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Methorics of the Precipitation Processes. XVII. A Study of the Simultaneous Precipitation of Silver Halides with Silver Cyanide and Silver Thiocyanate*

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Mixed »binary« systems were prepared by simultaneous precipitation of a silver halide with silver cyanide or silver thiocyanate and their growth was studied tyndallometrically. The concentration relations of halide and cyanide (or thiocyanate, respectively) components were changed over a large range. Some of these »binary« systems showed fairly reproducible precipitation curves that indicated the formation of mixed crystals, while in other cases only turbidity areas could be obtained.

INTRODUCTION

The phenomenology of the precipitation curves derived from the tyndallometric investigation of pure silver halide sols *in statu nascendi* was given by Težak[1] and his coworkers. The same was given for silver cyanide and silver thiocyanate sols by Težak and Stubičan[2,3]. We described the phenomena of simultaneous precipitation of mixed silver halides[4,5].

The simultaneous precipitation of AgBr and AgCN was investigated by Natta and Vecchia[6] and Schaum and Scheid[7], that of AgCl and AgCN by Natta and Vecchia, of AgBr and AgSCN by Schaum and Scheid, of AgCN and AgSCN by Marin and Duval[8]. These authors used X-ray[6], ultramicroscopic[7] and thermogravimetric[8] analysis. The subject of this paper is the tyndallometric analysis of such systems.

In Table I the solubility data[9] are given for five sparingly soluble silver salts which are being considered in this paper. By their combination ten

TABLE I

Solubility data of some sparingly soluble silver salts in mol/l

AgCl	AgCN	AgSCN	AgBr	AgI
1.1×10^{-5}	1.6×10^{-6}	1.1×10^{-6}	6.3×10^{-7}	1.5×10^{-7}

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»binary« systems can be obtained which are listed in Table II in the order of the decreasing solubility of their components. Systems AgCl-AgBr, AgCl-AgI and AgBr-AgI were already described in our previous papers[4,5]; the other ones are described in this paper.

TABLE II

»Binary« systems (AgA-AgB) of sparingly soluble silver salts listed in Table I

AgCl-AgCN AgCl-AgSCN AgCl-AgBr AgCl-AgI	AgCN-AgSCN AgCN-AgBr AgCN-AgI	AgSCN-AgBr AgSCN-AgI	AgBr-AgI

EXPERIMENTAL

A method already described[5] was used in this investigation. If the more soluble component of such a »binary« system is denoted as AgA and the less soluble one as AgB, the obtaining of these »binary« systems can be described as simultaneous mixing of $AgNO_3$, KA and KB. The concentration of $AgNO_3$ was always $2\times10^{-4}N$, thus defining the sol concentration (presuming that the *whole* potential solid phase underwent precipitation). The concentration of KA was always $4\times10^{-4}N$ (the *minimum concentration*[5] of the pure AgA system; only in the case A = CN it was $3\times10^{-4}N$ because of the well known complex forming tendency of AgCN): thus the sol particles always had negative charges — a fact that was verified by electrophoresis. The concentration of KB was varied from $3\times10^{-4}N$ to $3\times10^{-8}N$.

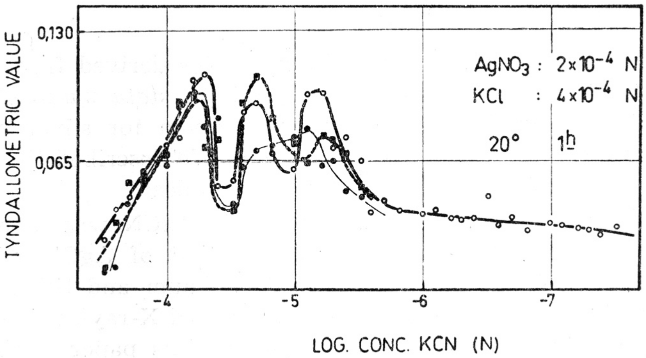

Fig. 1. Results of the twice repeated measurements of the system $AgNO_3$-KCl-KCN

AgCl-AgCN (Fig. 1). — This system showed three small maxima which were fairly reproducible. The three curves drawn represent attempts to reproduce the maxima. Turbidity was rather low in the whole concentration region of CN-ions.

AgCl-AgSCN (Fig. 2). — At greater concentrations of SCN-ions two distinct maxima appeared which were very well reproducible. The first one could be observed already after 10 minutes, while the second one arose only after a much longer time. After the maxima there was a minimum and then a constant low platform. The corresponding dyspersoidograms showed that the average size of the particles exactly followed the turbidity curves.

AgCl-AgBr. — See our last paper[5].

AgCl-AgI. — See our last paper[5].

AgCN-AgSCN (Fig. 3). — This very well reproducible system showed a distinct maximum developed already after 10 minutes. It was followed by a shallow minimum and that by a constant platform. After 1 hour the minimum area developed into two additional maxima.

AgCN-AgBr (Fig. 4). — Only a small maximum developed in this system. Turbidity was very low over the whole range of Br-ions concentration. The reproducibility of the measured turbidity was not good.

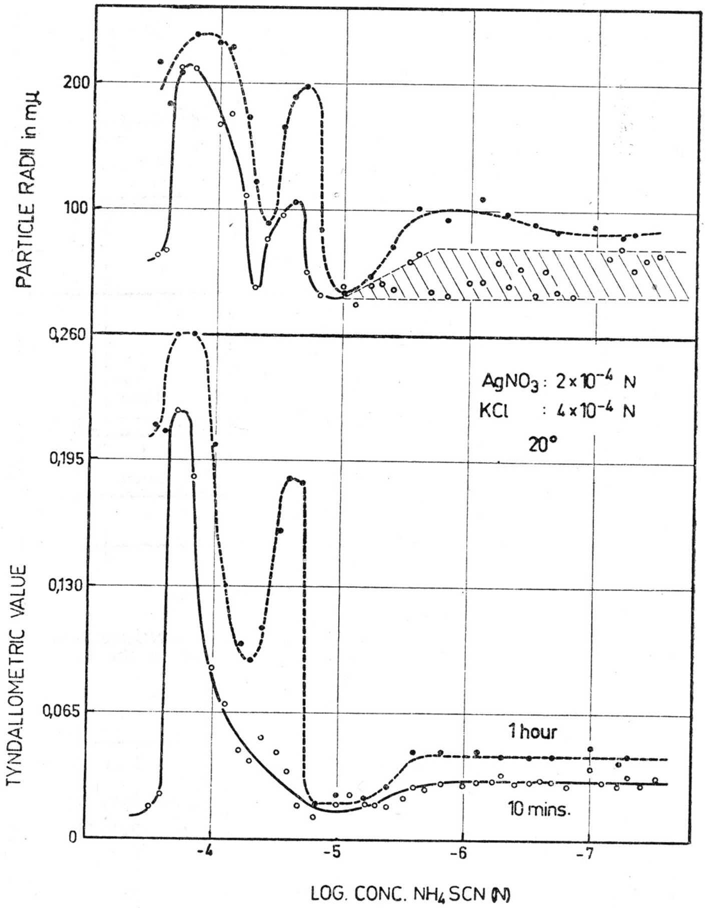

Fig. 2. Tyndallogram and dispesoidogram of the system $AgNO_3$-KCl-NH_4SCN.

AgCN-AgI (Fig. 5). — This system showed fairly stable sols. Even the 10 hours turbidity curve showed a deep minimum. The 1 hour turbidity has been measured twice to show the degree of reproducibility. The values were badly reproducible in the lower part of the concentration gradient. Turbidity was fairly low over the whole gradient.

AgSCN-AgBr (Fig. 6). — Reproducibility was very poor in the whole system which underwent quick precipitation in a short time. Double values are given for turbidity at both 5 and 10 minutes, showing the effects of uncontrolable factors. The average turbidity was very high over the whole concentration gradient of Br-ions (except at the left side of the diagram).

AgSCN-AgI (Fig. 7). — The turbidity values of this system were remarkably unreproducible but a linear general trend of the results plotted against the concentration gradient could be clearly distinguished; there were no maxima and no minima in this system. Turbidity grew gradually till it reached a high value at the end of the concentration gradient.

AgBr-AgI. — See our last paper[5].

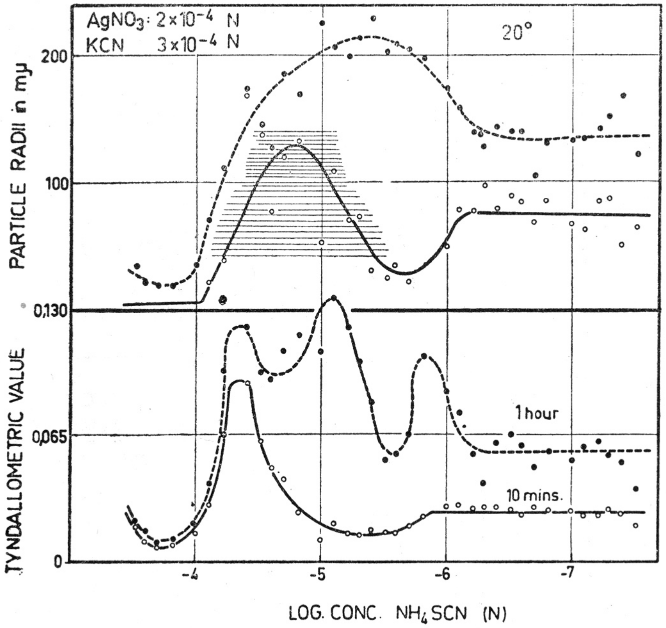

Fig. 3. Tyndallogram and dispersoidogram of the system $AgNO_3KCN-NH_4SCN$. The 10 minutes dispersity curve was drawn rather arbitrarily in the hatched area.

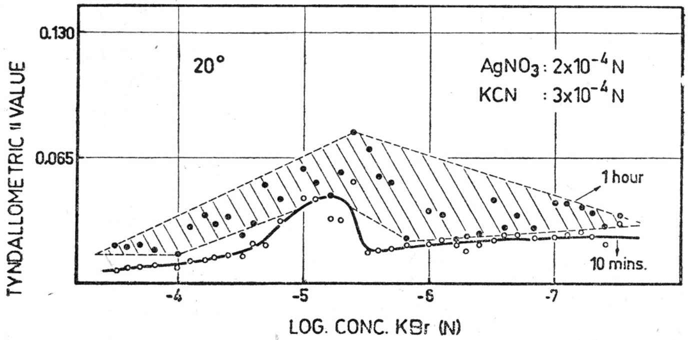

Fig. 4. Tyndallogram of the system $AgNO_3$-KCN-KBr

DISCUSSION

According to the reproducibility the investigated »binary« systems can be devided into two groups: the well reproducible ones (AgCl-AgSCN, AgCl-AgBr, AgCl-AgI, AgCN-AgSCN, AgBr-AgI) and the less reproducible ones (AgCl-AgCN, AgCN-AgBr, AgCN-AgI, AgSCN-AgBr, AgSCN-AgI).

The main uncontrolable factor that can influence the reproducibility of such systems is the way of mixing the reacting components ($AgNO_3$ and the mixture of KA and KB). Although it is done as uniformly as possible, the statistical distribution of various ions in the reacting volume at the very beginning of mixing will vary in a wide range from case to case. The con-

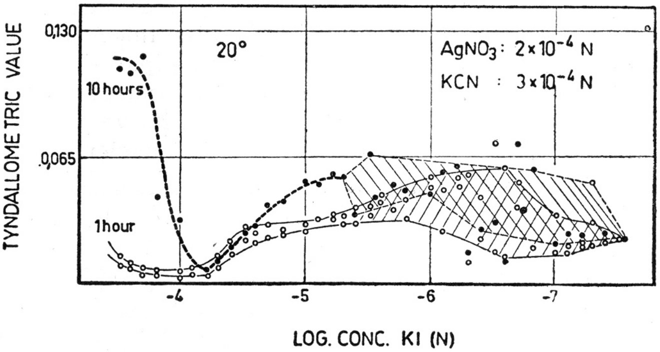

Fig. 5. Results of the repeated measurements of the system $AgNO_3$-KCN-KI

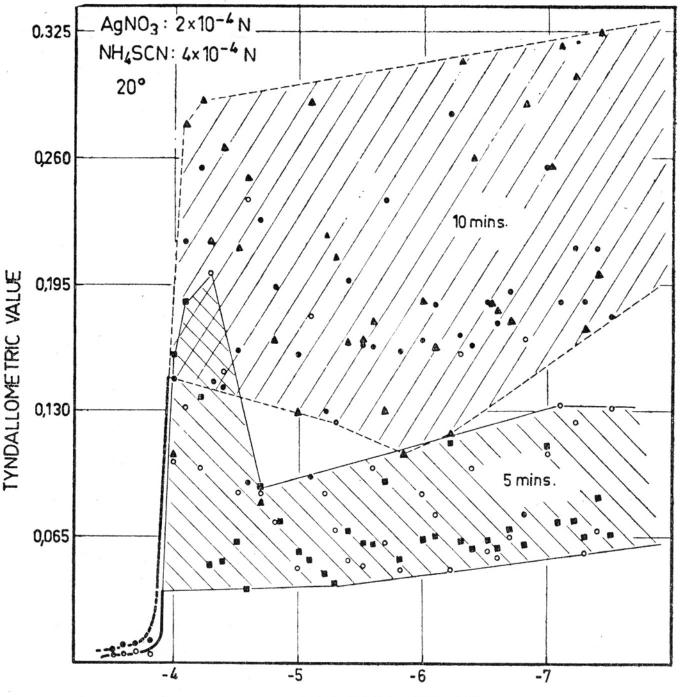

Fig. 6. Results of the repeated measurements of the system $AgNO_3$-NH_4SCN-KBr.

sequence of this unequal distribution is an unequal number of nuclei. If these nuclei grow by rapid crystallization into primary particles which — because of various factors — do not possess enough stability the resulting turbidity will show poor reproducibility. This is e. g. the case with the unstable silver thiocyanate sols[10].

In the system AgSCN-AgBr, therefore, there is a very large dissipation of experimental results showing the predominantly thiocyanate character of the system. In the system AgSCN-AgI similar dissipation can be observed beside a continuous change from stable AgI sols to unstable AgSCN sols with decreasing the concentration of I-ions. AgI — with its very low solubility — influences the precipitation by formation of the first nuclei.

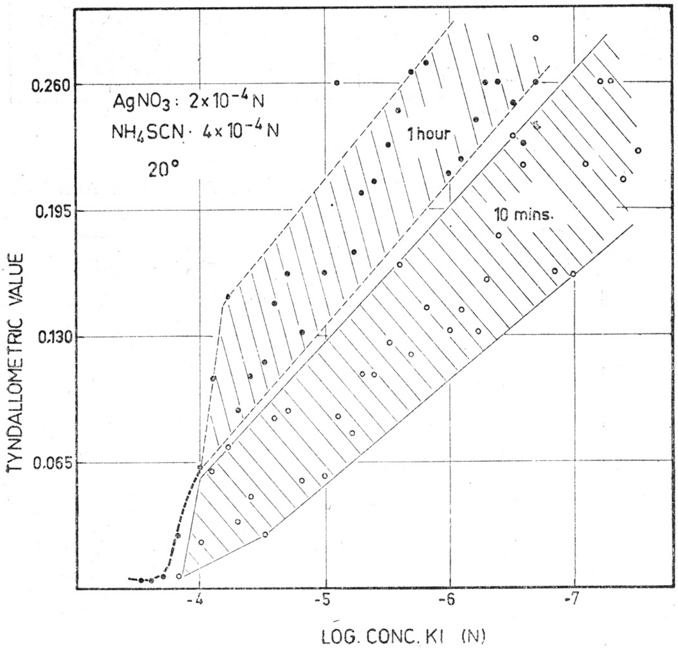

Fig. 7. Tyndallogram of the system $AgNO_3$-NH_4SCN-KI

In the systems AgCl-AgSCN and AgCN-AgSCN mixed crystals are probably formed. This is suggested by the appearance of well reproducible »secondary« maxima[1] (the ones on the right, appearing only after 1 hour, on Fig. 2 and 3) and also by low turbidity about the equivalence point of Ag-ions and SCN-ions, where AgSCN as the less soluble component should be in the state of unstable sol. These »secondary« maxima probably appear at those points of the concentration gradient, where the composition of mixed crystals represents a tyndallometric optimum. The same may be true for the maxima in the system AgCl-AgCN.

The formation of mixed crystals in the systems AgCl-AgBr, AgCl-AgI and AgBr-AgI has already been shown as very probable[5]. These results are in accord with the results of x-ray analysis of Pouradier and his coworkers[11], while mixed crystals of AgCN-AgSCN were found by Marin and Duval[8]. The formation of such mixed crystals depends on various factors, e. g. crystal lattice, ionic radii and ionic shape of the components, but mixed crystals were found also in cases where these factors were very different, e. g. AgCl-AgI[11] or AgCN-AgBr[6].

The first maxima of the system AgCl-AgSCN and AgCN-AgSCN (the ones on the left, appearing already after 10 minutes, on Fig. 2 and 3) as well as the 5 minutes maximum area in the system AgSCN-AgBr (Fig. 6) could be explained perhaps as isoelectric maxima[1] of AgB replaced from the equivalence point of Ag-ions and B-ions by the presence of A-ions.

The well-marked minima in the systems AgCl-AgSCN, AgCN-AgSCN and AgCN-AgI can be explained by such a distribution of crystallization nuclei which gives a minimum of turbidity, as a consequence. The corresponding dispersoidograms show indeed that the particles were very small at those points. Quite generally, the low turbidity in AgCl-AgCN, AgCN-AgSCN, AgCN-AgBr and AgCN-AgI systems can be ascribed to the presence of AgCN in the systems, the pure AgCN sol being very stable.

The main task of this report is to give the phenomenology of the precipitation of the investigated systems; the explanations given are mere hypothesis. It is not possible to state anything more certain before x-ray analysis is applied to these systems.

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IZVOD

Metorika precipitacionih procesa. XVII. Istodobna precipitacija argentum halogenida s argentum cianidom i argentum tiocianatom

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Istodobnom precipitacijom argentum halogenida s argentum cianidom ili argentum tiocianatom pripravljeni su miješani »binarni« sistemi i njihov je rast praćen tindalometrijski. Odnosi između koncentracija halogenidne i cianidne (odnosno tiocianatne) komponente mijenjali su se u širokom opsegu. Neki od tih »binarnih« sistema pokazuju precipitacione krivulje, koje se mogu dobro reproducirati, pa upućuju na stvaranje kristala mješanaca; u drugim slučajevima mogu se dobiti samo područja mutnoće.

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