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Investigation on Mixed Silver Halide, Silver Cyanide and Silver Thiocyanate Systems by means of Electron Microscope

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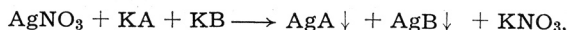
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Mixed systems of silver halides, silver cyanide and silver thiocyanate were investigated by means of electron microscope. The shape of the particles formed depends greatly on the ratio of concentrations of the reacting components. Even quite small amount of one substance can change the particle shape of another one. The most characteristic electron micrographs are reproduced.

In previous papers^{1,2} we described our tyndallometric investigation on the simultaneous precipitation of silver halides, silver cyanide and silver thiocyanate. The interpretation of the results obtained was difficult since only statistical phenomena of colloidal systems can be measured by tyndalometry and it is not possible to have any direct insight into the micro-mechanism of the processes involved. For this reason we tried to apply another technique which would enable us to observe *individual* particles of our systems. Thus we investigated all systems, possessing characteristic tyndalometric features, by means of electron microscope. The results of this investigation and the most characteristic of over a hundred pictures obtained are represented in this paper.

EXPERIMENTAL

We prepared our systems according to the scheme:



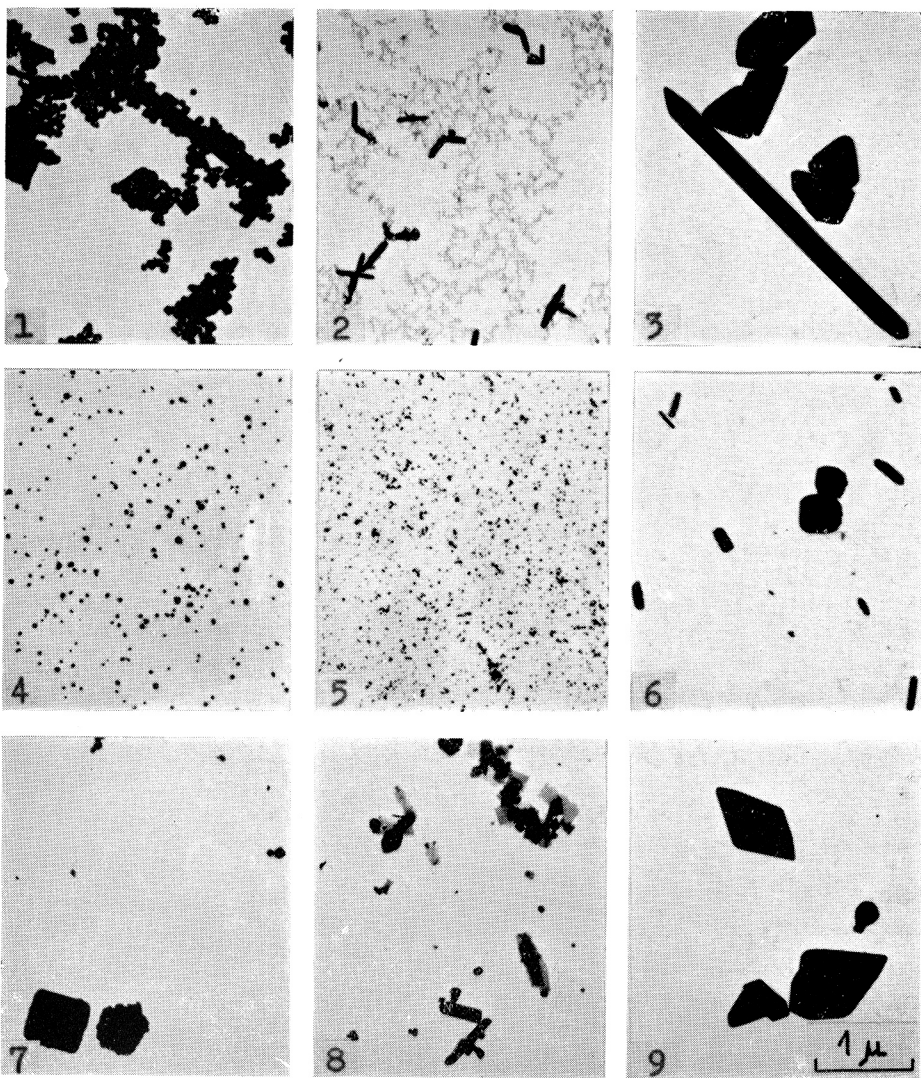
AgA representing the more soluble component of the system, AgB the less soluble one. The concentration of AgNO₃ was always 2×10⁻⁴N, that of KA 4×10⁻⁴N (except with A = CN = 3×10⁻⁴N), and that of KB was varied from 3×10⁻⁴ to 3×10⁻⁸N. The concentration gradient of B-ions included the point of equivalence where there was C_B = C_{Ag}. The systems were prepared for microscopic observation one hour after the mixing of the reacting components, always in the same way. The pictures were made with electron microscopic magnification 1,300x using the whole resolving power of the microscope and finally magnified to 13,000x. They are characteristic for the systems one hour old.

The electron micrographs are reproduced on Figs. 1 to 18 (see the plates included) and described in Table I.

DISCUSSION

In trying to interpret the results described one has to bear in mind that these systems suffer strong deformation when prepared for electron microscopic observation (because of enormous concentration change) and during the

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In all systems AgNO_3 : $2 \times 10^{-4} \text{ N}$.

Fig. 1. KCl : $4 \times 10^{-4} \text{ N}$.

Fig. 2. KCN : $3 \times 10^{-4} \text{ N}$.

Fig. 4. KBr : $4 \times 10^{-4} \text{ N}$.

Fig. 5. KI : $4 \times 10^{-4} \text{ N}$.

Fig. 7. KCl : $4 \times 10^{-4} \text{ N}$.
 KCN : $5 \times 10^{-5} \text{ N}$.

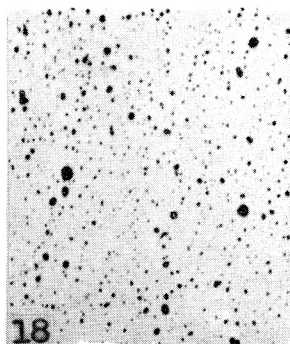
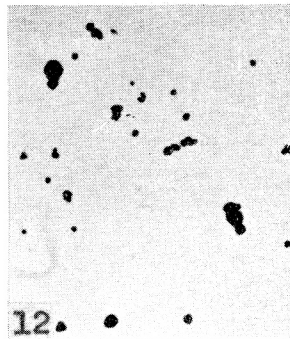
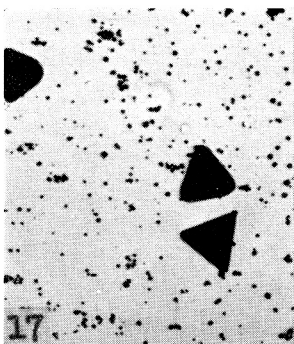
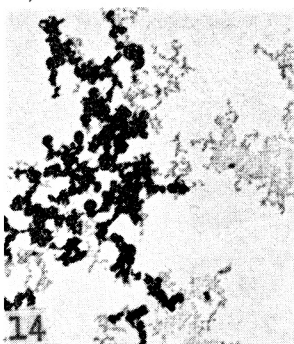
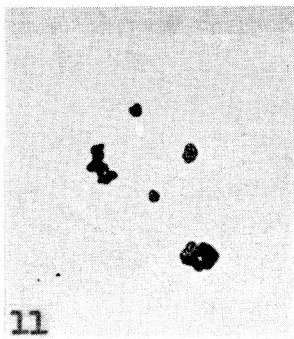
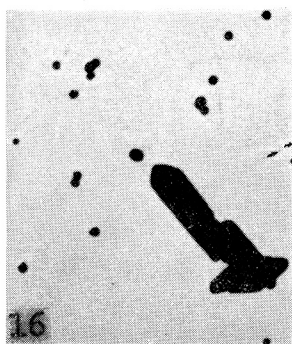
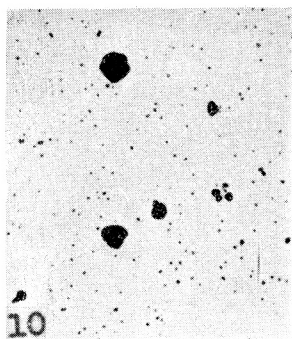
Fig. 8. KCl : $4 \times 10^{-4} \text{ N}$.
 NH_4SCN : $3 \times 10^{-4} \text{ N}$.

Fig. 3. NH_4SCN : $4 \times 10^{-4} \text{ N}$.

Fig. 6. KCl : $4 \times 10^{-4} \text{ N}$.
 KCN : $3 \times 10^{-4} \text{ N}$.

Fig. 9. KCl : $4 \times 10^{-4} \text{ N}$.
 NH_4SCN : $1.5 \times 10^{-4} \text{ N}$.

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In all systems AgNO_3 : $2 \times 10^{-4} \text{ N}$.

Fig. 10. KCl : $4 \times 10^{-4} \text{ N}$;
 KI : $3 \times 10^{-5} \text{ N}$.
 Fig. 13. KCN : $3 \times 10^{-4} \text{ N}$;
 NH_4SCN : $5 \times 10^{-5} \text{ N}$.
 Fig. 16. NH_4SCN : $4 \times 10^{-4} \text{ N}$;
 KBr : $3 \times 10^{-4} \text{ N}$.

Fig. 11. KCl : $4 \times 10^{-4} \text{ N}$;
 KI : $3 \times 10^{-7} \text{ N}$.
 Fig. 14. KCN : $3 \times 10^{-4} \text{ N}$;
 KBr : $6 \times 10^{-6} \text{ N}$.
 Fig. 17. NH_4SCN : $4 \times 10^{-4} \text{ N}$;
 KI : $1 \times 10^{-4} \text{ N}$.

Fig. 12. KCl : $4 \times 10^{-4} \text{ N}$;
 KI : $3 \times 10^{-8} \text{ N}$.
 Fig. 15. KCN : $3 \times 10^{-4} \text{ N}$;
 KI : $6 \times 10^{-5} \text{ N}$.
 Fig. 18. KBr : $4 \times 10^{-4} \text{ N}$;
 KI : $3 \times 10^{-5} \text{ N}$.

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TABLE I

System	$C_B > C_{Ag}$	$C_B < C_{Ag} \longrightarrow C_B < C_{Ag}$
Pure AgCl	small parallelograms; recrystallization into larger particles (Fig. 1)	
Pure AgCN	rhombohedral needles ^{3,4} ; tiny semi-transparent particles (Fig. 2)	
Pure AgSCN	large particles (about 1 μ long) with various shapes (Fig. 3)	
Pure AgBr	small particles with irre recognizable shape (Fig. 4)	
Pure AgI	small particles with irre recognizable shape (Fig. 5)	
AgCl—AgCN	needles of AgCN; a few parall. of AgCl (Fig. 6)	parallelograms of various sizes (Fig. 7)
AgCl—AgSCN	parallelogram slates, some very thin (semi-transp.); AgSCN partls.; small partls. with irre recognizable shape (Fig. 8)	AgSCN and AgCl particles independently, their ratio varying with changing C_B (Fig. 9)
AgCl—AgBr	small particles with irre recognizable shape	parallelograms of various sizes
AgCl—AgI	small particles with irre recognizable shape	small particles with irr. shape and larger ones (hexagonal* and parallels.); then only larger particles (Fig. 10—12)
AgCN—AgSCN	typical AgSCN particles	firstly only AgSCN partls., then partls. with hexagonal* shape, finally tiny semi-trpt. and larger ones (Fig. 13)
AgCN—AgBr	small particles with irre recognizable shape	aggregates of small partls. with irr. shape; tiny semi-trp. partls. (Fig. 14)
AgCN—AgI	small particles with irr. shape	aggregates of small particles with irr. shape; tiny semi-trp. particles (Fig. 15)
AgSCN—AgBr	AgSCN particles; smaller partls. with irr. shape (Fig. 16)	AgSCN particles
AgSCN—AgI	small pts. with irr. shape	AgSCN partls. and small pts. with irr. shape; finally only AgSCN particles (Fig. 17)
AgBr—AgI	small pts. with irr. shape	small and larger partls. with irr. shape, their ratio varying with changing C_B (Fig. 18)

* the term pertaining only to the shape of the particles, not necessarily to their crystal structure

observation itself (because of the impacts of electrons). The first obstacle is inevitable and the second one can be greatly reduced by careful operation with the electron beam. In spite of that, the pictures obtained were reproducible and the shape of the particles formed seems to be characteristic for the systems (one hour old). There is a definite change of the particle shape when the ratio between KA and KB is altered.

The most interesting features of the results described are a) the difference between the systems above the equivalence of Ag-ions and B-ions ($C_B > C_{Ag}$)

and those below it ($C_B < C_{Ag}$); b) the appearance of particles having shapes which correspond neither to AgA nor to AgB; c) the totally inhibited appearance of AgB in some systems, when quite small amount of AgA is present.

The pictures obtained cannot be a basis for any definite conclusions pertaining to the structure of the mixed precipitates. However, the mixed precipitates certainly show strong mutual influence of the components precipitated.

This paper represents the first attempt to give an electron microscopic insight into these mixed systems (only AgCl—AgBr and AgBr—AgI have been investigated by the means of electron microscope³). Other workers have investigated the systems with other techniques. There have also been electron microscopic investigations of the pure silver halides and silver thiocyanate systems⁴⁻⁶.

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IZVOD

**Istraživanja miješanih sistema argentum halogenida, argentum cianida
i argentum tiocianata pomoću elektronskog mikroskopa**

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Istraživani su miješani sistemi argentum halogenida, argentum cianida i argentum tiocianata pomoću elektronskog mikroskopa. Oblik nastalih čestica uvelike ovisi o omjeru koncentracija reagenata. Već malene količine neke komponente mogu promijeniti oblik čestica druge komponente. Reproducirane su najkarakterističnije slike dobivene pomoću elektronskog mikroskopa.

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