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Methorics of the Coagulation Processes. XIV. Simultaneous Coagulation of the Mixed Systems of Silver Halides, Silver Cyanide and Silver Thiocyanate by Monovalent Counter-ions*

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Tyndallometric investigation of the coagulation of the systems AgCl-AgBr, AgCl-AgI and AgCl-AgCN has shown that the less soluble component precipitates first and completely. If there are Ag-ions in excess of Br, I or CN ions, they will precipitate with Cl-ions present, which will then also stabilize the sol particles formed. In the system AgBr-AgI both components participate in building up the crystal lattice and stabilizing the particles. In the AgCl-AgSCN system the same mechanism can be presumed although not with such certainty.

INTRODUCTION

Proceeding with earlier investigations of mixed silver halide systems *in statu nascendi*^{1,2} we investigated the following systems: AgCl-AgBr, AgCl-AgI, AgCl-AgCN, AgCl-AgSCN and AgBr-AgI. The coagulation of the mixed systems mentioned above was carried on by neutral electrolyte (KNO₃). Our investigation verified the previous results although it was done with different concentration of the reacting components.

EXPERIMENTAL

When investigating our mixed systems we used an experimental technique already described^{3,4,5}.

The concentration of AgNO₃ on which the sol concentration was dependent was always constant ($2 \times 10^{-4}N$) during this investigation. The concentration of the component which made a more soluble precipitate with Ag-ions (KCl or KBr, respectively) was also constant ($2 \times 10^{-3}N$) in order to avoid the influence of changing the concentration of stabilizing ions. Series were prepared within particular systems with different concentrations ($0-2 \times 10^{-3}N$) of the component which made a less soluble precipitate with Ag-ions. The concentration of counter-ions (K⁺) was varied within such a particular series (taking into consideration the concentration of K-ions both in neutral electrolyte and in the reacting components). This concentration gradient of counter-ions was extended on both sides of the coagulation value^{4,5}. The critical time^{4,5} of the concentration tyndallograms was 10 minutes except in the case of the system AgCl-AgSCN where it was 1 minute.

AgCl-AgBr (Fig. 1). — Small addition of Br-ions to the pure chloride system did not change the coagulation value which remained nearly the same as for the pure AgCl system until the concentration of Br-ions became equal to the concen-

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tration of Ag-ions when it suddenly shifted to the coagulation value of the pure AgBr system.

AgCl-AgI (Fig. 2). — The shift of coagulation value caused by the addition of I-ions was analogous to the shift in the system AgCl-AgBr described above.

AgCl-AgCN (Fig. 3). — The addition of CN-ions to the pure chloride system left the chloride character of the coagulation curves untouched, and the coagulation values decreased slightly. When the concentration of CN-ions reached the concentration of Ag-ions the coagulation curves shifted to the curve of the pure cyanide system (undeveloped course).

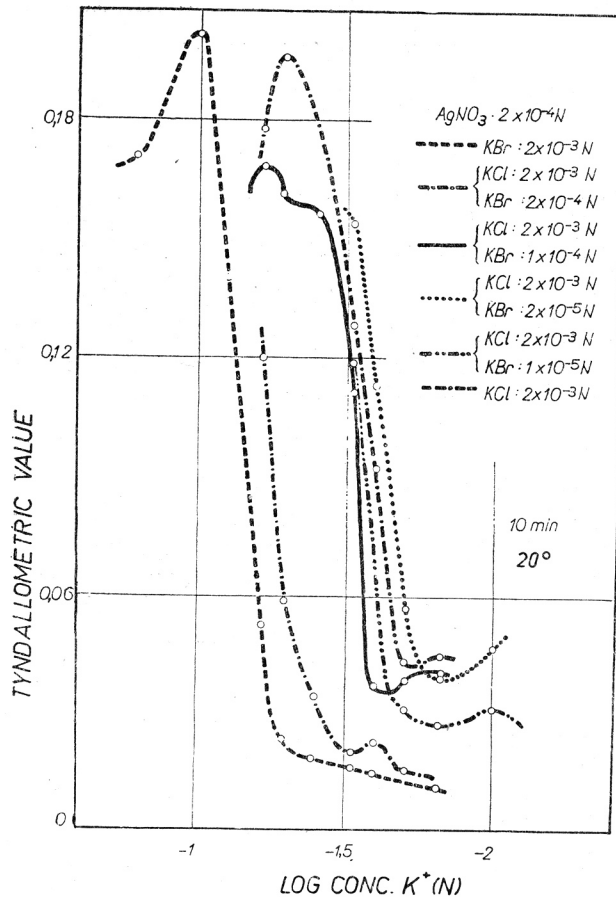


Fig. 1. Tyndallogram of the system $AgNO_3$ -KCl-KBr- KNO_3

AgCl-AgSCN (Fig. 4). — Small addition of SCN-ions to the pure chloride system suddenly reduced its turbidity. Further addition increased it again, and the coagulation curves gradually acquired thiocyanate character which was still not reached, however, at the concentration of SCN-ions equal to that of Ag-ions.

AgBr-AgI (Fig. 5). — Already small addition of I-ions to pure bromide system shifted the coagulation value of the system towards that of the pure AgI. Further addition of I-ions continued to shift the coagulation value until the value of pure AgI was reached.

DISCUSSION

The investigation of the mixed systems described above has shown that the precipitation of the solid phase is not analogous in all cases. The reason for it is in different solubilities of the components, different crystal lattice, different adsorbability, different stability of the sol etc.

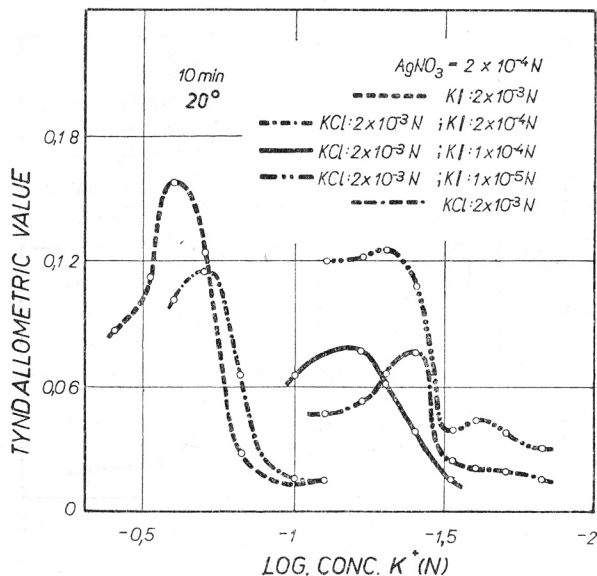


Fig. 2. Tyndallogram of the system $\text{AgNO}_3\text{-KCl-KI-KNO}_3$

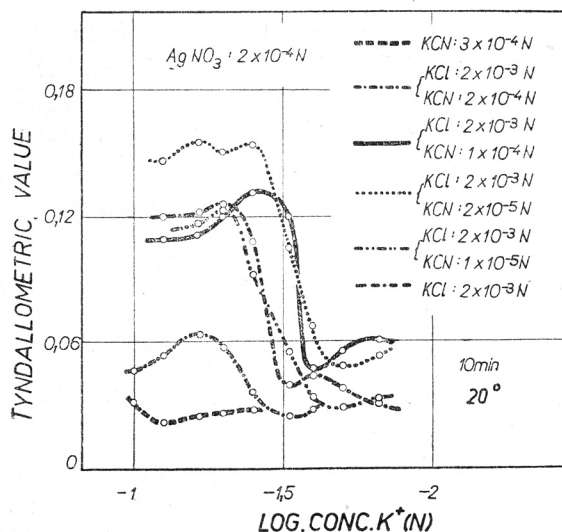


Fig. 3. Tyndallogram of the system $\text{AgNO}_3\text{-KCl-KCN-KNO}_3$

The fact that in the system AgCl-AgBr and AgCl-AgI coagulation value suddenly changes from the value of pure AgCl sol to that of pure AgBr sol (or AgI, respectively) when the addition of Br-ions (or I-ions, respectively) reaches the concentration of Ag-ions — indicates the original and entire

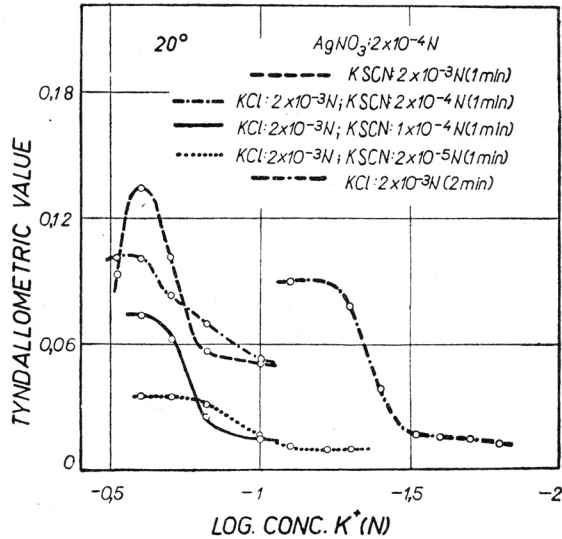


Fig. 4. Tyndallogram of the system $AgNO_3$ -KCl-KSCN-KNO₃

precipitation of the less soluble component. When there is not enough Br- or I-ions to react with all Ag-ions, Cl-ions participate in building up the crystal lattice and stabilize the particles. Thus the coagulation value does not differ a great deal from that of pure AgCl sol. After the equality of the concentrations of Ag-ions and Br-ions (or I-ions, respectively) has been reached there are still enough Br-ions (or I-ions, respectively) even for the stabilization of the particles and the coagulation value changes to that of pure AgBr (or AgI, respectively) system¹.

The behaviour of the system AgCl-AgCN can be explained in the same way.

Since the behaviour of the AgCl-AgSCN system is quite different from that of the systems described above, simultaneous precipitation of both components is to be presumed, maybe in the form of mixed crystals.

The continual change of coagulation values in the AgBr-AgI system can be explained only by mutual share of Br- and I-ions in building up the crystal lattice and stabilizing the sol particles, most probably in the form of mixed crystals.

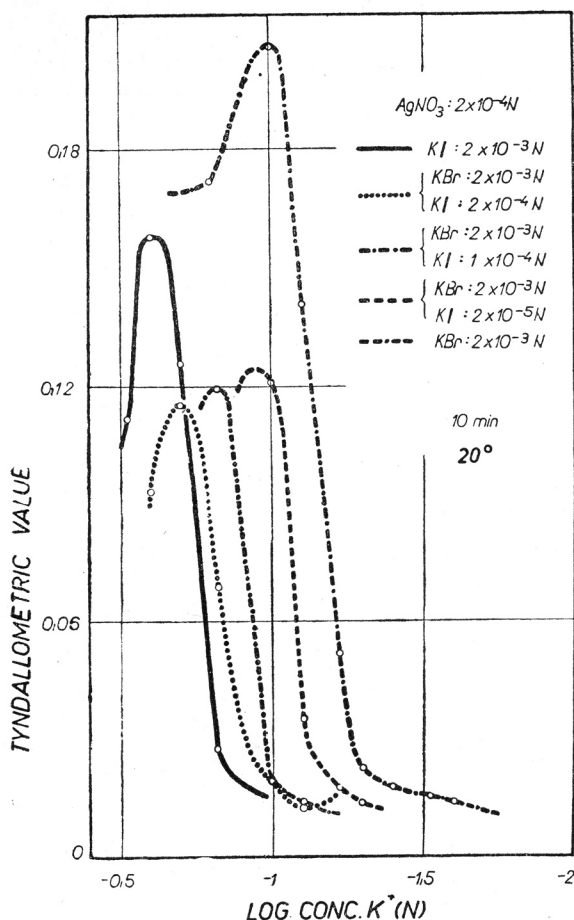


Fig. 5. Tyndallogram of the system $\text{AgNO}_3\text{-KBr-KI-KNO}_3$

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IZVOD

Metorika koagulacionih procesa. XIV. Istodobna koagulacija miješanih sistema argenti halogenida, argenti cianida i argenti tiocianata monovalentnim protu-ionima

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Tindalometrijska ispitivanja koagulacije sistema AgCl-AgBr , AgCl-AgJ i AgCl-AgCN pokazala su, da se teže topljiva komponenta izlučuje prva i to potpuno.

Ako Ag-iona ima u suvišku, u odnosu na prisutne Br, J ili CN ione, oni će se istaložiti s Cl-ionima, koji će ujedno stabilizirati čestice sola. U sistemu AgBr-AgJ obje komponente sudjeluju u izgradnji kristalne rešetke i u stabilizaciji čestica. U sistemu AgCl-AgSCN može se pretpostaviti isti mehanizam iako ne s tolikom sigurnošću.

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