Methorics of the Precipitation Processes. XVIII.
The Influence of Temperature and Concentration
on the Precipitation of Silver Bromide*

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The influence of temperature and concentration on the precipitation of silver bromide was investigated tyndallometrically. One could expect the disappearance of colloid-chemical effects and the emphasizing of crystallization phenomena in regions of small concentration. In general, both effects must be taken into consideration as competent for precipitation. The increase of temperature acts in the same way as the lowering of concentration, and interference of coagulation, crystallization and recrystallization processes can be observed.

INTRODUCTION

In continuation of our investigation on precipitation processes of silver halides in aqueous solutions we performed measurements at various temperatures with different concentrations of reacting components.

According to our previous papers[1] three stages in the precipitation processes can be distinguished: (1) nucleation, (2) growth and (3) aggregation. It may be expected with certainty that all three stages depend on temperature.

In the process of growth and aggregation several cases of particle mass increase must be distinguished. The particle can grow by direct phase transition of ions from liquid into solid (crystallization). Larger particles can be formed by the aggregation of smaller ones; the total area of solid phase can become remarkably smaller during this process (crystalline agglomeration), or the area does not change or changes only a little (coagulation). The third process of particle growing is recrystallization, i. e. the transition of ions from smaller particles to the larger ones through the solution.

All factors influencing the precipitation process are evidently dependent on temperature. Here the exceeding of a limit (Überschreitung[2]), defined as the difference between the chemical potentials of the precipitated matter in metastable liquid phase and the chemical potential of the same matter in phase equilibrium, must first be mentioned. In that difference especially the first term is dependent on temperature.

Überschreitung (exceeding) is one of the main factors governing the kinetics of nucleation and particle growth and is of great practical importance since it is proportional to the supersaturation and undercooling. The second factor which is important for the kinetics and mechanism of particle growth

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* Contribution No. 71 from the Laboratory of Physical Chemistry.

is the adsorption of ions on nuclei. Finally, the increase of temperature causes an increase of diffusion of matter in the methorical layer, an effect which obviously promotes the particle growth.

<div align="center">EXPERIMENTAL</div>

Tyndallometric measurements were applied to the investigation of solid phase formation. The experimental technique used was already described in our previous papers.[1] The measurements were performed with the C. Zeiss »Trübungsmesser«. The temperature was kept constant by a Hoeppler »Ultrathermostat« with an accuracy of $\pm 0.1^0$.

The mixing of the aqueous solutions of silver nitrate and potassium bromide was performed always by pouring the solution of silver nitrate into the solution of potassium bromide. The concentrations of these solutions were such that bromide-ions were usualy in excess, except in the equivalent region.

The measurements of particular systems were performed at constant temperatures in definite time intervals. The concentration of silver nitrate was 1×10^{-4}, 1×10^{-5} and 1×10^{-6} N. The concentration of potassium bromide was changed in a wide range up to a point a little under the equivalence. The temperature was 20, 40 and 60^0C.

<div align="center">RESULTS</div>

Figs. 1, 2 and 3 show the system with the concentration of silver nitrate 1×10^{-4} N. In the larger part of the system there is an excess of bromide-ions and the particles are, therefore, negatively charged. The results from Fig. 1
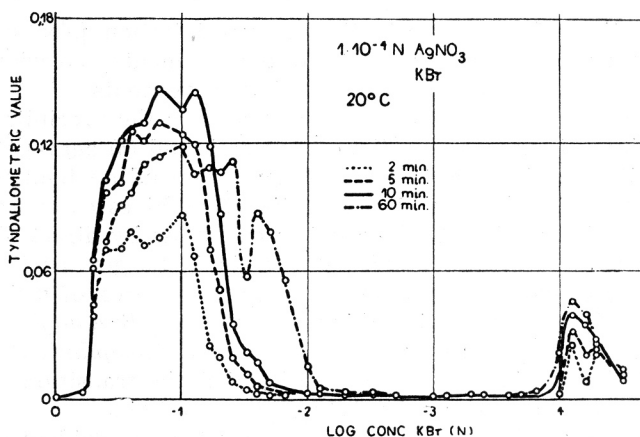

Fig. 1. Concentration tyndallogram of the system silver nitrate — potassium bromide at 20^0 C, concentration of silver nitrate 1×10^{-4} N.

agree with previous ones[3,4]. The precipitation diagram shows the region of complex solubility, the concentration maximum, the region of stable sol and the isoelectric maximum. The isoelectric maximum is displaced a little in the positive region of the precipitation diagram, a fact that also agrees with our previous results[5,6].

The general picture of the precipitation diagram remains the same with changing temperature (Figs. 2 and 3), but a shift of maxima boundaries can be observed. The isoelectric maximum shifts to the equivalence point and the

complex solubility boundary toward the lower concentration of potassium bromide.

On Figs. 4, 5 and 6 the tyndallometric curves for the system with the concentration of silver nitrate $1 \times 10^{-5} N$ are represented. Here longer time inter-
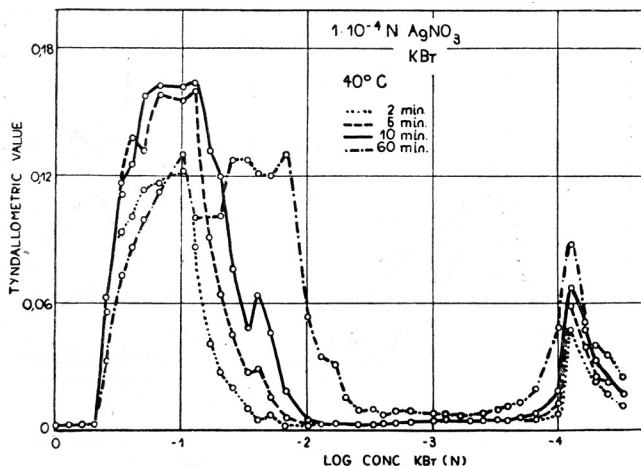

Fig. 2. Concentration tyndallogram of the system silver nitrate — potassium bromide at 40⁰ C, concentration of silver nitrate $1 \times 10^{-4} N$.

vals between the measurements were introduced because of the slowness of these processes. Fig. 4 shows the general precipitation diagram at 20⁰C with the following characteristics: the region of complex solubility reaches to the concentration of potassium bromide $2.5 \times 10^{-1} N$, then the concentration maxi-
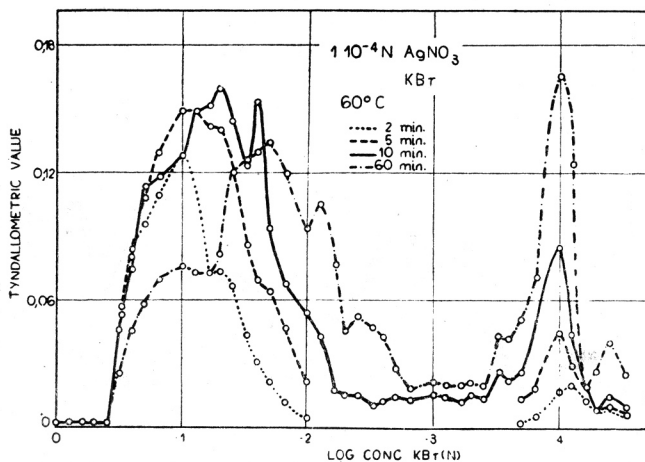

Fig. 3. Concentration tyndallogram of the system silver nitrate — potassium bromide at 60⁰ C, concentration of silver nitrate $1 \times 10^{-4} N$.

mum rises. The stable sol region lies between 1.5×10^{-3} and $2.5 \times 10^{-3} N$ potassium bromide and is narrower than that in the previous system. Then there comes a wide region of precipitation processes — the so-called *maximum at*

pBr 5 (analogous to the similar maximum found with silver iodide[7], named *maximum at pJ 8*) which reaches to the equivalence point. The concentration maximum is approximately at the same place as with the system with $1 \times 10^{-4} N$ silver nitrate.
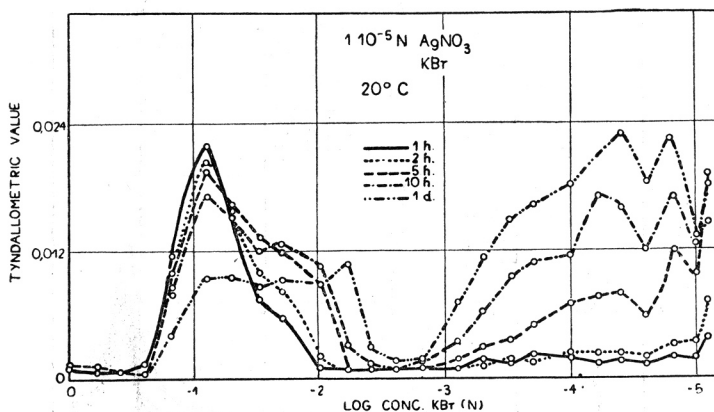

Fig. 4. Concentration tyndallogram of the system silver nitrate — potassium bromide at 20° C, concentration of silver nitrate $1 \times 10^{-5} N$.

The stable region disappears with rising temperature (*i. e.* the time of stability is shorter — Fig. 5). At the same time the concentration maximum becomes smaller and shifts toward the lower concentration of potassium bromide under the influence of complex solubility. The boundary of the maximum at pBr 5 was situated rather far in the positive region of the precipitation
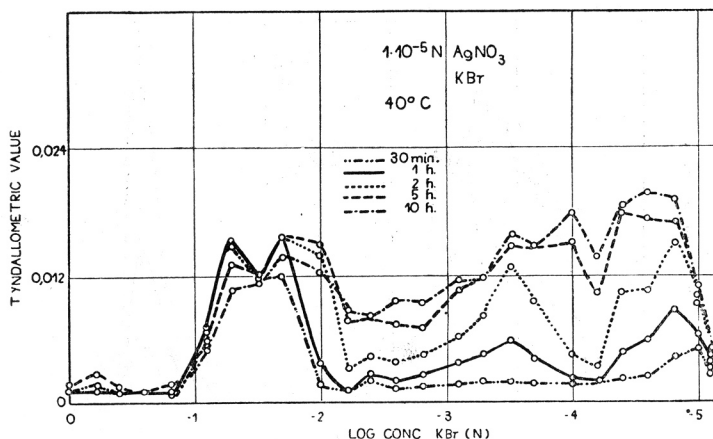

Fig. 5. Concentration tyndallogram of the system silver nitrate — potassium bromide at 40° C, concentration of silver nitrate $1 \times 10^{-5} N$.

diagram at 20°C,[8] while it was already near the equivalence point at 40°C. These effects were much more emphasized at 60°C (Fig. 6) where the concentration maximum was reduced to a small peak at $2 \times 10^{-2} N$ potassium bromide.

The maximum at pBr 5 shifted completely to the negative part of the precipitation diagram and was situated about $2.5 \times 10^{-5} N$ potassium bromide.

In the system with $1 \times 10^{-6} N$ silver nitrate the turbidities were so small, that the measurements were very unreliable. The residual turbidity of the
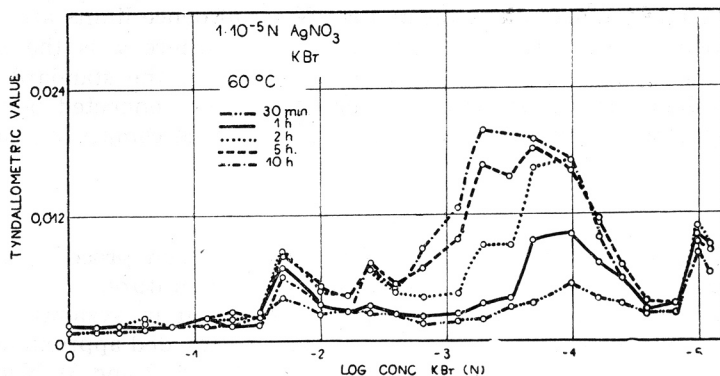

Fig. 6. Concentration tyndallogram of the system silver nitrate — potassium bromide at 60° C, concentration of silver nitrate $1 \times 10^{-5} N$.

solvent was in some cases over 50% of total turbidity; the optical irregularities of the test tubes influenced the results to a high degree, too. However, there is no doubt that the solid phase appears at this region of concentrations. We
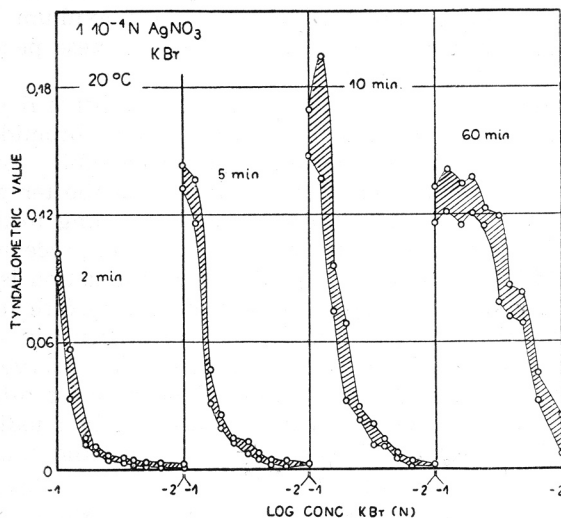
Fig. 7. Statistical analysis of the concentration tyndallogram of the system silver nitrate — potassium bromide at 20° C, concentration of silver nitrate $1 \times 10^{-4} N$.

observed visually the existence of Tyndall cones clearly different from the turbidities of the solute. At 20°C such a maximum appears at $5 \times 10^{-6} N$ potassium bromide and at 40°C shifts to $2.5 \times 10^{-5} N$, what agrees with the previously

published results[9]. At 60°C any appearance of solid phase could not be observed.

Fig. 7 shows a statistical analysis of a part of the system with $1 \times 10^{-4} N$ silver nitrate at 20°C. The analysis was applied to test the reproducibility of our results. The system was measured five times in the green spectral region. From these data the arithmetic mean and 95% confidence limits are estimated. The confidence limits are defined by ($\mu \pm t \cdot \sigma_\mu$), where μ is the arithmetic mean, t a parameter of the Student's distribution, σ_μ the standard deviation of the arithmetic mean estimated by the range. The connected points of the upper, resp. lower limits give the bands of confidence comprising 95% of the population.

DISCUSSION

We tried to explain the nature of the precipitation processes in various concentration regions and their dependence on temperature.

The colloid-chemical effects are fairly expressed in systems with great *Überschreitung* (exceeding) (the solubility product exceeded approximatively 10^5 times — system with $1 \times 10^{-4} N$ silver nitrate — Figs. 1, 2 and 3). Nucleation is rather fast and the incubation period vanishes in agreement with van Hook's measurements[10] at silver chromate. Except that, a great *Überschreitung* (exceeding) is favourable to form a great number of nuclei; as a consequence of this the phase surface is well developed. Here, therefore, there are very good conditions for the formation of a sol stable in a wide range of concentrations. It is sure, that the temperature sensitivity of the sol is partly due to the acceleration of the recrystallization processes. This is also shown by the characteristic peaks on the right part of the concentration maximum. With the higher temperature there is greater rate of appearance of these peaks (at 20°C they appear after 1 hour, at 60°C already after 2 minutes).

The shift of the isoelectric maximum into the positive region of the precipitation diagram is interpreted by the adsorption of bromide ions on silver bromide particles.[5] This interpretation seems acceptable, for the isoelectric maximum shifts to the equivalence point with rising the temperature.

It is possible to differentiate the processes according to their kinetics. At lower temperatures fast (coagulation) and slow (stable) processes can be clearly distinguished[11]. At higher temperatures the recrystallization is accelerated and the processes of coagulation and recrystallization interfere in a high degree. The determination of coagulation values[1] is very difficult in such cases where several processes interfere. Similar phenomena can be observed by comparison of the time tyndallograms of silver halides .The greatest difference between these two processes can be observed in the case of silver iodide, which is the most insoluble silver halide[12]. Silver chloride shows the smallest difference.

In the system with a smaller *Überschreitung* (exceeding) (silver nitrate concentration $1 \times 10^{-5} N$, solubility product exeeded 10^3 times) the concentration maxima are already very deformed by recrystallization processes (Figs. 4, 5 and 6). A rise of temperature favours the recrystallization and, at a sufficiently high temperature, it is not sure whether the processes do not become pure crystallization because in this region the solubility product is exceeded only 10 to 100 times (solubility product of silver bromide at 60°C calculated from the expression[13] $-\log K = 5702.2/T - 11.1822 + 0.014610\, T$; $K = 1.581 \times 10^{-11}$).

It seems, that the system is placed just in that critical concentration, where the colloid-chemical effects disappear and the pure crystallization processes begin to predominate; this is indicated by the strong temperature sensitivity of the processes.

The results from the system with $1 \times 10^{-6} N$ silver nitrate give only an information in which concentration region does the formation of solid phase appear. These concentrations are in the region of ionic solubility; the systems are very sensitive to the changes of temperature and concentration, what can be concluded from the remarkable shift of the maxima described above (so-called crystallisation maxima[9]). If the temperature rises sufficiently, *Über-schreitung* (exceeding) cannot be achieved. These measurements are on the boundary of the posibility of our apparatus and other ways for the measuring of small turbidities must be found.

REFERENCES

1. B. T e ž a k, E. M a t i j e v i ć and K. S c h u l z, *J. Phys. & Colloid Chem.* **55** (1951) 1557.
2. M. V o l m e r, *Kinetik der Phasenbildung,* T. Steinkopff, Dresden and Leipzig 1939, p. 76.
3. B. T e ž a k, *Arhiv kem.* **19** (1947) 19.
4. J. K r a t o h v i l, B. T e ž a k and V. B. V o u k, *Arhiv kem.* **26** (1954) 191.
5. B. T e ž a k, *Glasnik Hem. Društva, Beograd* **4** (1933) 137.
6. B. T e ž a k, E. M a t i j e v i ć, K. S c h u l z, M. M i r n i k, J. H e r a k, V. B. V o u k, M. S l u n j s k i, S. B a b i ć, J. K r a t o h v i l and T. P a l m a r, *J. Phys. Chem.* **57** (1953) 301.
7. M. M i r n i k and B. T e ž a k, *Arhiv kem.* **23** (1951) 44.
8. G. H. J o n k e r, *Thesis,* Utrecht 1943, p. 40.
9. B. T e ž a k, Discussions Faraday Soc. **18** (1954) 194.
10. A. van H o o k, *J. Phys. Chem.* **44** (1940) 751.
11. M. M i r n i k, F. F l a j š m a n, K. S c h u l z and B. T e ž a k, *J. Phys. Chem.* **60** (1956) 1473.
12. M. M i r n i k and B. T e ž a k, *Arhiv kem.* **21** (1949) 109.
13. B. B. O w e n and S. R. B r i n k l e y, *J. Am. Chem. Soc.* **60** (1938) 2237.

IZVOD

Metorika precipitacionih procesa. XVIII.
Utjecaj temperature i promjene koncentracija na precipitaciju srebrnog bromida

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Istraživan je utjecaj temperature i utjecaj promjene koncentracija na precipi-taciju srebrnog bromida pomoću tindalometrijske metode. Nađeno je, da se pri prije-lazu u područja nižih koncentracija gube koloidno-kemijski efekti i da sve više dolaze do izražaja pojave kristalizacije. U općem slučaju treba uvijek uzimati u obzir i jedne i druge efekte kao odlučne za proces precipitacije. I pri povišenju tempera-ture dolazi do miješanja procesa koagulacije, rekristalizacije i kristalizacije.

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