The Solubility of Silver Bromide in Aqueous Solutions of Potassium Bromide and Silver Nitrate at 20°C

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The solubility of silver bromide at 20° C in aqueous solutions of potassium bromide and silver nitrate has been measured over a concentration range from 2.5×10^{-7} M to 3.5 M for KBr and from 0.115 to 4.05 M for AgNO₃. A turbidimetric and an absorptiometric method were used. The influence of ionic strength on the complex solubility of silver bromide is briefly discussed.

The solubility of silver bromide in aqueous solutions of various soluble bromides has been measured by several authors. The first data of this kind may be found in papers by Schierholz[1], and Hellwig[2] who has also investigated the solubility of other silver halides in very concentrated solutions of alkali halides. Dede and Walther[3] have given some data on the solubility of silver bromide in potassium bromide, calcium bromide and hydrobromic acid solutions at different temperatures. The solubility of silver bromide in concentrated solutions (2M to 8M) of hydrobromic acid has been determined by Erber[4]. The most recent results are those of Chateau and Pouradier[5] and Leden[6]. In view of the fact that most solubility data of silver bromide in potassium bromide solutions found in literature cover only a limited concentration range of KBr (predominantly very high concentrations) we decided to reinvestigate this problem using a completely different method.

It seems that Hellwig[2] is the only author who has measured the solubility of silver bromide in aqueous solutions of silver nitrate.

EXPERIMENTAL

The usual method for determining the solubility of silver halides in aqueous solutions containing halide-ions consists in shaking solid silver halide with the solution of a soluble halide under well controlled experimental conditions (constant temperature, inert atmosphere, darkness, very pure chemicals etc.). The shaking is continued until the equilibrium is established, which is supposed to take several days. The saturated solution thus obtained is analysed for silver ion. We used a different, much simpler method similar to the procedure used by Težak et al.[7] for the preparation of coloidal solutions of silver halides *in statu nascendi*. This method was used by Stubičan[8] and Schulz[9] for determination of solubility of silver thiocyanate and silver iodide. It consists in mixing silver nitrate and alkali halide solutions of different concentration, and observing the turbidity of the mixed solution. The solubility is calculated from the concentration of alkali halide at which — for a given concentration of silver nitrate — the turbidity of the solution has disappeared. The optical arrangement used by Stubičan and Schulz for measuring the turbidity consisted of a Pulfrich photometer with a Zeiss nephelometric attachment. In addition to this we used a Beckman spectrophometer, Model DU. Both methods of measurement gave almost identical results. Turbidimetric

methods did not give satisfactory results if very small amounts of solid phase were involved ($<10^{-6}$ M AgBr) and had to be replaced by another method based on the absorption measurement in the UV-region[10]. A series of aqueous systems containing the same amount of silver nitrate and variable amounts of potassium bromide was prepared and the absorbance of the system measured at various wavelengths in UV. Potassium bromide solution of the same concentration served as reference solution. When the absorbance was plotted as a function of the concentration of potassium bromide in the system, a discontinuity in the curve could be seen indicating the formation of solid phase (AgBr) (or dissolution of the solid phase) (Fig. 1). Using this method we were able to observe the disappearance or formation of solid phase even if not more than 10^{-7} M AgBr was involved.
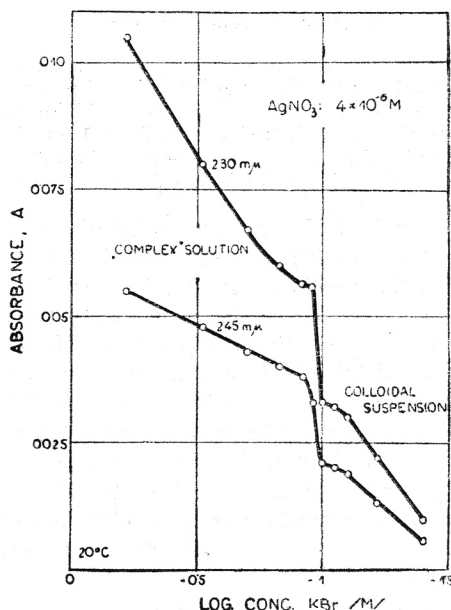

Fig. 1 The absorbance of the aqueous system containing 4×10^{-6} M AgNO₃ and KBr as a function of KBr concentration. The measurements were performed at 20° C one hour after mixing the reacting components. The discontinuity in the absorption curve indicates complex dissolution of the solid phase (AgBr). 1,0 cm absorption cells.

Chemicals of analytical purity grade were used in all experiments (»Erba« Potassium Bromide, »Baker's Analysed« Silver Nitrate). All measurements were performed at $20 \pm 0.1^{\circ}$ C. The specific conductance of distilled water was about 2.10^{-6} ohm⁻¹

<div align="center">RESULTS</div>

Table 1 gives the concentrations of potassium bromide at which — for a given concentration of silver nitrate (column 2) — the solid phase (AgBr) disappears. Similarly, Table 2 gives the concentrations of silver nitrate at which — for a given concentration of potassium bromide — the solid phase (AgBr) disappears. The results presented in Table 1 and Table 2 are also shown in Fig. 2, where the logarithm of silver nitrate concentration (ordi-

nates) is plotted against the logarithm of potassium bromide concentration at which the formation or disappearance of the solid phase is first noticeable (apscissae). The lower curve represents the solubility of silver bromide in

TABLE 1

The solubility of silver bromide in aqueous potassium bromide solutions

1	2	1	2
C_{KBr} (M)	C_{AgNO_3} (M)	C_{KBr} (M)	C_{AgNO_3} (M)
3,548	0,040	0,265	$2,0 \times 10^{-5}$
3,332	0,025	0,195	$1,0 \times 10^{-5}$
3,118	0,020	0,15	$6,0 \times 10^{-6}$
2,70	0,010	0,115	$4,0 \times 10^{-6}$
2,32	0,0060	0,0825	$2,5 \times 10^{-6}$
2,14	0,0040	0,048	$1,5 \times 10^{-6}$
1,73	0,0020	0,0275	$1,0 \times 10^{-6}$
1,38	0,0010	0,011	$4,0 \times 10^{-7}$
1,17	$6,0 \times 10^{-4}$	0,001	$1,0 \times 10^{-7}$
1,00	$4,0 \times 10^{-4}$	$1,0 \times 10^{-5}$	$1,0 \times 10^{-7}$
0,83	$2,0 \times 10^{-4}$	$4,0 \times 10^{-6}$	$2,5 \times 10^{-7}$
0,60	$1,0 \times 10^{-4}$	$2,5 \times 10^{-6}$	$4,0 \times 10^{-7}$
0,465	$6,0 \times 10^{-5}$	$1,0 \times 10^{-6}$	$1,0 \times 10^{-6}$
0,40	$4,0 \times 10^{-5}$	$2,5 \times 10^{-7}$	$4,0 \times 10^{-6}$

potassium bromide solutions; the upper curve shows the solubility of silver bromide in silver nitrate solutions. For the sake of comparison the results of Hellwig[2], Chateau and Pouradier[5] and Erber[4] are plotted in the same diagram.

TABLE 2

The solubility of silver bromide in aqueous silver nitrate solutions

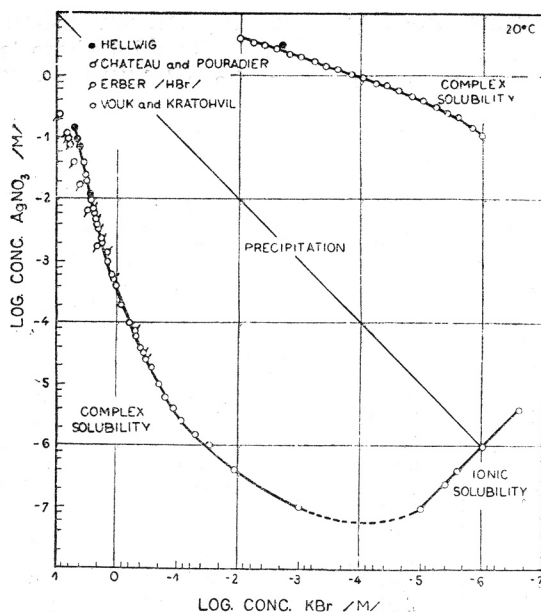| 1	2	1	2
C_{KBr} (M)	C_{AgNO_3} (M)	C_{KBr} (M)	C_{AgNO_3} (M)
0,01	4,05	$6,0 \times 10^{-5}$	0,75
0,006	3,45	$4,0 \times 10^{-5}$	0,69
0,004	3,16	$2,5 \times 10^{-5}$	0,57
0,0025	2,76	$1,5 \times 10^{-5}$	0,48
0,0015	2,25	$1,0 \times 10^{-5}$	0,42
0,001	2,01	$6,0 \times 10^{-6}$	0,315
$6,0 \times 10^{-4}$	1,68	$4,0 \times 10^{-6}$	0,25
$4,0 \times 10^{-4}$	1,44	$2,5 \times 10^{-6}$	0,215
$2,5 \times 10^{-4}$	1,29	$1,5 \times 10^{-6}$	0,145
$1,5 \times 10^{-4}$	1,08	$1,0 \times 10^{-6}$	0,115
$1,0 \times 10^{-4}$	0,93		

Fig. 2. The solubility of silver bromide in aqueous solutions of potassium bromide
(lower curve) and silver nitrate (upper curve).

DISCUSSION

The agreement between our results and the results obtained by some
other authors using different techniques is satisfactory although we did not
pay much attention to the time necessary for attaining the solubility equili-
brium. (Most of our measurements were performed not more than one hour
after mixing of the reacting components.) This seems to indicate that the
solubility equilibria are quickly established which is contrary to the assumption
of many other authors.

Four regions may be distinguished in Fig. 2: the precipitation region, the
region of complex solubility of silver bromide in potassium bromide, the
region of complex solubility of silver bromide in silver nitrate and the re-
gion where the solubility of silver bromide is governed by the solubility pro-
duct. The sensitivity of our optical arrangements was not sufficient for explo-
ring the region covering the potassium bromide concentrations from 1×10^{-3} M
to $1 \times 10^{-5} M$ and silver nitrate concentrations below 1×10^{-7} M. Therefore we
have not been able to determine the exact concentration value of KBr at
which the solubility product rule ceases to be valid. This transition region
has recently been investigated by Leden[6] using radioactive tracers, but his
results have not yet been published. Similarly we have not been able to find
out the trend of the solubility curve of silver bromide in silver nitrate solu-
tions for silver nitrate concentrations $< 1 \times 10^{-1}$ M and KBr concentrations
$< 1 \times 10^{-6}$ M. The solubility product value for silver bromide calculated from
our results amounts to $\sim 1 \times 10^{-12}$ at 20^{0} C, which is in fair agreement with
the most recent electrometric measurements[12] $(L = 0.508 \times 10^{-12}$ at 25^{0} C).

In the last ten years equilibria in complex solutions have often been inve-stigated in systems with constant — usually very high (up to I = 5.0) — ionic strength obtained by adding an »inert« electrolyte to the examined solution (»constant ionic medium method«[13]). This method facilitates theoretical inter-pretation of experimental results and was used in the study of complex solubility of silver chloride[14, 15], silver bromide[6] and silver iodide[11]. The com-parison of results obtained under these conditions with results of Kendall and Sloan[16] and Forbes[17, 18] for silver chloride and Schulz and Težak[9] for silver iodide justifies the assumption that the solubility curve of silver bromide would not have been essentially different had we used the constant ionic medium method, except in the region of ionic solubility which is strongly de-pendent on the ionic strength of the medium.

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IZVOD

Topljivost srebrnog bromida u otopinama kalium bromida i srebrnog nitrata kod 20⁰ C

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Odredili smo topljivost srebrnog bromida u otopinama kalium bromida i sre-brnog nitrata kod 20⁰ C. Mjerenja smo izvršili u koncentracionom području 4.0×10^{-2} M — $1,0 \times 10^{-7}$ M srebrnog bromida u otopinama kalium bromida; odnosno $1,0 \times 10^{-2}$ M — $1,0 \times 10^{-6}$ M srebrnog bromida u otopinama srebrnog nitrata. Odredili smo područje

koncentracija kalium bromida, u kojem promjene ionske topljivosti srebrnog bromida slijede zakon o djelovanju masa.

Dobiveni podaci potpuno se podudaraju s rezultatima drugih autora. Raspravljen je utjecaj ionske jakosti otopine na kompleksnu topljivost srebrnog bromida u vezi s određivanjima topljivosti u otopinama konstantne ionske jakosti.

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