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## Methorics of the Precipitation Processes. XII. Mutual Influence of Silver Halides in Precipitation Processes\*

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Our investigations into the mutual influence of silver halides on precipitation processes, using sols *in statu nascendi*, included the systems AgBr-AgI and AgCl-AgI.

The general result of our investigations is that those halide ions which make the least soluble salt with Ag-ions are preferred in building up the crystal lattice of silver halides. If such ions are in excess over the Ag-ions in the system, then neither the crystal growth nor the coagulation of sol particles will much depend upon the presence of other halide ions. This dependence is small in the system AgBr-AgI and almost vanishes in the system AgCl-AgI.

### INTRODUCTION

It has been known for a long time that small addition of AgI to the bromine photographic emulsion considerably increases its sensitivity. Mixed crystals of silver halides have, therefore, been investigated by many authors using various techniques<sup>1-11</sup>. Their results are very different. We approached the problem from the point of view of colloid chemistry and tried to solve it by using a method described in previous papers.<sup>12,13,14</sup> The problem was interesting, since even small quantities of iodides, for instance, could widely change the course of the formation and coagulation of AgBr owing to the much smaller solubility of AgI. The solubilities of silver halides in the series AgCl-AgBr-AgI have the ratios  $1 : 5.5 \times 10^{-2} : 7.7 \times 10^{-4}$

### EXPERIMENTAL

The system AgBr-AgI was investigated first. With  $2 \times 10^{-4}$  N AgNO<sub>3</sub> we observed that already an addition of 1 N-%\*\* KI to KBr increased the coagulation value of the system from  $3.8 \times 10^{-2}$  N to  $8 \times 10^{-2}$  N (Fig. 1). This effect was constant even when KI additions were decreased to 0.4 N-%.

The change of the one hour coagulation curve was characteristic too. While pure AgBr coagulated in one hour in the whole concentration region of counterions used (introduced as KBr), the sol obtained with small additions of I-ions remained stable for more than one hour in lower regions of the gradient.

When the percentage of I-additions was varied from series to series, a shift of a new maximum with changes in the quantity of I-ions added was observed (4-hours coagulation curves in fig. 2). This maximum appeared strictly at the point where KI was equivalent to AgNO<sub>3</sub>.

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\*\* N-% denotes the percentage of one halide component in the mixture of halides when their concentrations are expressed in normalities.

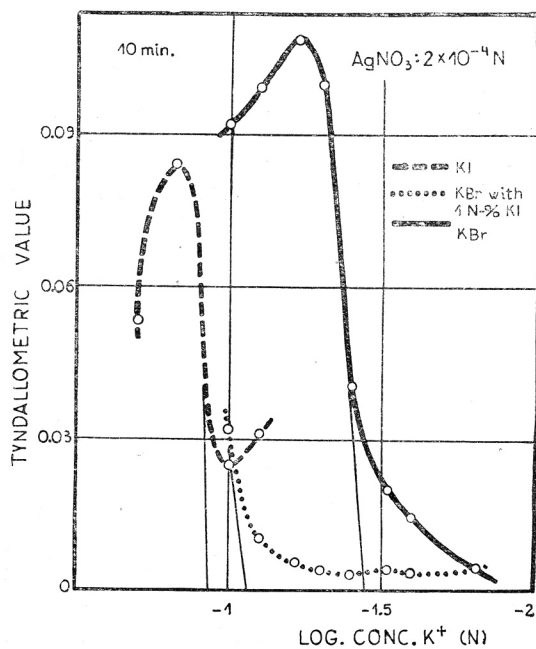


Fig. 1. The influence of KI addition to the system  $\text{AgNO}_3\text{-KBr}$ .

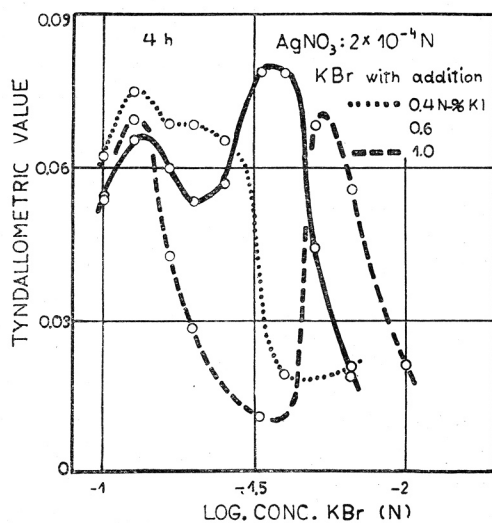


Fig. 2. Isoelectric maxima of  $\text{AgI}$  appearing in the system  $\text{AgNO}_3\text{-KBr-KI}$ .

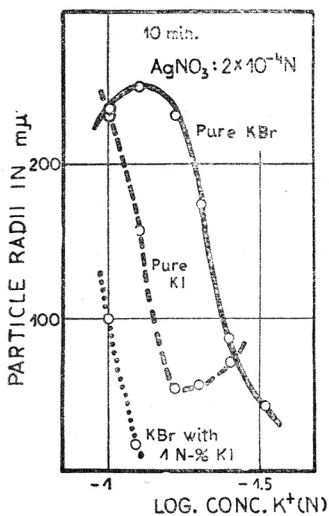


Fig. 3.

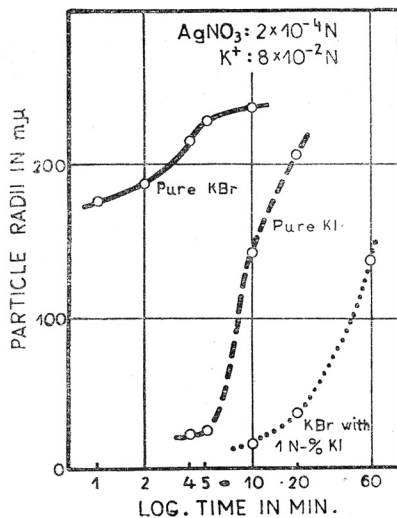


Fig. 4.

Fig. 3. Concentration dispersoidograms of the systems  $\text{AgNO}_3\text{-KBr}$ ,  $\text{AgNO}_3\text{-KI}$  and  $\text{AgNO}_3\text{-KBr-KI}$ .  
 Fig. 4. Time dispersoidograms of the systems  $\text{AgNO}_3\text{-KBr}$ ,  $\text{AgNO}_3\text{-KI}$  and  $\text{AgNO}_3\text{-KBr-KI}$ .

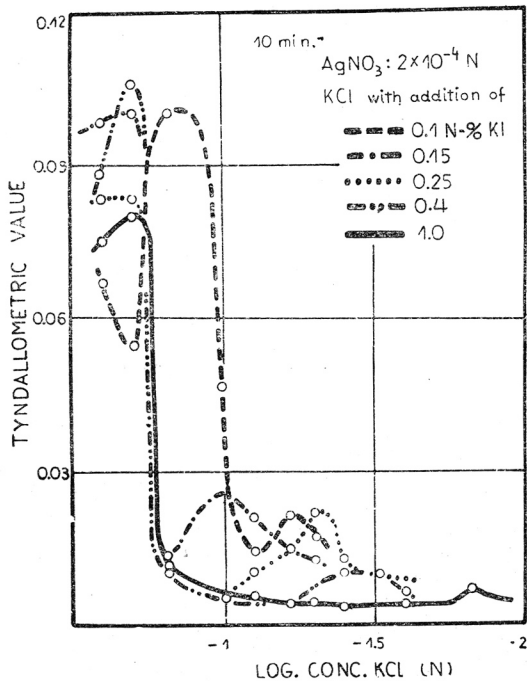


Fig. 5. Isoelectric maxima of  $\text{AgI}$  appearing in the system  $\text{AgNO}_3\text{-KCl-KI}$ .

Small I<sup>-</sup>-additions also affected the size of colloidal particles and the rate of their growth (fig. 3 and 4).

After this we started to investigate the influence of KI additions to KCl. Here the iodide character of the coagulation curves was still more pronounced, with the coagulation value of  $16 \times 10^{-2} N$  KCl. We also observed a regular shift of the AgI maximum with changes in the quantity of KI addition. Both phenomena are shown in fig. 5.

Then we performed many measurements with counter-ions introduced as  $KNO_3$  while the concentrations of halide ions were constant i.e.  $C_{Br^-} + C_{I^-} = \text{const.} = 2 \times C_{Ag^+} = 4 \times 10^{-4} N$ . A shift in coagulation values of the systems with an increase in the ratio between I<sup>-</sup> and Br<sup>-</sup> ions was observed again.<sup>12</sup> Additions of the order 1 N-% KI to KBr rapidly pushed the coagulation values towards higher concentrations. With larger additions (of the order 10 N-%) the coagulation values only slowly increased until the value for pure AgI was reached at 50 N-% KI (equivalence with  $AgNO_3$ ).

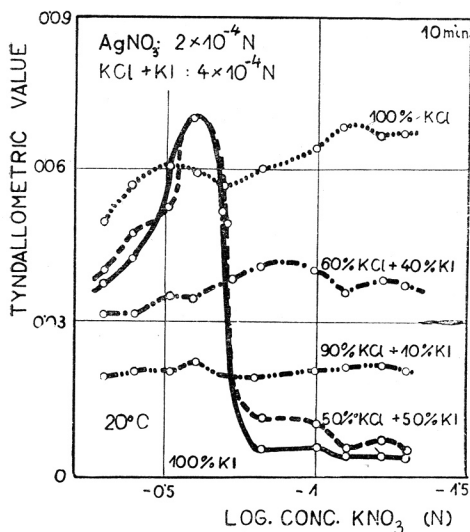


Fig. 6.

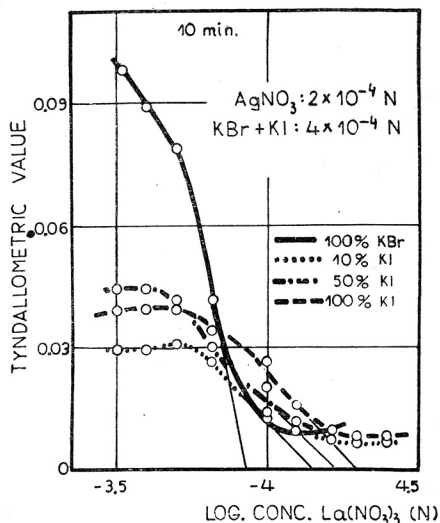


Fig. 7.

Fig. 6. The influence of KI addition to the system  $AgNO_3$ -KCl- $KNO_3$ .

Fig. 7. The influence of KI addition to the system  $AgNO_3$ -KBr- $La(NO_3)_3$ .

With AgCl these influences were much more pronounced. In the whole concentration gradient ( $5-50 \times 10^{-2} N$   $KNO_3$ ) pure AgCl coagulated completely (fig. 6). Already 1 N-% KI in the halide mixture considerably decreased the turbidity but the systems coagulated in the whole region. Further additions, up to 40 N-% KI, did not change the picture essentially. At 50 N-% KI, however, the curves rapidly acquired an iodide character with a decline in concentration maximum and a coagulation value of  $18 \times 10^{-2} N$ .

The situation was quite reverse when trivalent La-ion was taken instead of monovalent K-ion, as counter-ion. The coagulation value for pure AgBr was at very low concentrations,  $12 \times 10^{-5} N$   $La(NO_3)_3$ . The additions of I<sup>-</sup> ions decreased it gradually to the coagulation value for pure AgI,  $4 \times 10^{-5} N$  (fig. 7). With the AgCl-AgI systems the situation was similar.

## DISCUSSION

The principal question to be explained is the strong influence of very small additions of some halide ions to the other ones during the coagulation process of their silver salts. The comparison of our results with those of Taboury and his collaborators<sup>15,16,17</sup> and the senior author (B. T.)<sup>18</sup> and S. Kratochvil<sup>19</sup> suggests that induced formation of solid phase occurred in our systems too. Here, however, apart from the difference in the ease of crystal formation, the differences in solubility and adsorbability require consideration.

When the concentration gradient of counter-ions was obtained by KBr or KCl, there was an excess of I-ions over Ag-ions in spite of their small concentration. Thus AgI was preferably formed and I-ions were preferably adsorbed on AgI particles. The coagulation curves, therefore, had a predominantly iodide character (high coagulation value and a much increased sol stability). Yet Br-ions had also a share, to some extent, in these processes, because of their great excess.

The particles of AgI were much smaller than those of AgBr, but prevailed widely in number (AgI having a much smaller solubility product). The particles of our systems with small I<sup>-</sup>-additions were, in turn, smaller than those of AgI itself, and even the rate of their growth was smaller. This may be explained by the fact that in such mixed systems the comparatively low concentration of I-ions caused no appreciable complex solubility of AgI particles formed and there was, therefore, a much larger number of nuclei which could only slowly re-grow into coarser particles.

The preferability of I-ions in the formation of solid phase and in the adsorption on it was also confirmed by the appearance of new maxima at that point on the halide ions gradient where I-ions were in equivalence with Ag-ions, and by the fact that these maxima shifted regularly with the change in I<sup>-</sup>-percentage, following exactly the equivalence point with Ag-ions. There is no doubt that they were isoelectric maxima of AgI.

In AgCl-AgI systems the influence of iodide additions was more pronounced because of the greater difference in solubility between AgCl and AgI than between AgBr and AgI.

When the concentration gradient of counter-ions was obtained by KNO<sub>3</sub>, and twice as many halide ions were taken as Ag-ions, there was not enough I-ions to react with all Ag-ions and thus Br- or Cl-ions participated in building up the crystal lattice also. At 50 N-% iodides the I-ions were in equivalence with Ag-ions. The systems, therefore, did not behave as pure iodide systems before this composition was reached.

With trivalent La-ions as counter-ions the effects were different. The coagulation values of our systems were shifted to a much lower concentration region of counter-ions (two powers of 10 lower). This is in agreement with the Schulze-Hardy rule. The coagulation values decreased with the increase in the number of I-ions. This is natural, for trivalent ions have a lower coagulation value for AgI than for AgBr or AgCl. The reason for that has been discussed in a previous paper by the senior author (B.T.)<sup>20</sup>.

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## IZVOD

## Metorika precipitacionih procesa. XII.

## Medusobni utjecaj argenticum halogenida kod precipitacionih procesa

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Naša istraživanja međusobnog utjecaja argenticum halogenida kod precipitacionih procesa obuhvatila su sisteme AgBr-AgI i AgCl-AgI. Radili smo sa solovima *in statu nascendi*.

Općeniti je rezultat naših istraživanja, da prilikom izgradnje kristalne rešetke argenticum halogenida prvenstvo imaju oni halogenid ioni, koji s argenticum ionima daju najteže topljivu sol. Ako takvih iona ima u sistemu u suvišku nad argenticum ionima, ne će ni kristalni rast ni koagulacija čestica sola u znatnoj mjeri ovisiti o prisutnosti drugih halogenidnih iona. Kod sistema AgBr-AgI ta je ovisnost malena, a kod sistema AgCl-AgI gotovo iščezava.

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