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Methorics of the Precipitation Processes. XIV. New Maxima on the Precipitation Curves of Mixed Silver Halides*

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Series of mixed silver halide colloidal systems were prepared and their growth was studied tyndallometrically. The concentration relations of halide components were changed from system to system. Certain relations favour the precipitation of mixed silver halide crystals. The increase of temperature influences the precipitation, changing the rate of the growth of colloidal particles and their ionic solubility at the same time.

INTRODUCTION

In continuation of our previous investigations on the influence of small additions of certain halide ions to other ones upon the precipitation of silver halides[1] we also investigated the region of small concentration of the variable component on both sides of the equivalence point. The influence of counter-ions is negligible in this region; the processes which occur are mainly crystallization processes. When investigating the region bellow the equivalence point we performed our measurements in such a way that the sol concentration did not decrease and the charge of the sol particles remained negative.

EXPERIMENTAL

It has been known that silver halides show a stability region in their precipitation curves[2]; this region spreads from the concentration maximum to the isoelectric maximum. But after a certain time these systems also undergo visible precipitation. In Fig. 1 the 1-hour curve represents the subsequent precipitation of AgCl, which forms the most unstable sol among silver halides. A minimum situated just before the isoelectric maximum is fairly remarkable. Since these concentrations of halide ions, where the minimum appears, i. e. $8\times10^{-4} - 3\times10^{-4}$ *N*, are important in our further discussion we shall call them *minimum concentrations* throughout this paper.

The introduction of iodide ions, even in concentrations as small as 0,03 *N*-%, changes the curve essentially, and the minimum area disappears. The new curve shifts regularly with increasing the percentage of iodide ions. But since this shift cannot be followed into the region of positively charged sols, the effect mentioned above disappears completely at 1 *N*-% iodide addition, and the minimum appears again.

We simplified our further work by keeping — within a series — at a constant level not only the Ag-component but also the more soluble halide component. The concentration of the less soluble halide component was systematically reduced

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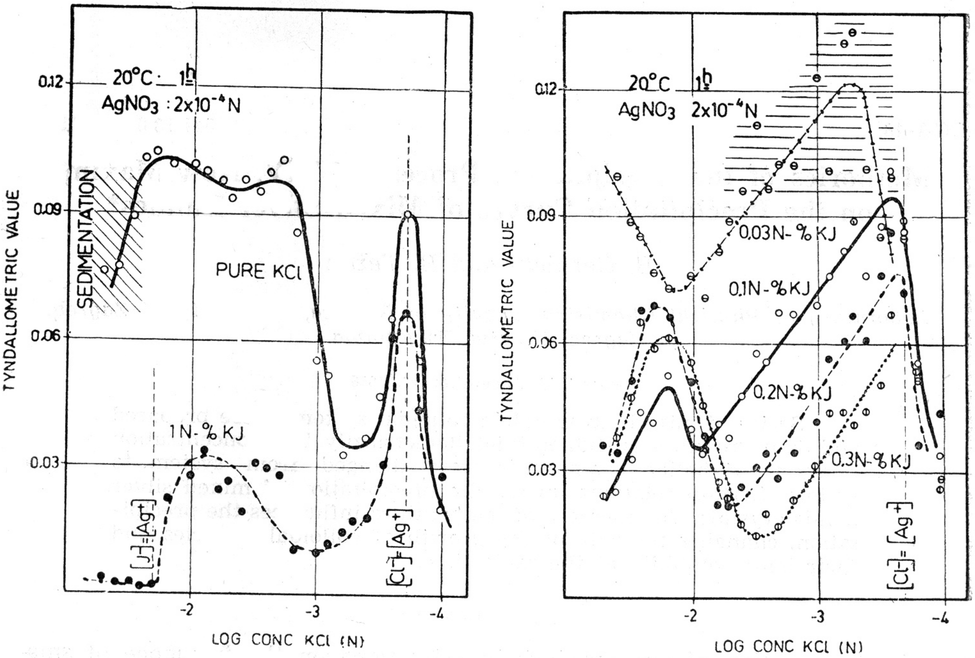

Fig. 1. The effect of iodide addition to the AgCl system. (The curve for 0,03 N-% was drawn in analogy with other curves in the hatched area).

from a value lying a little above the equivalence point by three or four decades. Accordingly, our measurements can be devided into three groups, denoted as *a, b, c*. The concentration of $AgNO_3$ was constant in all three groups, i. e. $2 \times 10^{-4}\,N$, and the concentration of the constant halide component was always higher than that of $AgNO_3$ so that the sol particles always had a negative charge.

a) KCl const., KI var. These series were performed with two chloride ion concentrations: $2 \times 10^{-3}\,N$ and $4 \times 10^{-4}\,N$. Fig. 2 shows that only the smaller one, which is the minimum concentration for the pure AgCl system, enables the detection of two maxima, a small one at about $3 \times 10^{-5}\,N$, and a high one at about $2 \times 10^{-7}\,N$. At the higher one, the curve tends to a platform at low concentrations of KI. The dispersoidograms of these systems show a fair concordance with the corresponding tyndallograms.

Fig. 3 shows the influence of temperature on the formation of these maxima. KCl has the minimum concentration. When temperature is increased the maxima become higher, then decline. A slight shift to higher concentrations can also be observed. Temperature influences also the rate of the growth of these systems. While they grow approximatively for one hour at room temperature, then stagnate and start sedimenting, the same process takes about 20 minutes at 40° and 10 minutes at 60°.

It was observed that the systems before the equivalence point assume a transparent yellow colour right at the beginning.

b) KCl const., KBr var. The precipitation curves of these systems, in Fig. 4, show only one maximum, at about $4 \times 10^{-6}\,N$. This, again, can be observed only with the minimum concentration of KCl. The dispersoidograms only partly follow the corresponding tyndallograms.

Fig. 5 shows the influence of temperature on these systems. When temperature was increased the maximum shifted remarkably into the region of higher concentrations, first becoming higher, then declining again. The influence of temperature on the rate of the growth of these systems was the same as in the case *a)*.

There were no yellow systems in this case.

c) KBr const., KI var. In this case we took $4 \times 10^{-4}\,N$ as the concentration of KBr in analogy with the minimum concentration of KCl in case *a)* and *b)*. These systems grow very slowly; Fig. 6 shows their growth within the first 20 hours. At least two distinct maxima are apparent: a smaller one at $1 \times 10^{-4}\,N$, and a higher one at $3 \times 10^{-5}\,N$.

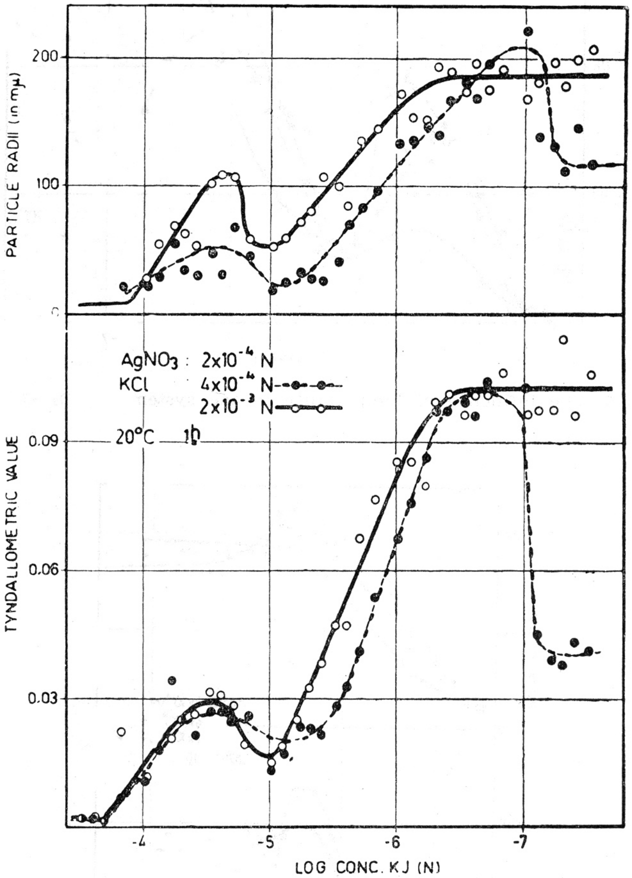

Fig. 2. The effect of changing the relation between the concentrations of Cl- and I-ions in the system $AgNO_3$-KCl-KI.

These systems are strongly influenced by temperature. The maxima become higher and larger with increasing temperature, but especially the rate of their growth is highly increased, as shown in Figs. 7 and 8.

Yellow systems appeared as in the case *a)*.

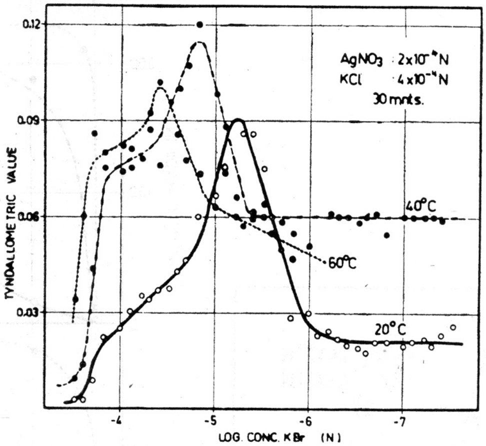

Fig. 5. The influence of temperature in the system $AgNO_3$-KCl-KBr.

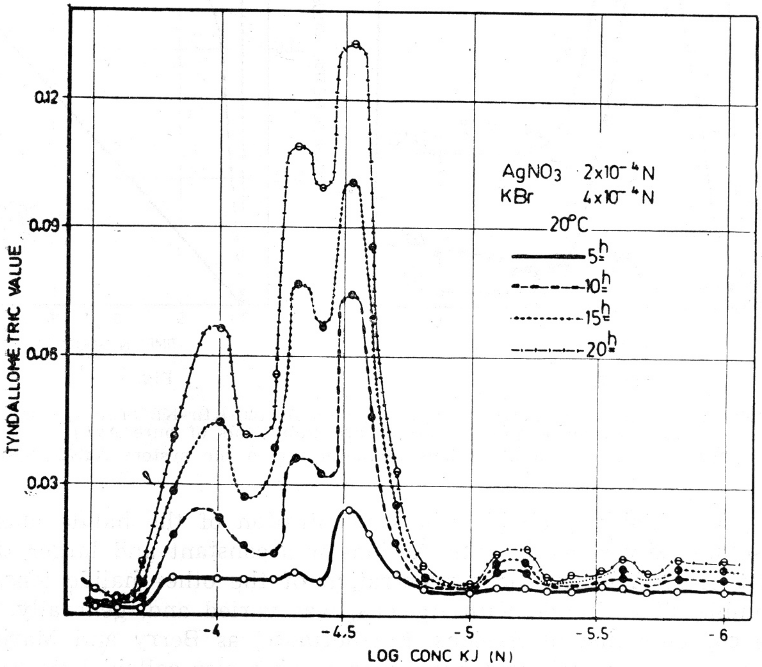

Fig. 6. The effect of changing the relation between the concentrations of Br- and I-ions in the system $AgNO_3$-KBr-KI.

DISCUSSION

The new maxima which were obtained show that there exist certain well-defined concentration realtions favouring the precipitation of mixed silver halide crystals. There are several facts that make the assumption of

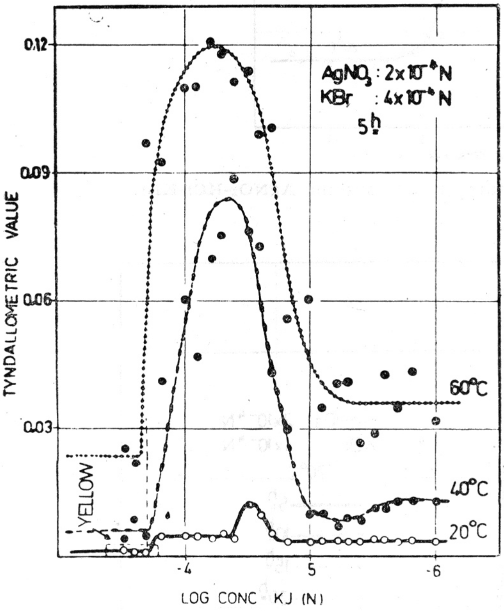

Fig. 7.

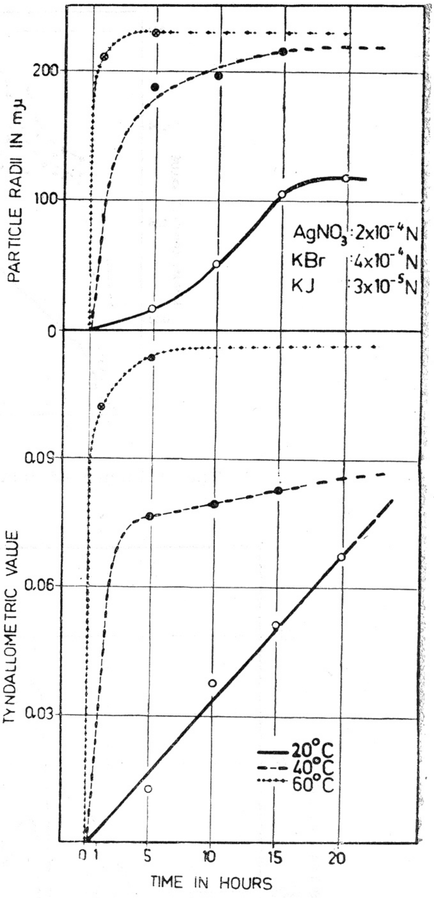

Fig. 8.

Fig. 7. The influence of temperature in the system $AgNO_3$-KBr-KI. (The systems above the equivalence point, 2×10^{-4} *N*, are stable sols of pure AgI.)

Fig. 8. The rate of growth at various temperatures in the system $AgNO_3$-KBr-KI.

mixed crystals highly probable: the concentration of the halide ions giving a more soluble silver halide with Ag-ions was constant and larger than the concentration of Ag-ions; the concentration of the other halide ions, giving a less soluble silver halide with Ag-ions, was varied and, generally, smaller than the concentration of Ag-ions. Furthermore, as Berry and Marino[3] and Pouradier and his coworkers[4-6] have shown, whenever colloidal silver halides come in contact with each other, redistribution occurs resulting in the formation of mixed silver halide crystals.

It seems obvious that certain concentration relations between the less and the more soluble halide component favour the formation of mixed silver halide crystals; hence maxima appear at the corresponding points of the concentration gradient. The tyndallometric method, however, enables only the estimation of the average composition of the solid phase (presuming that the *whole* potential solid phase has undergone precipitation), and does not enable the estimation of the number of phases, of their particular composition and of their percentual share. It would be necessary, therefore, to apply the radiotracer method and X-ray analysis to this problem before saying anything essential about the character of these maxima.

Here only some external features of the maxima can be discussed. They begin to rise after the equivalence point (2×10^{-4} *N*) when there is not enough I-ions (Br-ions, in case *b*) to form pure silver halide with Ag-ions. The systems seem to represent pure AgI (AgBr, in case *b*) before the equivalence point, because of the smaller solubility of AgI (and AgBr, respectively). This is, in the case of AgI, suggested also by the very low turbidity and yellowish colour of these systems, which is typical of small AgI colloidal particles with adsorbed I-ions. After the equivalence point Cl-ions (Br-ions, in case *c*) also take share in precipitating Ag-ions and mixed crystals are formed. When the concentration of the less soluble component becomes too low its influence suddenly vanishes and there is a low platform after the maxima corresponding to the *minimum concentration* of the more soluble component.

In case *a* and *b* the increase of temperature first favours the precipitation since the rate of crystallization and, perhaps, of thermal coagulation is increased. Further increase of temperature, however, makes the increase of ionic solubility predominant. In case *c* the increase of temperature favours the precipitation very much, which explains the considerable difficulty in the precipitation of these systems. The reason for this influence cannot be given before the composition of particular phases is better known. The same is truth about the change in composition of the systems in maxima with increasing temperature, in case *b*.

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IZVOD

Metorika precipitacionih procesa. XIV. Novi maksimumi na taložnoj krivulji miješanih agentum halogenida.

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Pripravljeni su nizovi koloidnih miješanih sistema argentum halogenida i njihov rast je praćen tindalometrijski. Odnosi koncentracija halogenidnih komponenata mijenjali su se od sistema do sistema. Izvjesni odnosi pogoduju precipitaciji kristala mješanaca argentum halogenida. Povišenje temperature utječe na precipitaciju mijenjajući brzinu rasta koloidnih čestica i njihovu ionsku topljivost.

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