

The Complex Solubility and the Composition of Aqueous Complex Solutions of Silver Halides and Silver Thiocyanate*

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The numerous data on complex solubility of silver halides and silver thiocyanate in aqueous solutions have been systematized and the solubility curves constructed. The data are discussed in relation to the experimental techniques used, to the effect of the ionic strength, and to the influence of the accompanying cations from halide component. The comparison of the solubility curves for various silver halides and silver thiocyanate has been made.

In order to evaluate the composition of the complex solutions and to determine the stability constants of the soluble complex ionic species present, use was made of a simple graphical method. By this method the solubility data from the literature as well as from the own determinations are interpreted and the results of the interpretation compared with the conclusions of other authors. The reliability of the interpretation of the solubility data is discussed.

In the course of the investigation of the precipitation processes of silver halides and silver thiocyanate the need has arisen for knowing the data of complex solubility of these precipitates in the solutions with excess of the one of the ionic constituents of crystal lattice. The data of complex solubility together with the data for the ionic solubility define the solubility curve of a heteropolar precipitate and at the same time the concentration region in which the formation of the solid phase can proceed at all.

By inspecting the relevant literature we could not find a systematic, thorough and comparing review of the data, obtained by various techniques and by various authors, of complex solubility of silver halides and silver thiocyanate in aqueous solutions. It seemed worthwhile to make such a review using the data from the literature as well as the results of our determinations.^{1, 2, 3}

We considered also that it would be of interest to investigate the region of the complex solutions of silver halides and silver thiocyanate in order to obtain some insight into the composition and the character of the soluble complex ionic species present. For this reason we elaborated a direct gra-

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phical method for the evaluation of the composition of complex solutions. This method made possible also the determination of the stability constants of the complex ions.

THE SOLUBILITY CURVES OF SILVER HALIDES AND SILVER THIOCYANATE IN AQUEOUS SOLUTIONS

As the graphical presentation of data is more convenient for our purposes than the tabulation we are giving them in the diagrams: logarithm of the total concentration of silver ions versus logarithm of the total concentration of halide or thiocyanate ions (Fig. 1., 2., 3., 4., 5., and 6.).

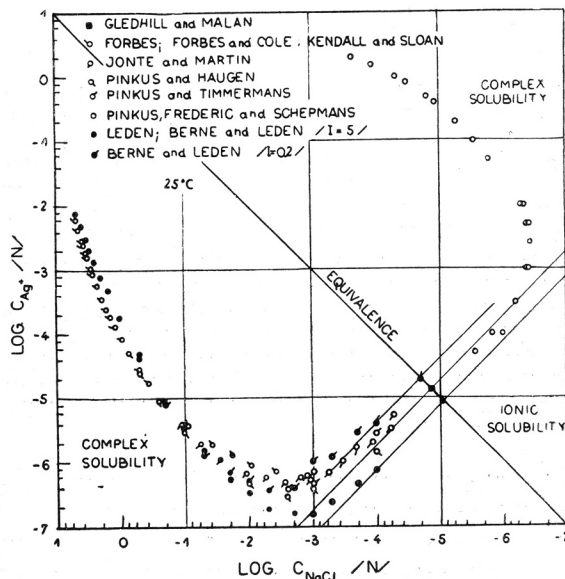


Fig. 1. Solubility curve of silver chloride in aqueous solutions according to the data of Forbes,⁴ Forbes and Cole,⁵ Kendall and Sloan,⁶ Pinkus and Haugen,⁷ Pinkus and Timmermans,⁸ Pinkus, Frederic and Schepmans,⁹ Jonte and Martin,¹⁰ Leden,¹¹ Berne and Leden,¹² and Gledhill and Malan.¹³

The data presented in Figs. 1. to 6. have been obtained by means of various experimental techniques (by observing Tyndall effect^{1, 2, 3, 4, 5, 8, 9, 17, 20}, by analyses of the saturated solutions of solid precipitate^{6, 7, 11, 14, 15, 16, 18, 19, 20, 21, 22}, or by using radioactive tracers^{10, 12, 18}). However, we can note the satisfactory agreement between the data of various authors except at the solubility minima (for AgCl and AgBr). But just in these concentration regions the experimental difficulties and uncertainties are considerable¹⁸. The effect of the ionic strength can be noted also at the solubility minima as well as in the ionic solubility region (provided that the differences observed are not due to the experimental errors). With increasing concentration of the solid phase the influence of ionic strength is considerably diminished or almost completely absent.

It is very interesting to compare the complex solubility curves of silver chloride in the solutions of various soluble chlorides (Fig. 2. and 3.). It is evident that complex solubility of silver chloride increases in the order: $\text{HCl} < \text{NaCl} < \text{LiCl}$, $\text{KCl} < \text{NH}_4\text{Cl}$, and $\text{MgCl}_2 < \text{CaCl}_2 < \text{SrCl}_2 < \text{BaCl}_2$, respectively. These series correspond (except LiCl) to the increase in size of the accompanying cations from the alkali and alkaline earth metal groups of the periodic system of elements. The influence of the accompanying cation from halide component decreases with the increasing dilution of the solutions. It may be possibly connected with the sterical factors.

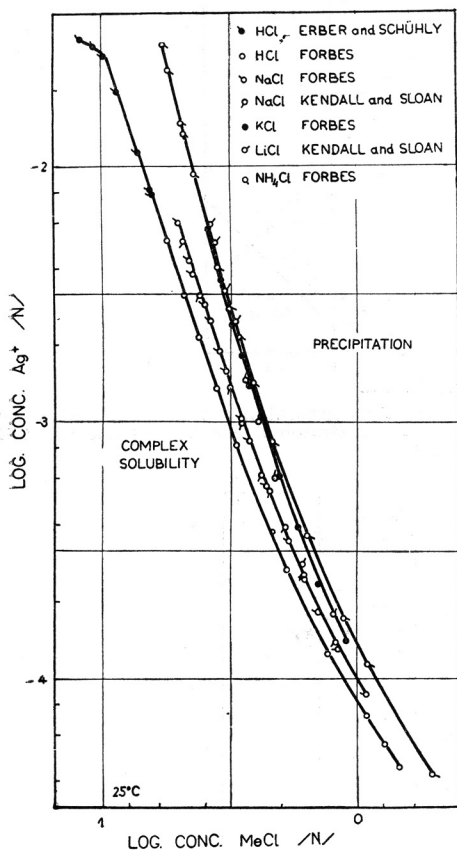


Fig. 1.

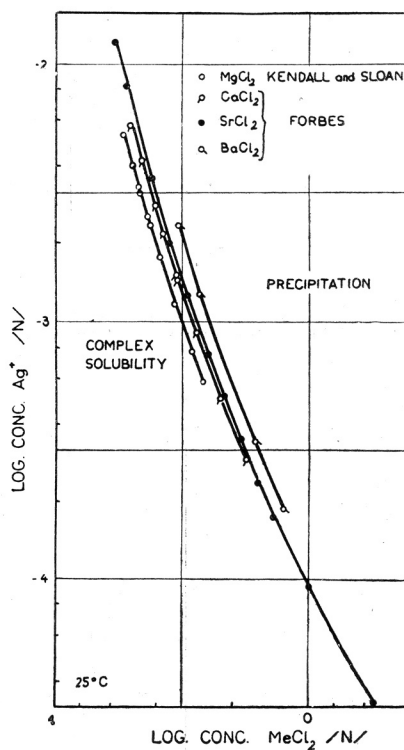


Fig. 2.

Fig. 3. Complex solubility of silver chloride in aqueous solutions of MgCl_2 , CaCl_2 , SrCl_2 and BaCl_2 according to the data of Forbes⁴ and Kendall and Sloan.⁶

Fig. 7. represents the solubility curves of all silver halides and silver thiocyanate. For constructing this diagram we have chosen the data obtained with the solutions of uncontrolled ionic strength because these data are more numerous and more complete. From Fig. 7. the following conclusions can be made:

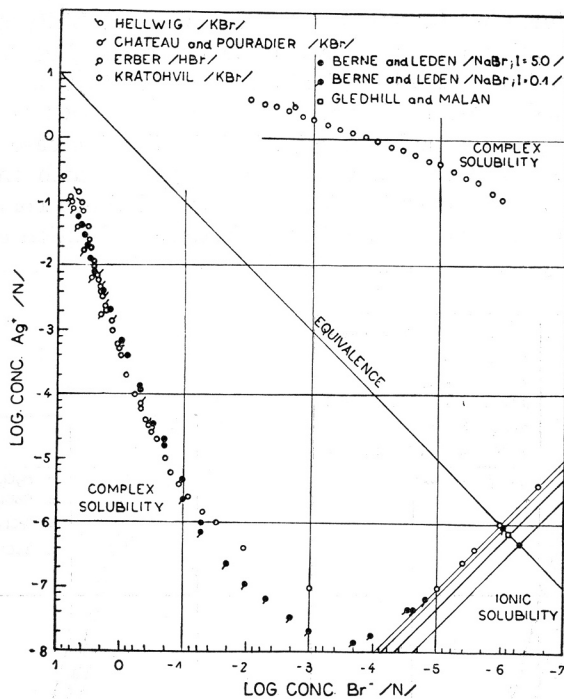


Fig. 4. Solubility curve of silver bromide in aqueous solutions according to the data of Hellwig,¹⁵ Erber,¹⁶ Chateau and Pouradier,¹⁷ Berne and Leden,¹⁸ Vok, Kratohvil and Težak,² and Gledhill and Malan.¹³

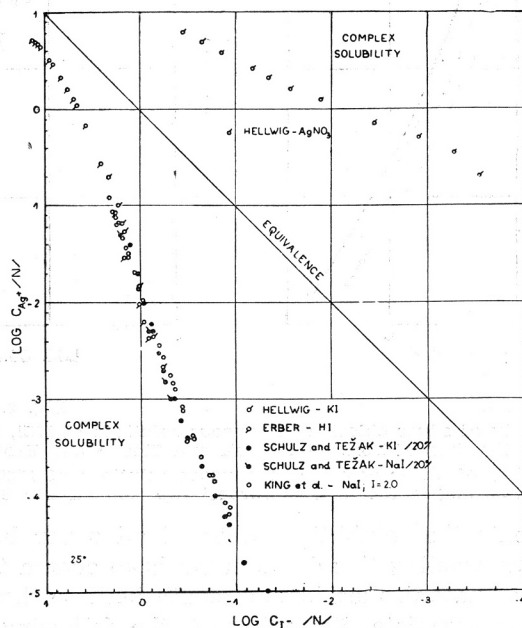


Fig. 5. Solubility curve of silver iodide in aqueous solutions according to the data of Hellwig,¹⁵ Erber,¹⁹ King, Krall and Pandow,²⁰ and Schulz and Težak.¹

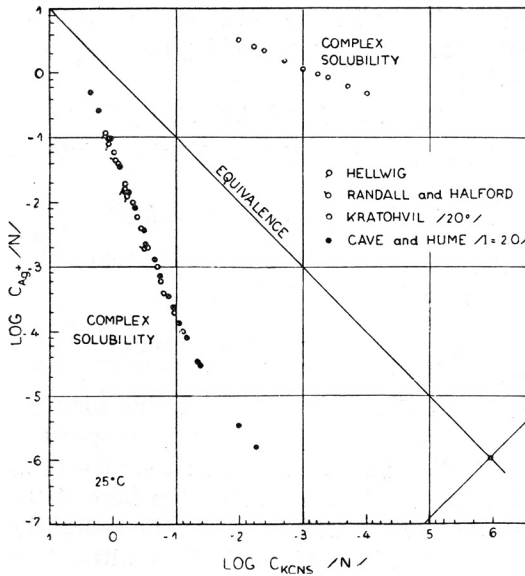


Fig. 6. Solubility curve of silver thiocyanate in aqueous solutions according to the data of Hellwig,¹⁵ Randall and Halford,²¹ Cave and Hume²² and Kratochvil.³

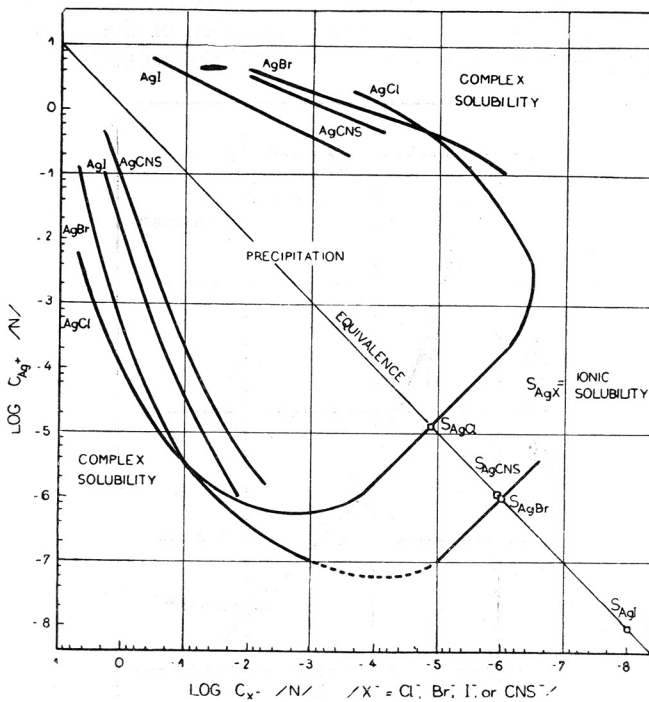
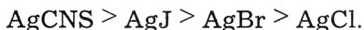
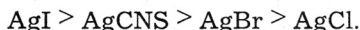


Fig. 7. A schematic diagram representing the solubility curves of silver halides and silver thiocyanate in aqueous solutions according to the data from Figs. 1., 4., 5., and 6.

a) The complex solubility in the solutions of the corresponding soluble halide or thiocyanate (for amounts of solid phase greater than $\sim 10^{-5} M$) increases in the order:



b) Increase of the complex solubility in the solutions of silver nitrate is in the order:



c) More silver ions are necessary for dissolving the same amount of solid phase than halide or thiocyanate ions.

THE COMPOSITION OF AQUEOUS COMPLEX SOLUTIONS OF SILVER HALIDES AND SILVER THIOCYANATE AND THE STABILITY OF COMPLEX IONS

In order to evaluate the composition of the complex solutions and to determine the constitution of the soluble complex species and their stability in the various concentration ranges, we made use of a new, simple, graphical method. To illustrate this method it seems the best to use an example. We have chosen the data of our determinations of the solubility of silver bromide in the solutions of potassium bromide and silver nitrate³, completed with the results of Hellwig¹⁵ and Chateau and Pouradier¹⁷.

We were interested, namely, in the changes of the concentration ratios of the precipitating components at the boundary of the solubility region and the precipitation region. If the logarithm of the concentration ratios of silver and bromide ions are plotted against the logarithm of the corresponding concentrations of bromide ions in excess (Fig. 8.), the solubility curve dissolves

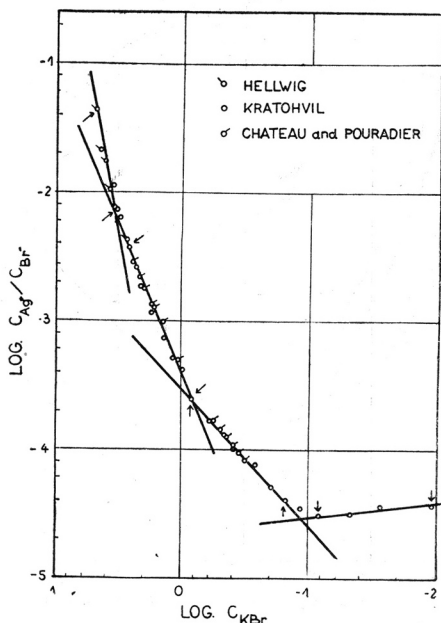


Fig. 8. Plot of the concentration ratios of silver and bromide ions at the solubility boundary versus the corresponding concentrations of bromide ions.

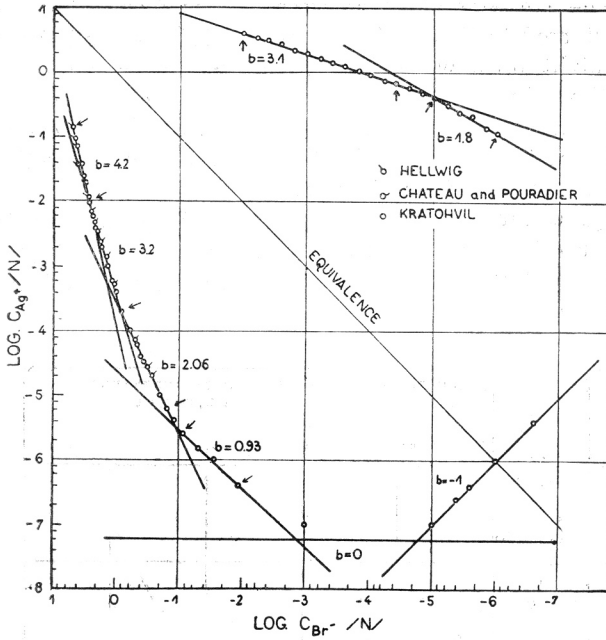


Fig. 9. Solubility curve of silver bromide in aqueous solutions of potassium bromide and silver nitrate approximated by the secants having coordinates determined by Fig. 8 (lower curve) and Fig. 10. (upper curve). b is the slope of a secant.

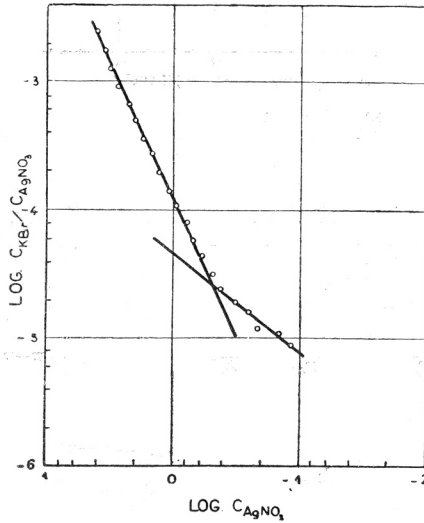


Fig. 10. Plot of the concentration ratios of bromide and silver ions at the solubility boundary versus the corresponding concentrations of silver ions.

into several intersecting straight lines. The intersection points are marked with arrows. The corresponding abscissa values (concentrations of bromide ions) were transferred to the solubility curve of Fig. 4. and through the points so obtained straight lines were drawn (Fig. 9., lower part). These lines are the secants of the solubility curve but in the majority of cases they deviate very little from the curve because of small curvature. By each secant of the Fig. 9. the value of its slope is indicated. It is striking that these values are nearly the whole numbers in each case.

The same procedure was performed with the solubility data for silver bromide in silver nitrate solutions (Fig. 10. and upper part of Fig. 9.). From Fig. 11. it is apparent that the same could be done with other silver halides and silver thiocyanate.

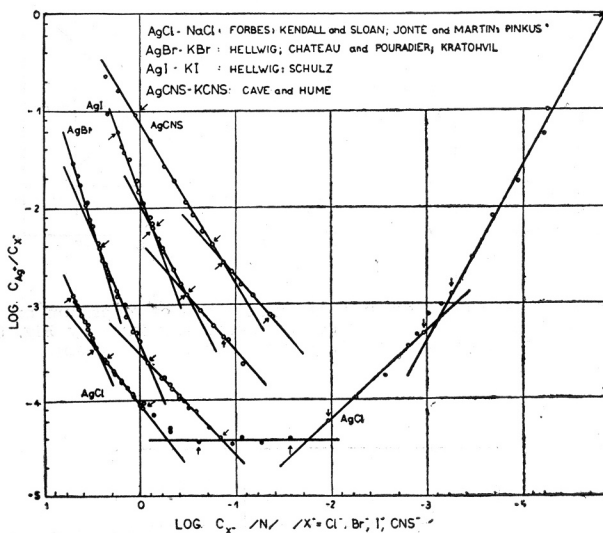


Fig. 11. Plot of the concentration ratios of silver and halide, resp. thiocyanate ions at the solubility boundaries versus the corresponding concentrations of halide, resp. thiocyanate ions.

Now the question arises about the physical significance of these straight lines (secants) and the values of their slopes respectively.

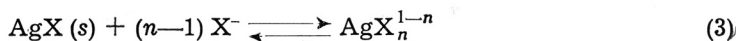
If the ions Ag^+ and X^- ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$ or CNS^-) form complexes with one another, then in the saturated solutions with excess of X^- ions the following equilibria should exist for the dissolution of the solid AgX ^{11, 18}



with the equilibria constants

$$k_{m, n-m} = \frac{[\text{Ag}_m \text{X}_n^{m-n}]}{[\text{X}^-]^{n-m}} \quad (2)$$

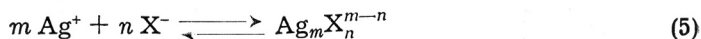
If no polynuclear complexes ($m > 1$) are formed in the solution, but only mononuclear ($m = 1$), the dissolution equilibria may be represented by



with the equilibria constants

$$k_{1, n-1} = \frac{[\text{AgX}_n^{1-n}]}{[\text{X}]^{n-1}} \quad (4)$$

The stability constants of the complex species (reciprocal values of the dissociation constants of the complex) are defined by the following equilibria:



$$\beta_{m, n} = \frac{[\text{Ag}_m \text{X}_n^{m-n}]}{[\text{Ag}^+]^m [\text{X}^-]^n} \quad (6)$$

where m and n have the same values as in (1) and (2). Dividing eq. (2) by eq. (6) we obtain

$$\frac{k_{m, n-m}}{\beta_{m, n}} = [\text{Ag}^+]^m [\text{X}^-]^m = L^m \quad (7)$$

(L = solubility product), which in the case of mononuclear complexes becomes

$$\frac{k_{1, n-1}}{\beta_{1, n}} = [\text{Ag}^+] [\text{X}^-] = L \quad (8)$$

It follows from the eq. (7) or (8) that by knowing the equilibria constants of dissolution and the solubility product it is possible to compute the stability constants.

The equations of the straight lines of Fig. 9. (lower part) are:

$$\log [\text{Ag}^+] = \log a + b \log [\text{X}^-] \quad (9)$$

where $\log a$ is the segment on the ordinate and b the slope of the straight line. If only mononuclear complexes are formed in solution, i. e. if the dissolution equilibria may be represented by (3) and (4), then

$$[\text{AgX}_n^{1-n}] = [\text{Ag}^+] \quad (10)$$

By taking logarithms of both sides of the eq. (4) and using eq. (10) we obtain

$$\log [\text{Ag}^+] = \log k_{1, n-1} + (n-1) \log [\text{X}^-] \quad (11)$$

By comparing eq. (9) and (11) we see that

$$a = k_{1, n-1} \quad (12)$$

$$b = n - 1 \quad (13)$$

It means that the values of the slopes of the straight lines (secants) by which the solubility curve is approximated represent the number of ligands minus one, bound to the central ion in mononuclear complex. This complex predominates in the concentration region of the component in excess defined

TABLE I
The results of the interpretation of the solubility data for silver chloride
in aqueous solutions

| Author | Ref. | $C_{Cl} (N)$ | Complex | Stab. const. $\beta_{m,n}$ Solubility Potention | Graphical method (Kratohvil, Težak, Vouk) | | | |
|--|------|---------------|---------------|--|---|--------------|---------------|-------------------|
| | | | | | Slope $\frac{b}{b}$ | $C_{Cl} (N)$ | Complex | $\beta_{m,n}$ |
| Bodländer and Eberlein Forbes (NaCl) | 23 | about 4 | $AgCl_4^{3-}$ | 5×10^5 | | | | |
| | 4 | 1—5 | $AgCl_3^{2-}$ | | 2.2 | 1—2.5 | $AgCl_3^{2-}$ | 5.1×10^5 |
| | | | $AgCl_4^{3-}$ | | 3.1 | > 3 | $AgCl_4^{3-}$ | 2.0×10^5 |
| | | | $AgCl_5^{4-}$ | | | | | |
| Forbes and Cole (NaCl) | 5 | < 0.04 | $AgCl(aq)$ | | 1.1 | 0.05—0.5 | $AgCl_2^{-}$ | 3.1×10^5 |
| | | 0.1—0.5 | $AgCl_2^{-}$ | 2×10^5 | | | | |
| Forbes; | 4 | < 0.5 | $AgCl(aq)$ | | | | | |
| Forbes and Cole (HCl) | 5 | | $AgCl_2^{-}$ | | 0.94 | 0.01—0.5 | $AgCl_2^{-}$ | 2.2×10^5 |
| | | | $AgCl_3^{2-}$ | | 1.9 | 0.6—2 | $AgCl_3^{2-}$ | 4.5×10^5 |
| | | | $AgCl_4^{3-}$ | | 2.98 | 3—6 | $AgCl_4^{3-}$ | 1.7×10^5 |
| | | $AgCl_5^{4-}$ | | | | | | |
| Erber and Schühly (HCl) | 14 | 5—12.5 | $AgCl_4^{3-}$ | 8×10^5 | 2.98 | 6—10 | $AgCl_4^{3-}$ | 1.7×10^5 |
| Pinkus and Timmermans (HCl) | 8 | | | | 0.0 | 0.001—0.01 | $AgCl(aq)$ | 3.4×10^3 |
| | | | | | 0.94 | 0.01—0.5 | $AgCl_2^{-}$ | 2.2×10^5 |

TABLE II

The results of the interpretation of the solubility data for silver bromide
in aqueous solutions.

| Author | Ref. | $C_{Br} (N)$ | Complex | Stab. const. $\beta_{m,n}$ Solubility Potentiom. | Graphical method (Kratohvil, Težak, Vouk) | | | | | | | |
|------------------------------|------|--------------|-----------------|---|---|--------------|-------------------------------------|---|------|----------|---------------|-------------------|
| | | | | | Slope b | $C_{Br} (N)$ | Complex | $\beta_{m,n}$ | | | | |
| Hellwig | 15 | > 2 | $AgBr_3^{2-}$ | | 4.2 | > 2 | $AgBr_5^{4-}$ or $Ag_2Br_6^{4-}$ | 3.0×10^8 3.0×10^{20} | | | | |
| Bodländer and Eberlein | 23 | ? | $AgBr_4^{3-}$ | 8.5×10^8 | | | | | | | | |
| Erber (HBr) | 16 | 2—9 | $Ag_2Br_6^{4-}$ | 1.3×10^{10} | 3.3 | 2—9 | $AgBr_4^{3-}$ | 3.2×10^8 | | | | |
| Chateau and Pouradier | 17 | < 0.5 | $AgBr_3^{2-}$ | 5.3×10^8 | 2.2 | 0.3—0.6 | $AgBr_3^{2-}$ | 7.0×10^8 | | | | |
| | | | | | 3.0 | 0.8—2.5 | $AgBr_4^{3-}$ | 9.6×10^8 | | | | |
| Berne and Leden (I = 5.0) | 18 | < 0.5 | $AgBr_2^{-}$ | 1.7×10^7 | | | | | | | | |
| | | | | | 0.5—3 | } | 1.2×10^9 | 8.0×10^8 | 1.92 | 0.05—0.3 | $AgBr_3^{2-}$ | 1.5×10^9 |
| | | | | | | | 1.6×10^9 | 1.4×10^9 | 2.76 | 1—5 | $AgBr_4^{3-}$ | 3.0×10^9 |
| | | | | | | | | $\sim 10^{20}$ | | | | |
| > 3 | | | | | | | | | | | | |

| | | | | | | | | |
|--------------------------------|----|---------------------|---------------------------------|-------------------|------|----------------|---|---|
| Berne and Leden (I = 0.1) | 18 | < 0.1 | AgBr(aq) | 1.4×10^4 | 0.0 | 0.0001—0.001 | AgBr(aq) | 2.0×10^4 |
| | | < 0.1 | AgBr ₂ ⁻ | 1.3×10^7 | 0.8 | 0.001—0.01 | AgBr ₂ ⁻ | 4.4×10^6 |
| Vouk, Kratochvil and Težak | 2 | | | | 1.7 | 0.05—0.1 | AgBr ₃ ²⁻ | 1.2×10^8 |
| | | | | | 0.0 | 0.00002—0.0004 | AgBr(aq) | 1.2×10^5 |
| | | | | | 0.93 | 0.01—0.1 | AgBr ₂ ⁻ | 5.0×10^7 |
| | | | | | 2.06 | 0.1—0.8 | AgBr ₃ ²⁻ | 5.7×10^8 |
| | | | | | 3.2 | 0.8—2.5 | AgBr ₄ ³⁻ | 8.0×10^8 |
| | | | | | 4.2 | 2.5—5 | AgBr ₅ ⁴⁻ or Ag ₂ Br ₆ ⁴⁻ | 3.2×10^8 3.2×10^{20} |
| Vouk, Kratochvil and Težak | 2 | C _{Ag} (N) | | | 1.8 | 0.1—0.4 | Ag ₃ Br ²⁺ | 1.0×10^8 |
| | | | | | 3.06 | 0.6—4 | Ag ₄ Br ³⁺ | 2.4×10^8 |
| Hellwig | 15 | ? | Ag ₂ Br ⁺ | 5.0×10^9 | | | | |
| (Interpretation: Yatsimirskii) | 26 | | | | | | | |

TABLE III

The results of the interpretation of the solubility data for silver iodide
in aqueous solutions

| Author | Ref. | $C_I (N)$ | Complex | Stab. const. $\beta_{m,n}$ Solubility Potentiom. | Graphical method (Kratohvil, Težak, Vouk) | | | |
|---------------------------|------|-----------|--------------------------|---|---|-----------|-----------------------------------|--|
| | | | | | Slope b | $C_I (N)$ | Complex | $\beta_{m,n}$ |
| Hellwig | 15 | 0.3—2 | AgI_2^- | 5.5×10^{15} | 3.0 | 0.3—0.8 | AgI_4^{3-} | 1.0×10^{14} |
| | | | AgI_3^{2-} | | 3.83 | 0.8—2 | AgI_5^{4-} or $Ag_2I_6^{4-}$ | 1.5×10^{14} 7.0×10^{20} |
| Bodländer and Eberlein | 23 | ? | AgI_4^{3-} | 5.5×10^{15} | | | | |
| | | ? | $Ag_2I_4^{2-}$ | | | | | |
| | | ? | $Ag_2I_4^{3-}$ | | | | | |
| | | ? | $Ag_2I_6^{4-}$ | | | | | |
| | | ? | $Ag_2I_7^{5-}$ | | $\sim 10^{30}$ | | | |
| Korenman | 25 | ? | AgI_4^{3-} | 2.5×10^{14} | | | | |
| King, Krall and Pandow | 20 | < 1 | AgI_3^{2-} | | 1.94 | 0.1—0.25 | AgI_3^{2-} | 4.0×10^{13} |
| | | > 1 | polynuclear complexes | | 2.93 | 0.4—2 | AgI_4^{3-} | 1.4×10^{14} |

| | | | | | | | | |
|--|----|---|------------------------------|-----------------------|------|---------------------|--|----------------------|
| Erber (HI) | 19 | 0.8—13 | $\text{Ag}_2\text{I}_6^{4-}$ | 1.0×10^{15} | 3.8 | 0.8—3 | AgI_5^{4-} | 9.0×10^{13} |
| | | | | | | | or $\text{Ag}_2\text{I}_6^{4-}$ | 4.5×10^{32} |
| | | | | | 1.8 | 4.5—7 | AgI_3^{2-} | 8.0×10^{14} |
| | | | | | | | (ratio $C_{\text{Ag}} : C_{\text{I}} = 1 : 3$ to $1 : 4.1$) | |
| | | | | | 0.87 | 10—13 | AgI_2^{--} | 5.5×10^{15} |
| | | (ratio $C_{\text{Ag}} : C_{\text{I}} = 1 : 2.5$) | | | | | | |
| Schulz and Težak | 1 | | | | 2.1 | 0.1—0.3 | AgI_3^{2-} | 4.0×10^{13} |
| | | | | | 3.0 | 0.3—0.7 | AgI_4^{3-} | 1.1×10^{14} |
| | | | | | 4.1 | 0.8—1.2 | AgI_5^{4-} | 1.4×10^{14} |
| | | | | | | | or $\text{Ag}_2\text{I}_6^{4-}$ | 7.0×10^{29} |
| Hellwig (Interpretation: Yatsimirskii) | 15 | $C_{\text{Ag}} (N)$ | Ag_3I^{2+} | 1.25×10^{14} | 2.0 | $C_{\text{Ag}} (N)$ | Ag_3I^{2+} | 1.0×10^{14} |
| | 26 | 0.2—6 | | | | | | |

TABLE IV
 The results of the interpretation of the solubility data for silver thiocyanate
 in aqueous solutions.

| Author | Ref. | $C_{\text{CNS}} (N)$ | Complex | Stab. const. $\beta_{m,n}$ Solubility Potentiom. | Graphical method (Kratohvil, Težak, Vouk) | | | |
|---------------------------------|------|----------------------|-----------------------|---|---|----------------------|-----------------------|----------------------|
| | | | | | Slope b | $C_{\text{CNS}} (N)$ | Complex | $\beta_{m,n}$ |
| Hellwig | 15 | 0.6—1.2 | AgCNS_2^- | | 2.82 | 0.6—1.2 | AgCNS_4^{3-} | 5.0×10^{10} |
| Randall and Halford | 21 | | | | 2.87 | 0.3—1 | AgCNS_4^{3-} | 5.0×10^{10} |
| Bodländer and Eberlein | 23 | ? | AgCNS_2^- | 6.0×10^9 | | | | |
| | | | AgCNS_4^{3-} | 1.4×10^{11} 1.5×10^{11} | | | | |
| Ferrel, Ridgion and Riley | 27 | 0.6—0.9 | AgCNS_2^- | 4.0×10^{10} | | | | |
| | | | AgCNS_3^{2-} | 6.0×10^{10} | | | | |
| Cave and Hume | 22 | < 0.2 | AgCNS_2^- | 1.5×10^8 | | | | |
| | | < 0.2 | AgCNS_3^{2-} | 2.0×10^9 | 2.1 | 0.04—0.13 | AgCNS_3^{2-} | 2.0×10^{10} |
| | | > 0.2 | AgCNS_4^{3-} | 1.0×10^{10} | 2.8 | 0.2—2 | AgCNS_4^{3-} | 6.0×10^{10} |
| Kratohvil | 3 | | | | 2.1 | 0.08—0.15 | AgCNS_3^{2-} | 2.0×10^{10} |
| | | | | | 2.8 | 0.15—1 | AgCNS_4^{3-} | 6.0×10^{10} |

by the corresponding apscissa values of the points through which the secants are laid.

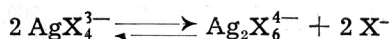
Thus the possibility is given for determining the composition of the complex species present from the solubility curve of silver halides and silver thiocyanate.

According to the eq. (12) the segment on the ordinate represents the equilibrium constant of dissolution of AgX and the formation constant of the corresponding complex respectively. By means of the relation (8) it is possible to compute the stability constants of the mononuclear complex ions of silver halides and silver thiocyanate.

Naturally, quite analogous considerations and relations are valid for the solubility of silver halides and silver thiocyanate in solutions with excess of silver ions .

It is necessary to point out that in each concentration region of the component in excess, defined by the limiting points of the secant, besides the dominant complex the presence of other complexes is also possible. That may be the reason for the difference of the values of slopes from whole numbers. Between the regions determined by each line (secant) there may be very often small transition regions without any dominant complex species.

The slope of the steepest line on the Fig. 9. is $b = 4.2$, meaning that in the corresponding concentration region of bromide ions the complex AgBr_5^{4-} predominates. As the probability for the existence of such a complex is small we have to assume the formation of polynuclear complexes at high concentrations of the component in excess, e. g. according to the following equilibrium:¹⁸



For the formation constants of polynuclear complexes eq. (2) is valid. If we suppose that

$$[\text{Ag}_m\text{X}_n^{m-n}] = \frac{1}{m} [\text{Ag}^+] \tag{14}$$

we can write

$$k_{m, n-m} = \frac{[\text{Ag}^+]}{m [\text{X}^-]^{n-m}} = \frac{a}{m} \tag{15}$$

where a is the segment on the ordinate. If the values of m are assumed or if they are known from other sources, e. g. from potentiometric measurements, then the slope of the straight line ($n-m$) in eq. (15) will represent the total number of ligands (n) minus the number of silver ions (m) bounding these ligands. The value of a/m gives the possibility of computing the stability constants $\beta_{m, n}$ by means of eq. (7).

By using the procedure described previously we have interpreted the data of our own determinations of complex solubility and the data of other authors whose results were represented in Fig. 1. to 6. Tables I, II, III, and IV give the results of the interpretation of the solubility data of the various authors as well

as the results of the potentiometric measurements in the complex solutions of silver halides and silver thiocyanate. In each table the author's name, the reference, the concentration range of the component in excess in which the measurements were performed and the corresponding stability constants $\beta_{m,n}$ are indicated. On the right side of each table the results of the interpretation of the solubility data using the graphical method described above are also given.

It is evident from these tables that the interpretation of the complex solubility data by various methods led to essentially the same results and that the agreement between the values of the stability constants computed by our method and the values determined by other authors is quite satisfactory.

With regard to our graphical interpretation of the experimental results it is necessary to remark that we are not able to establish with certainty the presence of the polynuclear complex ions. The same holds also for other methods of interpretation of the solubility data. Thus, the conclusions obtained from the experiments at high concentrations of the component in excess, where the formation of polynuclear complexes is most probable, are not necessarily always the correct ones and the only possible (e. g. the data of Erber, especially for silver iodide). But if we take into account that maximal coordination number of silver is four, and that at high concentrations we approach the ratio $[\text{Ag}] : [\text{X}] = m : n$, where m and n are numbers even smaller than 5, and if we make use of the results from other experiments, e. g. potentiometric measurements, then the conclusions obtained from the interpretation of the solubility data at high concentrations can be accepted with confidence.

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IZVOD

Kompleksna topljivost i sastav kompleksnih vodenih otopina argentum halogenida i argentum rodanida

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Sredili smo mnogobrojne podatke iz literature za kompleksnu topljivost argentum halogenida i argentum rodanida i načinili krivulje topljivosti (apscisa: log. ukupne koncentracije halogenid, odnosno rodanid iona; ordinata: log. ukupne koncentracije argentum iona) (Sl. 1. do 6.). Diskutirali smo podatke topljivosti s obzirom na upotrebene eksperimentalne metode, utjecaj ionske jakosti i utjecaj popratnih kationa iz halogenidne komponente. Usporedili smo krivulje topljivosti za različite argentum halogenide i argentum rodanid (Sl. 7.).

Da bismo odredili sastav kompleksnih otopina i izračunali konstante stabiliteta prisutnih kompleksnih iona, razradili smo jednu jednostavnu, grafičku metodu. Obradom eksperimentalnih podataka konstatirali smo, naime, da se krivulje topljivosti argentum halogenida i rodanida mogu aproksimirati nizom sekanti, čije se vrijednosti nagiba malo razlikuju od cijelih brojeva (Sl. 8. do 11.), a predstavljaju broj liganada manje jedan vezanih u mononuklearni kompleksni ion. Taj kompleks dominira u koncentracijskom području komponente u suvišku, definiranom koordinatama točaka na krivulji topljivosti, kroz koje je povučena sekanta. Na taj smo način obradili podatke iz literature i rezultate interpretacije usporedili sa zaključcima drugih autora (Tabl. I. do IV.). Konstatirali smo, da se rezultati podudaraju kako s obzirom na sastav prisutnih kompleksa, tako i s obzirom na vrijednosti odgovarajućih konstanti stabiliteta.

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