40.7*; 0.0300, 1.214, *25.8*, *32.6*; 0.0426, 1.432, *20.3*, *25.9*; 0.0548, 1.605, *16.6*, *21.3*; 0.0686, 1.788, *13.3*, *17.1*; 0.0815, 1.940, *10.8*, *13.8*; 0.1021, 2.161, *7.8*, *10.0*;

Series 3, cell type II

0, 0.494, *60.2*, *71.1*; 0, 0.701, *44.8*, *54.7*; 0, 0.903, *34.0*, *42.4*; 0, 1.143, *24.6*, *31.2*; 0, 1.356, *18.0*, *23.1*; 0.0352, 1.391, *20.8*, *26.5*; 0.0352, 1.567, *15.8*, *20.3*; 0.0352, 1.710, *12.3*, *15.7*; 0.0352, 1.856, *9.1*, *11.6*; 0.0352, 2.029, *5.5*, *7.0*; 0.0352, 2.188, *2.6*, *3.1*;

Series 4, cell type II

0, 0.766, *40.6*, *50.0*; 0, 0.988, *30.2*, *37.9*; 0, 1.204, *22.5*, *28.6*; 0, 1.422, *16.2*, *20.8*; 0, 1.656, *10.3*, *13.3*; 0.0589, 1.715, *13.9*, *17.8*; 0.0589, 1.844, *11.1*, *14.2*; 0.0589, 1.978, *8.0*, *10.2*; 0.0589, 2.122, *5.3*, *6.7*; 0.0589, 2.350, *1.2*, *1.4*;

Series 5, cell type II

0, 0.893, *34.4*, *42.8*; 0, 1.161, *23.8*, *30.2*; 0, 1.411, *16.5*, *21.1*; 0, 1.652, *10.5*, *13.5*; 0, 1.877, *5.8*, *7.3*; 0.0764, 1.953, *10.0*, *12.8*; 0.0764, 2.101, *6.7*, *8.7*; 0.0764, 2.255, *4.0*, *5.0*; 0.0764, 2.400, *1.4*, *1.6*;

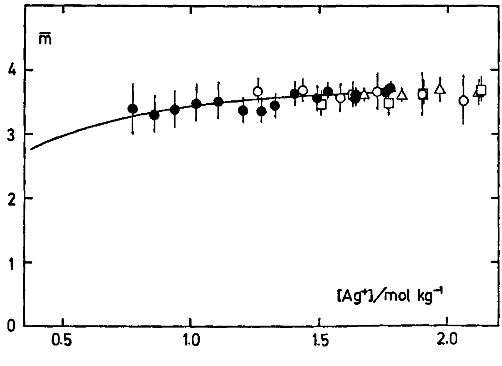

Fig. 1. Ligand numbers $\bar{m}$ determined by emf measurements. Symbols: melts saturated in AgBr (●); C_{Br} = 76.4 mmol kg^{-1} (△); C_{Br} = 58.9 mmol kg^{-1} (□); C_{Br} = 35.2 mmol kg^{-1} (○). The solid curve is calculated by use of the stability constants of Table 3.

Table 2. Solubility and distribution data.

$\frac{C_{Ag}}{\text{mol kg}^{-1}}$	$\frac{C_{Br}}{\text{mol kg}^{-1}}$	$x_2 \times 10^2$	a_1	f_1	$a_2 \times 10^2$	f_2	$\bar{m}$	$\frac{[Ag^+]}{\text{mol kg}^{-1}}$	$\frac{[Ag^+][Br^-] \times 10^7}{(\text{mol kg}^{-1})^2}$
0.2860	0.00201	0.03	1.000	1.000			2.57	0.2808	3.00
0.402	0.00297	0.05	1.000	1.000			2.81	0.394	3.00
0.495	0.00440	0.13	1.000	1.001			2.96	0.482	3.00
0.590	0.00662	0.27	0.999	1.002			3.08	0.570	3.00
0.695	0.00924	0.42	0.999	1.003			3.18	0.666	3.00
0.792	0.01195	0.43	0.998	1.002	0.15	0.34	3.27	0.753	2.99
0.900	0.01563	0.83	0.997	1.005	0.17	0.20	3.34	0.848	2.99
1.008	0.02018	0.85	0.996	1.004	0.19	0.22	3.40	0.939	2.99
1.110	0.02470	0.90	0.995	1.004	0.20	0.22	3.45	1.025	2.99
1.200	0.02922	1.40	0.995	1.009	0.20	0.14	3.48	1.098	2.98
1.297	0.03466	1.79	0.993	1.011	0.21	0.12	3.52	1.175	2.98
1.404	0.0419	1.93	0.992	1.012	0.23	0.12	3.55	1.255	2.98
1.501	0.0476	2.37	0.991	1.015	0.26	0.11	3.58	1.331	2.97
1.623	0.0560	2.31	0.989	1.012	0.28	0.12	3.60	1.421	2.97
1.713	0.0627	2.62	0.987	1.014	0.29	0.11	3.62	1.486	2.96
1.824	0.0716	2.70	0.986	1.013	0.30	0.11	3.64	1.563	2.96
1.931	0.0805	2.96	0.984	1.014	0.32	0.11	3.66	1.636	2.95
2.044	0.0914	3.10	0.983	1.014	0.34	0.11	3.67	1.708	2.95
2.186	0.1044	3.32	0.981	1.015	0.36	0.11	3.69	1.801	2.94

± 0.2 as estimated from a reasonable assumption of random errors in E_{corr} of about ± 0.3 mV. As seen from Fig. 1, $\bar{m}$ increases with $[Ag^+]$ from 3.3 to 3.7 in the concentration range investigated. Within the limits of experimental errors no systematic dependence of $\bar{m}$ on C_{Br} at constant $[Ag^+]$ can be detected. This feature is taken as an indication of the absence of polynuclear complexes $Ag_mBr_n^{(m-n)+}$ in observable amounts with a possible exception for species having $m/n \approx 3.5$.

No attempts at a further quantitative evaluation of the $\bar{m}$-data in terms of definite stability constants have been made, but the important features of Fig. 1 which have been stressed here, give strong support to the interpretation of the solubility data.

Solubility and distribution measurements. All data pertaining to the solubility and distribution measurements are collected in Table 2. As indicated by the magnitude of x_2 there is a small but significant solubility of $AgNO_3$ in AgBr, and the following two heterogeneous equilibria have to be considered in the treatment of the data:

$$AgBr(ss) \rightleftharpoons Ag^+ + Br^-$$

$$K_1' = [Ag^+][Br^-]a_1^{-1} \qquad (2)$$

$$AgNO_3(ss) \rightleftharpoons Ag^+ + NO_3^-$$

$$K_2' = [Ag^+]a(NO_3)a_2^{-1} \qquad (3)$$

Following the general principles outlined previously,[3] we set d ln $a(NO_3) = 0$, since NO_3^- is effectively the only anion present in the nitrate melt. Taking the standard state for silver bromide to be pure solid AgBr, we arrive at

$$\ln a_{1j} = \int_{\ln [Ag^+]_0}^{\ln [Ag^+]_j} -(x_2/x_1)\, \mathrm{d} \ln [Ag^+] \qquad (4)$$

(The subscript j is used to indicate different quantities referring to the same actual system, and $[Ag^+]_0$ refers to a system with $x_2 = 0$).

Since the experimental study was restricted to a range where K_1' and β_1 cannot be determined these constants have been taken from the thorough investigations of Cigén and Mannerstrand,[1,2] *viz.* $K_1' = 3.00 \times 10^{-7}$ (mol kg^{-1})^2 and $\beta_1 = 267$ (mol kg^{-1})$^{-1}$. The data have been treated according to

$$(C_{Br}K_1'^{-1}a_1^{-1} - [Ag^+]^{-1} - \beta_1)[Ag^+]^{-1} = \sum_{m=2}^{M} k_m[Ag^+]^{(m-2)} \qquad (5)$$

From the least squares treatment of the left hand member as a function of $[Ag^+]$ it became evident that the summation in the right hand member had to be carried out to $M = 4$, *viz.* complexes with ion charges + 1, + 2, and + 3

Table 3. Over-all stability constants for complexes $Ag_mBr^{(m-1)+}$ in alkali metal nitrate melts at 280 °C. The errors quoted are three standard deviations from the least squares calculations.

	$\beta_1 \times 10^{-2}$ $(\text{mol kg}^{-1})^{-1}$	$\beta_2 \times 10^{-4}$ $(\text{mol kg}^{-1})^{-2}$	$\beta_3 \times 10^{-4}$ $(\text{mol kg}^{-1})^{-3}$	$\beta_4 \times 10^{-4}$ $(\text{mol kg}^{-1})^{-4}$
This work, $(K,Na)NO_3$	2.67 [a]	1.1 ± 0.4	2.2 ± 0.8	4.5 ± 0.5
Ref. 40, solubility data, $(K,Na)NO_3$ [b]	3.5	0.8	2.4	–
Ref. 35, emf data, KNO_3 [c]	2.6	2.9	–	–
Ref. 34, emf data, $NaNO_3$ [c]	1.9	1.9	–	–

[a] From Ref. 2. [b] Interpolated values from experimental determinations at 275 and 300 °C. [c] Apparent stability constants, extrapolated from investigations in the range 400–500 °C.

should be considered. Since an existence of polynuclear (polybromic) species $Ag_mBr_n^{(m-n)+}$ would require $m/n \approx 3.5$, to be in accordance with the potentiometric data, such species would have ion charges $\geq +5$. Therefore, it is concluded that only monobromic complexes are present in significant amounts. The solubilities are well reproduced assuming a stepwise formation of complexes Ag_2Br^+, Ag_3Br^{2+}, and Ag_4Br^{3+} and the parameters k_m of eqn. (5) are thus identified as β_m. Starting with $[Ag^+] \approx C_{Ag} - 3C_{Br}$ the calculations were iterated according to eqns. (4) and (5) to yield the final set of stability constants β_m and free ligand concentrations $[Ag^+]$. The constants are given in Table 3.

Since no conclusive evidence is found for specific halide-alkali metal ion interactions in mixed halide nitrate melts,[46–48] and since the calculations indicate that all complexes are present in fairly large relative amounts, no serious errors in the stability constants due to the "solvation effects" should be expected.[3]

The over-all constants $\beta_2 - \beta_4$, which are collected in Table 3, are all of the same order of magnitude. Hence, all complexes Ag_2Br^+, Ag_3Br^{2+} and Ag_4Br^{3+} are present simultaneously in comparable amounts in most of the melts investigated, which is the main reason why the uncertainties in β_2 and β_3 are rather large although the spread in experimental solubility data is fairly low. Table 3 also includes β-values interpolated from the sets of constants determined by Sinistri and Pezzati[40] by solubility measurements at 275 and 300 °C. For β_2 and β_3 the agreement with their data is very good. It is also obvious that Sinistri and coworkers did not extend their measurements to the composition range where Ag_4Br^{3+} had to be considered.

The distribution of Ag(I) between the two phases has been treated as follows. Firstly, the activities a_2 were estimated by integrating the relation

$$d \ln f_2 = -(x_1/x_2)\, d \ln f_1 \qquad (6)$$

Since x_1/x_2 appeared to be well approximated by

$$x_1/x_2 = [\sum_{\nu=0}^{2} b_\nu (\ln f_1)^\nu]^{-1} \qquad (7)$$

the integration was performed analytically from the lower limit ($\ln f_2 = 0$; $\ln f_1 = 0$), *i.e.* the standard state for $AgNO_3$ is chosen to be in accordance with the condition $\lim_{x_1 \to 0} f_2 = 1$.

For the most dilute solutions the errors in x_2 and hence in $\ln f_1$ prevent meaningful calculations. For that reason a_2 and f_2 have been omitted in Table 2 for these systems.

Secondly, setting $a(NO_3) = 1$, the heterogeneous equilibrium constant K_2' is calculated as the average value of $[Ag^+]a_2^{-1}$, yielding $K_2' = (5.2 \pm 0.6) \times 10^2$ mol kg^{-1}. From K_1' and K_2' a conditional equilibrium constant K_{12}' for the anion exchange reaction

$$AgBr(ss) + NO_3^- \rightleftharpoons AgNO_3(ss) + Br^-$$

is obtained as $K_{12}' = 5.8 \times 10^{-10}$ mol kg^{-1}.

Table 4. The stepwise stability constants and quotients in molten alkali nitrate and aqueous solution.

Medium	Quantity	$m=1$	$m=2$	$m=3$	$m=4$
H_2O, 20 °C, $I=0$	K_m/M^{-1}	2.4×10^4 [a]	475 [b]	12 [b]	–
$(K,Na)NO_3(l)$, 280 °C	$K_m/(\text{mol kg}^{-1})^{-1}$	267 [c]	40	2	2
H_2O, 20 °C, $I=0$	$K_m/K_{(m+1)}$	50	40	–	–
$(K,Na)NO_3(l)$, 280 °C	$K_m/K_{(m+1)}$	7	20	1	–

[a] Determined at 25 °C, Ref. 44. [b] Ref. 6. [c] Ref. 2.

DISCUSSION

The potentiometric ligand concentration measurements in melts concentrated in solutes have clearly demonstrated the absence of systematic dependence of $\bar{m}$ on C_{Br} in the composition range where a quantitative treatment of the complex equilibria is meaningful. Such a dependence should be expected if polybromic species with ion charges $\leq +3$ were present in significant amounts. The β-values of Table 3 have been used to compute ligand numbers $\bar{m}$, and the corresponding graph of $\bar{m}$ *vs.* $[Ag^+]$ is included in Fig. 1 to illustrate the perfect agreement between the emf and solubility measurements as interpreted in terms of mononuclear complexes only. It might, however, seem reasonable to expect polybromic complex cations to be formed with the bromine atoms joined *via* a Br–Ag–Br linkage – an arrangement which has recently been found in solid Ag_2BrNO_3. This compound contains trigonal bipyramidal Ag_5Br-polyhedra, linked together by edges and corners.[45]

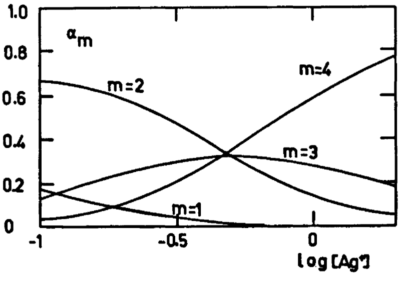

Fig. 2. The distribution of bromide on different complex ions. $\alpha_m=[Ag_mBr^{(m-1)+}]C_{Br}^{-1}$.

The relative distribution of bromide in different species is shown in Fig. 2 and the stepwise stability constants and quotients between them are collected in Table 4, where the relevant comparisons with aqueous solution data can also be made. In water no preference for Br to coordinate a certain number of ligands can be observed, whereas $m=2$ seems to be somewhat preferred at the expense of 3 in fused nitrate media, where Ag_3Br^{2+} amounts to at most about 30 % of C_{Br}.

Finally it should be noted that although three terms in the right hand member of eqn. (5) were found to describe the solubilities sufficiently well in the composition range investigated, there is no obvious reason why the complex formation curve should stop definitely at $\bar{m}=4$. The structures of the solid compounds $Ag_3I(NO_3)_2$[21] and Ag_2BrNO_3[45] suggest that a larger maximum coordination number might be possible.

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