A Solubility Study of the Complex Formation between Silver and Bromide Ions in Alkali Nitrate Melts

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The reaction between solid silver bromide and bromide ions in a fused equimolar mixture of potassium nitrate and sodium nitrate as solvent was studied at 280°C. The change in solubility of the slightly soluble silver bromide, when the concentration of bromide ions was increased by adding a varying excess of an equimolar mixture of potassium bromide and sodium bromide, was interpreted as the formation of complexes between silver bromide and bromide ions. The following over all complexity constants β were obtained: $\beta_{1,1} = 267$ (m^{-1}); $\beta_{2,1} = 2.3 \times 10^4$ (m^{-2}); $\beta_{3,1} = 6.7 \times 10^4$ (m^{-3}); $\beta_{6,2} = 2.2 \times 10^{10}$ (m^{-7}). For the solubility product of silver bromide the value 2.7×10^{-7} (m^2) was obtained.

In a previous paper [1] the complex formation between silver ions and bromide ions in molten alkali nitrate as solvent was studied by the aid of a potentiometric method. However, it seems desirable to investigate the complex formation with different methods, since the knowledge of complex formation in fused media solvents is hitherto very incomplete. Among other methods used we may mention freezing point depression, [2]conductance,[3] spectrophotometric,[4] and solubility [5-9] methods.

In this paper we will report the results of an investigation of the complex formation between silver ions and bromide ions studied with a solubility method. The solubility of silver bromide was studied as a function of the concentration of the free bromide ions in the solution using an equimolar mixture of potassium nitrate and sodium nitrate as solvent. The concentration of the ligand was varied over the range $c_{Br} = 0.001-2$ (m), which is a larger range than what is found in most investigation of complex formation in melts. The variation of the solubility of silver bromide, when the bromide concentration is raised, is well consistent with the opinion that complex species are formed.

EQUATIONS FOR THE CALCULATION OF THE COMPLEXITY CONSTANTS

Solubility measurements constitute a comparatively easy way to obtain some information of complex formation in solutions. However, this method cannot be generally used to evaluate the individual complexity constants if polynuclear complexes are formed.

If a sparingly soluble salt MA(s) can be dissolved by complex formation with the ligand A we obtain for the over-all equilibria

$$mMA(s) + (n-1)A \rightleftharpoons M_mA_{m+n-1} \tag{1}$$

and for the equilibrium (concentration) constants

$$K_{s,m+n-1,m} = [M_mA_{m+n-1}]/[A]^{n-1} \tag{2}$$

The solubility S_{MA} can be described by the expression

$$S_{MA} = \sum_{m=1} \sum_{n=0} mK_{s,m+n-1,m}[A]^{n-1} \tag{3}$$

where the limits of summation have to be judged from experimental data.
If no polynuclear complexes are formed, eqn. (3) is simplified to

$$S_{MA} = \sum_{n=0} K_{s,n}[A]^{n-1} \tag{4}$$

and the equilibrium constants can be computed by graphical methods or by a "trial and error"-procedure from measurements of the solubility.

The concentration of free ligand A can be obtained from

$$[A] = C_A - \bar{n}C_M = c_A - (\bar{n}-1)S_{MA} \tag{5}$$

where
C_A = the total concentration of the ligand A
C_M = » » » » » metal M
c_A = the concentration of the salt containing the ligand ion added to the solution
$\bar{n}$ = the ligand number
For a mononuclear system the ligand number is defined as

$$\bar{n} = (C_A-[A])/C_M = (C_A-[A])/S_{MA} = \sum_{n=1} nK_{s,n}[A]^{n-1} / \sum_{n=0} K_{s,n}[A]^{n-1} \tag{6}$$

By differentiating eqn. (4) with respect to [A] and combining with eqn. (6) we obtain

$$\frac{d(\log S_{MA})}{d(\log [A])} = \frac{\sum_{n=0} (n-1)K_{s,n}[A]^{n-1}}{\sum_{n=0} K_{s,n}[A]^{n-1}} = \bar{n}-1 \tag{7}$$

Thus the value of $\bar{n}$ can be obtained from a graph of the function $\log S_{MA}(\log [A])$.

As a first approximation we take $[A] = c_A$. A graph of $\log S_{MA}(\log c_A)$ gives a value of $\bar{n}$ and when inserting this $\bar{n}$-value in eqn. (5) an approximate value of $[A] = [A]_1$ is found. In the next approximation the function $\log S_{MA}(\log [A]_1)$ is drawn and a more accurate value of $\bar{n}$ is obtained, and so on.

EXPERIMENTAL

Chemicals. All chemicals used were reagent grade or prepared from reagent grade materials. *Silver bromide* was prepared from silver nitrate and potassium bromide, in hot aqueous solution, thoroughly washed and dried. The solid silver bromide was stored in black-painted bottles. The used salts, *potassium nitrate, sodium nitrate, potassium bromide,* and *sodium bromide* were dried for days or weeks at 120°C and stored in desiccators.

Apparatus. The used apparatus was essentially the same as in Ref.[1] with the exception that the reaction vessel was a large Pyrex test tube.

Measurements. An excess of silver bromide was added to 50.0 g of the solvent, an equimolar mixture of potassium nitrate and sodium nitrate, containing a known concentration of bromide ions, and then the mixture was stirred for 10—45 h at 280°C. The bromide ions were added as an equimolar mixture of potassium and sodium bromide in order to keep the fraction of potassium and sodium ions constant in the melt. The constancy of the solubility, within experimental errors, indicated that equilibrium was attained in less than 6 h. When experimentally possible, equilibrium was also attained in such a way that AgBr was precipitated when more bromide was added to the solutions.

The undissolved silver bromide was allowed to settle for at least one hour after that the glass stirrer was stopped. With a pre-heated pipette samples were taken from the melt and analysed for their silver content. The absence of undissolved particles of silver bromide was reasonably assured by visual observation of the molten samples and by reproducible analyses.

The samples were cooled and the thus solidified melts were then weighed and dissolved in an aqueous solution containing potassium cyanide in excess for the formation of silver cyanide complexes. Then the samples were analysed.

Analyses. The solubility S_{AgBr} of solid silver bromide was determined by electro-analyses when $S_{AgBr} \gtrsim 10^{-3}$ (m) and by a radioassay technique, using silver bromide labeled with ^{110m}Ag (from A.E.R.E., Harwell, England) when $S_{AgBr} \lesssim 10^{-3}$ (m).

Table 1. The solubility S_{AgBr} of silver bromide in alkali nitrate melts at 280°C for different bromide concentrations c_{Br}.

c_{Br} m	$\bar{n}$	[Br⁻] m	$10^4 \times S_{AgBr,exp.}$ m	$10^4 \times S_{AgBr,calc.}$ m	Method[a]
2.00	2.89	1.78	1144 ± 20	1160	E
1.50	2.84	1.38	636 ± 15	623	E
1.00	2.76	0.949	290 ± 5	280	E, R
0.600	2.63	0.581	119 ± 5	114	E
0.400	2.52	0.391	59.1 ± 1.2	59.7	E, R
0.200	2.32	0.197	22.2 ± 0.5	22.4	E, R
0.100	2.12	0.0990	10.1 ± 0.2	9.72	E, R
0.0600	1.97	0.0595	5.72 ± 0.05	5.72	R
0.0400	1.85	0.0397	3.93 ± 0.05	3.96	R
0.0200	1.59	0.0199	2.45 ± 0.05	2.41	R
0.00995	1.26	0.00991	1.78 ± 0.03	1.79	R
0.00609	1.00	0.00609	1.67 ± 0.03	1.68	R
0.00595	0.99	0.00596	1.74 ± 0.05	1.68	R
0.00407	0.79	0.00411	1.74 ± 0.04	1.75	R
0.00398	0.78	0.00401	1.71 ± 0.04	1.76	R
0.00200	0.49	0.00211	2.20 ± 0.05	2.23	R
0.00096	0.30	0.00118	3.21 ± 0.05	3.17	R
0	0.14	0.00052	6.01 ± 0.07	6.03	R

[a] E denotes electroanalytically determined solubilities. R denotes radiochemically determined solubilities.

Table 2. The values of the equilibrium constants (defined in eqn. (2)).

$K_{s,0}$	=	$(2.70 \pm 0.10) \times 10^{-7}$ (m²)
$K_{s,1,1}$	=	$(8.0 \pm 0.3) \times 10^{-5}$ (m)
$K_{s,2,1}$	=	$(7.0 \pm 0.2) \times 10^{-3}$
$K_{s,3,1}$	=	$(2.0 \pm 0.1) \times 10^{-2}$ (m⁻¹)
$K_{s,6,2}$	=	$(2 \pm 1) \times 10^{-3}$ (m⁻³)

One comment may be made regarding the determinations where labeled silver bromide was used. Because of the radioactive silver the silver bromide grew dark from radio-chemical effects. When the active silver bromide was older than 10−12 days the solubility measurements could not be reproduced. Therefore, both active silver bromide and silver nitrate solutions were used as quickly as possible.

The solubility at a given concentration of alkali bromides was determined at least twice. When the determinations could be made by both electroanalyses and radioactivity measurements they agreed within experimental errors.

RESULTS AND DISCUSSION

The results of the measurements are given in Table 1 where the accuracy has been judged from the reproducibility of the determinations.

The final computation of the equilibrium constants was made using an electronic high-speed computer (SMIL). When doing this we used the knowledge about the complex system that the e.m.f. measurement had given us (Ref.[1]). The constants were also evaluated with graphical methods. Both methods gave constants which were in good agreement. The obtained constants are gathered in Table 2.

In Table 1 the values of $S_{AgBr.calc.}$ are obtained from eqn. (3) using the constants given in Table 2. The $\bar{n}$-values in Table 1 are calculated, using the constants in Table 2, from the $\bar{n}$ expression that is valid if polynuclear complexes are formed

$$\bar{n} = \frac{\sum\limits_{m=1} \sum\limits_{n=-m+2} (m+n-1)K_{s,m+n-1,m}[A]^{n-1}}{\sum\limits_{m=1} \sum\limits_{n=0} mK_{s,m+n-1,m}[A]^{n-1}} \tag{9}$$

A graphical representation of the measurements is shown in Fig. 1. In a logarithmic diagram the concentration of each complex M_mA_{m+n-1} can be described by a straight line with the integer slope $(n-1)$ since eqn. (2) can be written

$$\log [M_mA_{m+n-1}] = \log K_{s,m+n-1,m} + (n-1) \log [A] \tag{10}$$

The value of the solubility product $K_{s,0}$ of silver bromide was checked potentiometrically and found to be $K_{s,0} = (3.00 \pm 0.10) \times 10^{-7}$ (m²). From solubility measurements $K_{s,0} = 2.70 \pm 0.10) \times 10^{-7}$ (m²) was obtained. Flengas and Rideal [10] have also determined the solubility product of silver bromide. They found $K_{s,0} = 7.61 \times 10^{-8}$ (m²) at 250°C and they calculated ΔH to 21.30 kcal/mole for the dissolvation. If Flengas and Rideal's values are extrapolated to 280°C we obtain $K_{s,0} = 2.3 \times 10^{-7}$ (m²). The value of $K_{s,0}$ obtained by Blander and Luchsinger [11] at 250°C gives, extrapolated to 280°C, $K_{s,0} = 3.2 \times 10^{-7}$ (m²).

Table 3. The values of the consecutive constants (defined in eqn. (12)) for mononuclear species and the over-all complexity constants (defined in eqn. (11)).

$K_1 = 267$ (m^{-1})	$\beta_{1,1} = 267$ (m^{-1})
$K_2 = 88$ (m^{-1})	$\beta_{2,1} = 2.3 \times 10^4$ (m^{-2})
$K_3 = 2.9$ (m^{-1})	$\beta_{3,1} = 6.7 \times 10^4$ (m^{-3})
	$\beta_{6,2} = 2.2 \times 10^{10}$ (m^{-7})

The potentiometric measurements in unsaturated solutions (Ref.[1]) could be described by assuming the four complex species AgBr, $AgBr_2^-$, $AgBr_3^{2-}$, and $Ag_2Br_6^{4-}$. The present solubility measurements are also consistent with these complex species but it should be remembered that the existence of polynuclear complexes can not be proved from solubility measurements only.

The over-all complexity constants, denoted

$$\beta_{m+n-1,m} = [M_m A_{m+n-1}]/[M]^m [A]^{m+n-1} = K_{s,m+n-1,m}/K_{s,0}{}^m \qquad (11)$$

have also been calculated. $K_{s,0}$ is the solubility product of MA. In the calculations the value $K_{s,0} = 3.00 \times 10^{-7}$ (m^2) obtained from potentiometric measurements has been used. In Table 3 the β-values are given together with the consecutive constants

$$K_n = [MA_n]/[MA_{n-1}] [A] \qquad (12)$$

A comparison between the values of the constants obtained with different methods and by different investigators is given in Ref.[1]

In Figs. 1 and 2 the ligand number $\bar{n}$ is drawn as a function of log [Br$^-$]. Fig. 2 also shows the distribution of the different species in the silver-bromide system as a function of log [Br$^-$].
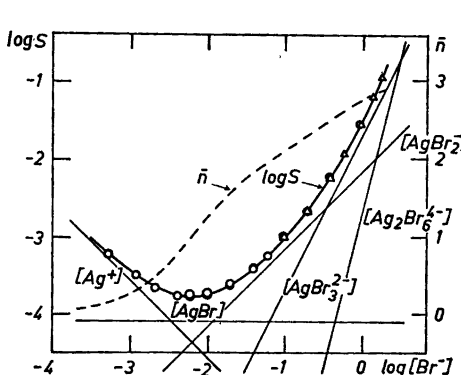

Fig. 1. A logaritmic diagram of the concentrations of the different species, the solubility S_{AgBr} and the ligand number $\bar{n}$ as functions of the bromide ion concentration.
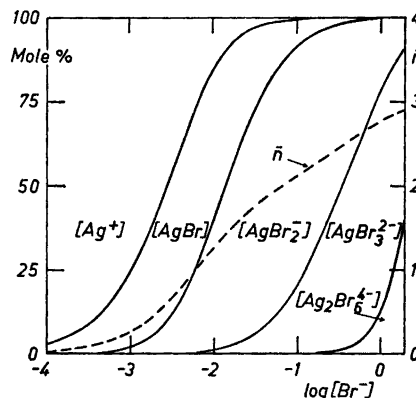
Fig. 2. The distribution in mole % of the silver on the different species as a function of log [Br$^-$] and the ligand number $\bar{n}$ as a function of log [Br$^-$]. Saturated solutions.

The ligand number $\bar{n}$ never exceeds the value 2.9 in the undertaken measurements (see Table 1). In aqueous solution the co-ordination number of the silver ion is four [12] in respect of halide ions but in nitrate melts no more than three bromide ions seem to be attached to the silver ion in the complexes.

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