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Characterization of the Precipitation Processes of Negatively Charged Silver Bromide by the Influence of Non-Ionic Surface-Active Agent and Temperature Change*

V. Hrust and B. Težak

Department of Physical Chemistry, Institute of Chemistry, University of Zagreb, POB 163, Zagreb, Croatia, Yugoslavia

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The kinetics of precipitation in sols *in statu nascendi* was studied near the complex solubility limit of the negatively charged silver bromide precipitate.

Different precipitation processes were observed by the analysis of the critical time of precipitation and were characterized by the influence of the non-ionic surface-active agent Triton-X-305 and by the change of temperature during the precipitation.

The results show that two processes of the growth of secondary structures from primary particles take place in relation to the potassium bromide concentrations in excess: aggregation which takes place at lower, and crystallization which occurs at higher concentrations of potassium bromide in excess.

INTRODUCTION

The »precipitation body« of silver bromide has been studied by Težak *et al.*[1-4]. The processes of growth have been investigated in various concentration regions. Several maxima of turbidity appear in dependence on the concentration of reacting components: concentration, transition, isoelectric and crystallization maximum. The 'concentration maximum' takes place at the limit of the complex solubility region, when the concentration of the component in excess has reached the coagulation value.

The influence of non-ionic surface-active agent (SAA) Triton-X-305 (T-X-305) and change in temperature on the precipitation of negatively charged AgBr sol *in statu nascendi* have been examined in order to characterize the processes appearing in connection with the concentrations of reacting components within the 'concentration maximum'.

The stability of inorganic hydrophobic colloids in the presence of various SAA has been studied by many authors[5-8] and it has been found that they can flocculate and protect colloids from aggregation. We have used this fact in order to differentiate various kinds of precipitation processes within the 'concentration maximum'.

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EXPERIMENTAL

Measurements were done on a Zeiss tyndallometer connected to a Pulfrich photometer. The photomicrografs were done on a Zeiss light microscope. The systems were kept at constant temperature by a Hoeppler ultrathermostate. The adsorption isotherm of T-X-305 was done on the Pye-Unicam SP 1800 spectrophotometer.

The sols *in statu nascendi* were prepared as described by Težak[9] and the kinetics of precipitation was studied.

Aqueous solutions of $AgNO_3$ and KBr were prepared by dissolving dry salts (p. a. »Merck« Darmstadt) in bidistilled water and standarized potentiometrically.

The non-ionic SAA T-X-305 is a member of the octylphenoxyethanol series with 30 oxyethylene units. It was obtained from Rohm & Haas Co., USA, as a 70% water solution, and was not further purified.

RESULTS

The results of measurements are presented in Figures 1 to 7. The sol concentration was always 1.0×10^{-4} mol dm^{-3} and the excess of potassium bromide was varied.

Figure 1 shows the growth of negatively charged silver bromide precipitate in the region of the negative 'concentration maximum'. The tyndallometric values are plotted against time.

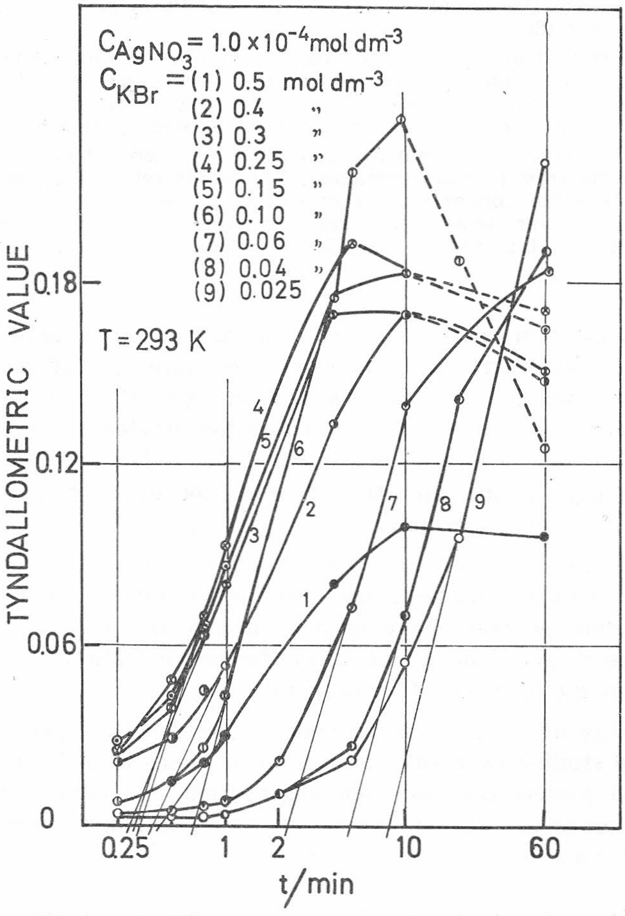

Figure 1. The time-tyndallograms for: $AgNO_3$—KBr (various concentrations).

The concentration of silver nitrate was 1.0×10^{-4} mol dm^{-3} and that of potassium bromide varied from 2.0×10^{-2} to 5.0×10^{-1} mol dm^{-3}. The critical times of precipitation (t_c) were defined by drawing a tangent to the steepest part of the tyndallometric - time curves (Figures 1, 2, 3). The influence of T-X-305 on the kinetics of precipitation of AgBr sols is shown in Figure 2.

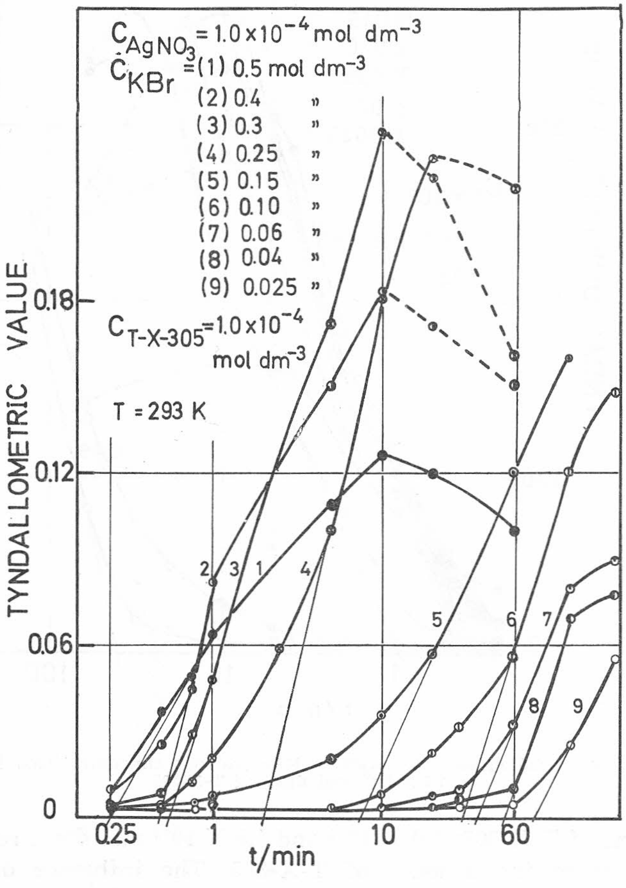

Figure 2. The time-tyndallograms for: $AgNO_3$—KBr (various concentrations) in the presence of 1.0×10^{-4} mol dm^{-3} of T-X-305.

and 3. Two different concentrations of T-X-305 were used. The concentration of 1.0×10^{-4} mol dm^{-3} of T-X-305 usually stabilized AgBr sols, thus the t_c of the systems became higher in relation to sols without T-X-305. Near the complex solubility limit the stabilizing action of T-X-305 disappeared. In the presence of 1.0×10^{-5} mol dm^{-3} of T-X-305 the processes of growth became faster from critical coagulation concentration (c. c. c.) of potassium ion to the complex solubility. Below c. c. c. only the sabilization action of T-X-305 was observed.

In Figure 4. t_c (from Figures 1, 2, 3) are plotted against the concentrations of potassium bromide. Curves 1 and 2 show t_c in the presence of two different

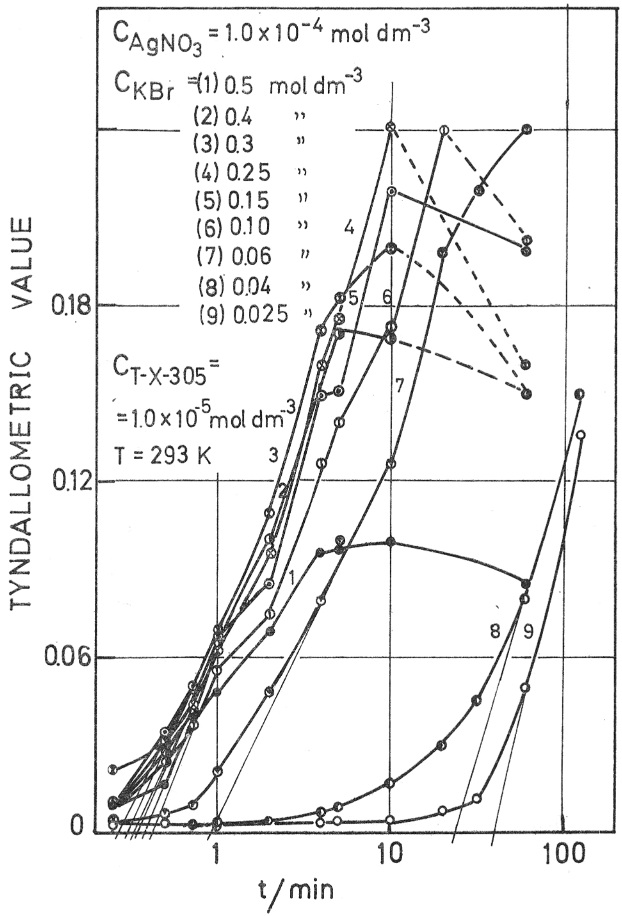

Figure 3. The time-tyndallograms for: $AgNO_3$—KBr (various concentrations) in the presence of 1.0×10^{-5} mol dm^{-3} of T-X-305.

concentrations of T-X-305: 1.0×10^{-4} and 1.0×10^{-5} mol dm^{-3}, respectively, and t_c for systems in the absence of T-X-305. The influence of various concentrations of T-X-305 on the negatively charged silver bromide precipitate from the stable region to the complex solubility region is shown in Figure 5. The concentrations of T-X-305 were varied from 10^{-6} to 4.0×10^{-3} mol dm^{-3} and stabilization and flocculation concentrations, (c. s. c.) and (c. f. c.), respectively, were determined by drawing a tangent to the steepest part of the concentration tyndallograms, 10 minutes after mixing the reacting components. In Figure 6 the c. s. c. of T-X-305 are plotted against the concentrations of potassium bromide. Also the 'concentration maximum' of AgBr is shown for 10 minutes after mixing, and the characteristic regions of the 'concentration maximum' are marked. The c. s. c. are presented in order to show the influence of T-X-305 on the precipitation processes within various regions of the 'concentration maximum'.

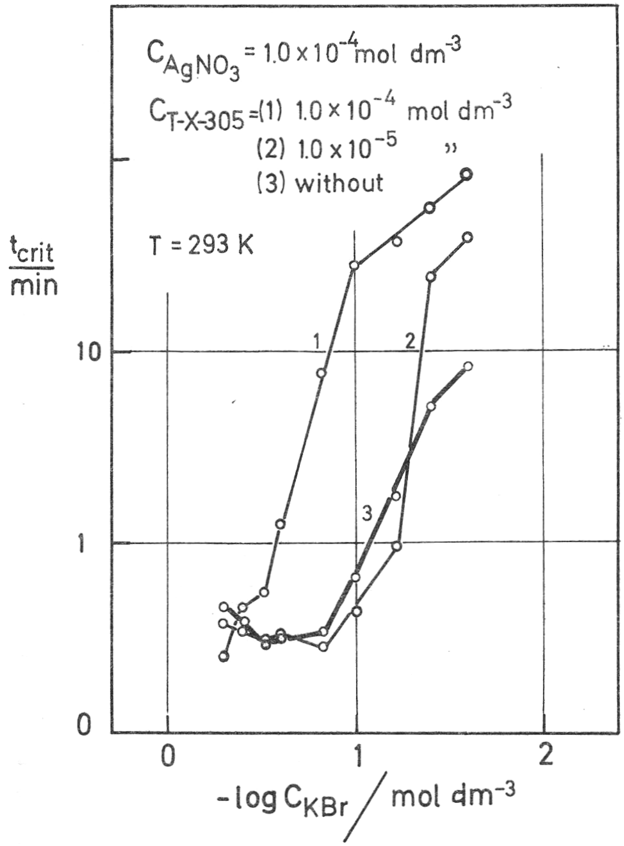

Figure 4. Critical times of precipitation in the absence and presence of T-X-305.

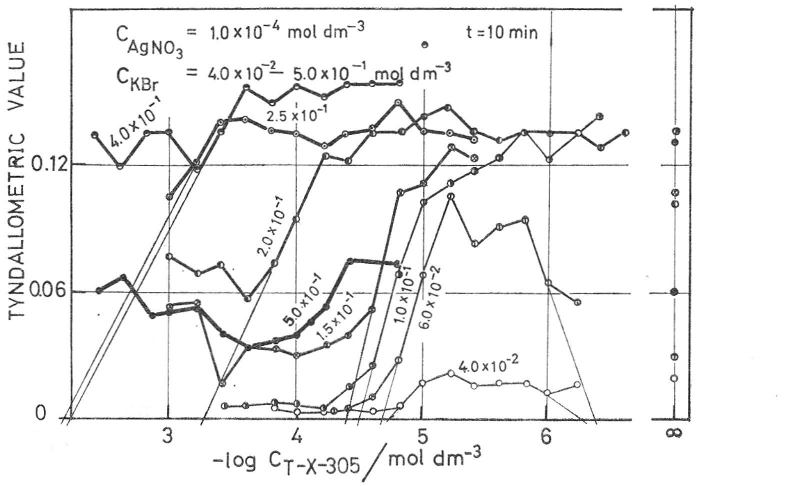

Figure 5. The influence of various concentrations of T-X-305 on the AgBr precipitate.

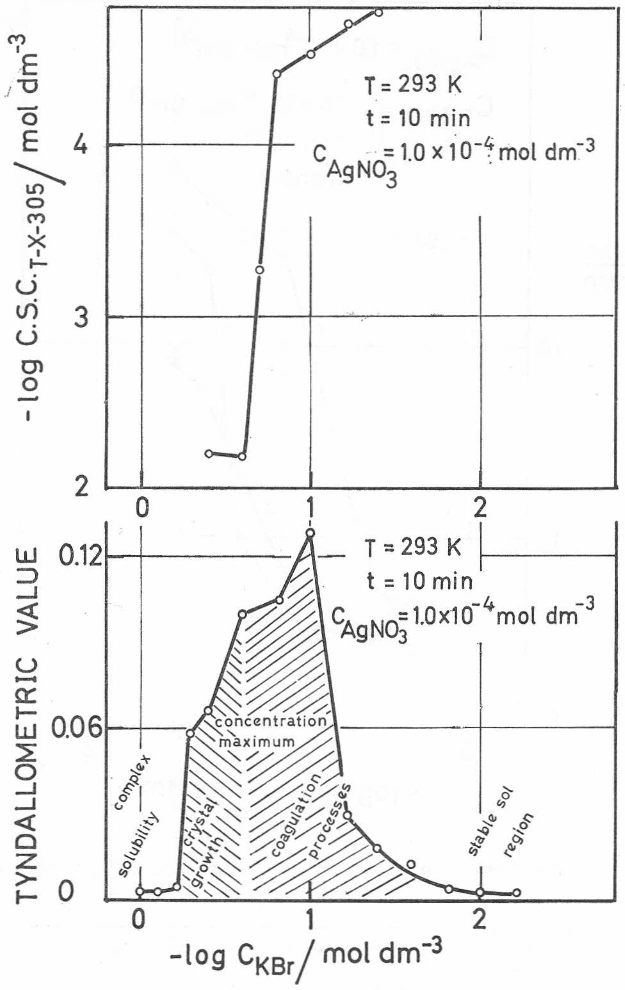

Figure 6. The picture of the 'concentration maximum' of AgBr without T-X-305. The characteristic precipitation regions are marked (ordinate axis: tyndallometric value). The stabilization values of T-X-305 for this precipitation system are shown in the same Figure (ordinate axis: c. s. c. values).

In Figure 7 the influence of temperature on precipitation in the region of the 'concentration maximum' is shown. After 60 minutes the temperature of the systems was elevated to 363 K for 10 minutes. The measurements of such systems showed a shift of the complex solubility limit to the lower concentrations of KBr. This is the soluble part of the 'concentration maximum' (curve 2). After cooling the systems to 293 K for 60 minutes the tyndallometric values were practically unchanged (curve 3) but from the complex solution the appearence of crystals was observed. The photomicrographs of crystals are presented in the same figure.

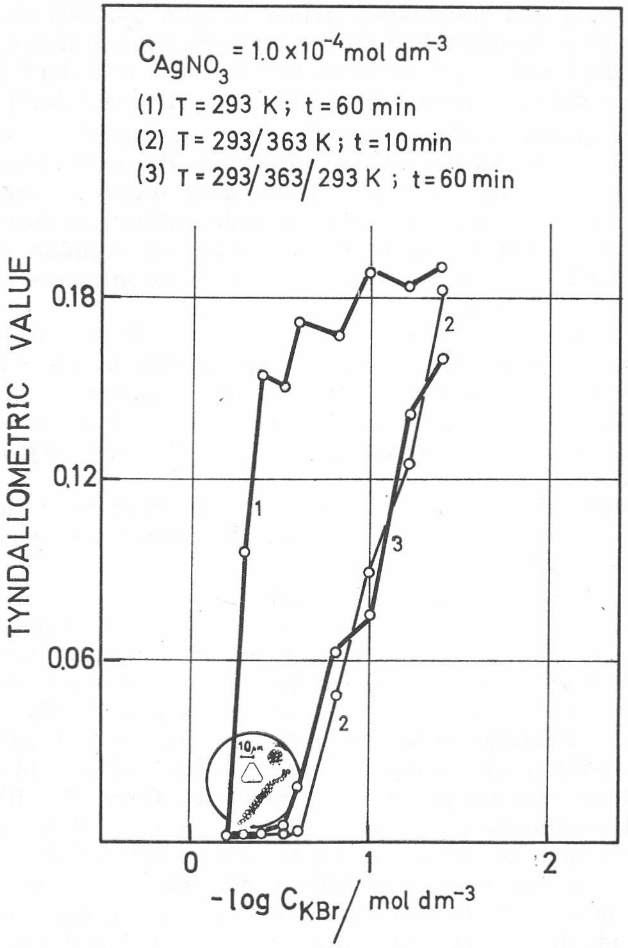

Figure 7. The influence of temperature change on the growth of precipitate in the 'concentration maximum'.

DISCUSSION

The kinetics of the growth of the precipitate in the region of the negative 'concentration maximum' of silver bromide has not yet been studied in detail. Težak and Matijević[9,10,11] have studied the kinetics of coagulation and observed a shift of the critical coagulation region to the stable region as a function of time and dielectric constant of the medium.

The growth of the precipitate in the region of the 'concentration maximum' was examined in greater detail in this study. The different processes of growth were characterized by the effects of non-ionic SAA T-X-305, and by change in temperature.

The influence of non-ionic SAA on positive and negative silver iodide sols was studied previously by Mathai and Ottewill[8] and an increase in the stability of sols was found.

The stabilizing and flocculation action of SAA T-X-305 on silver iodide sols were found[12] to be dependent on the sol concentration (c. s. c. between 10^{-4} and 10^{-5} mol dm^{-3} and c. f. c. between 10^{-6} and 10^{-7} mol dm^{-3} for negatively charged silver iodide sols from 1.0×10^{-4} to 2.0×10^{-3} mol dm^{-3}).

Our investigations have shown that by varying the concentration of T-X-305, stabilization and flocculation effects on the silver bromide sols can be found. The c. s. c. and c. f. c. are of the same order of magnitude as for silver iodide sols and it was found that the stabilization and flocculation action of T-X-305 was related to the excess of potassium bromide. Two different concentrations of T-X-305 were used for studying the influence on the kinetics of precipitation of AgBr sols.

The concentration of 1.0×10^{-5} mol dm^{-3} of T-X-305 (flocculation) was obtained for a sensitive part, and the concentration of 1.0×10^{-4} mol dm^{-3} of T-X-305 (stabilization) was obtained for a non-sensitive part of the adsorption isotherm. Both concentrations of T-X-305 showed a decrease either in the flocculation or in the stabilization effects in the same region of the concentration maximum (Figure 4).

The influence of cationic surfactants, if they exist as impurities, can be synergistic; the concentrations of cationic impurities are not high enough for a significant coagulation action.

The kinetic curves (from tyndallometric value — time diagrams) show different processes of precipitation in systems with and without T-X-305. By t_c- analysis a better view of the precipitation processes is given. By plotting t_c *versus* potassium bromide concentration three curves are derived (Figure 4). Curve 3 presents precipitation processes without T-X-305, while curves 1 and 2 present precipitation processes in the presence of two different concentrations of T-X-305, respectively. The curves consist of several straight lines, which characterize various precipitation processes. Curve 3 (without T-X-305) has several discontinuities. A straight line below c.c.c. shows slower aggregation processes towards the stable region, where T-X-305 shows stabilization action only. t_c become lower as KBr concentrations become higher. The straight line about c.c.c. shows coagulation processes. t_c reach each minimum value in the middle of the 'concentration maximum' and rise again to the complex solubility, as crystallization processes take place. Curve 1 is composed of three straight lines, one of them representing aggregation (in the concentration range from 2.5×10^{-2} to 1.0×10^{-1} mol dm^{-3} of KBr), the second one mixed, and the third one crystallization processes. Curve 2 gives a better distinction between the aggregation processes; slower aggregation below the c.c.c. and faster coagulation processes above the c.c.c., where T-X-305 also shows a flocculation action. The c.s.c. of T-X-305 *versus* the concentrations of potassium bromide (Figure 6) show another way to determine different precipitation processes in the region of the 'concentration maximum' and are found to be between 6.0×10^{-5} and 1.0×10^{-5} mol dm^{-3} for the aggregation processes, while they rise rapidly from the concentration of 1.5×10^{-1} to 2.5×10^{-1} mol dm^{-3} of KBr and reach the value of 8.0×10^{-3} mol dm^{-3}. The rapid rise of c.s.c. takes place in the region of mixed processes, while the stabilization action of T-X-305 disappeares. In this region crystallization processes were supposed. By means of the analysis of t_c and c.s.c. the growth processes of secondary structures can be differentiated from primary particles in the region of the 'concentration maximum' according to Težak's five subsystems of precipitation[13]. Crystal growth takes place from the dominant complex species ($AgBr_3^{2-}$ as computed graphically[14]).

The temperature change effects supply additonal data about the crystallization processes near the complex solubility limit. A change in the temperature of sols from 293 K to 363 K causes the solubility of the precipitate of a part of the 'concentration maximum'. The shift of the complex solubility limit is found to be to the concentration of 2.5×10^{-1} mol dm^{-3} of KBr. A partly soluble precipitate was found in the 2.5×10^{-1} to 1.5×10^{-1} mol dm^{-3} range. From the latter concentration towards the lower concentrations of KBr rapid aggregation takes place at higher temperatures. By cooling the systems from 363 K to 293 K and by using light microscope, two different shapes of crystals (quite often monodisperse), that had been grown from complex species, were obserwed.

CONCLUSION

Previous studies of Težak and coworkers indicated that the 'concentration maximum' of AgBr precipitate is formed on the complex solubility limit and that it is characterized by fast aggregation processes of the primary structures by the influence of the coagulation action of potassium ion.

In this paper the kinetics of precipitation of AgBr sols in the region of the 'concentration maximum' was examined. It was found that in addition to the coagulation processes crystal growth and the aggregation of small crystallites occured in this region. By the analysis of t_c for sols in the presence and absence of T-X-305 and by the analysis of c. s. c. the regions of aggregation, crystallization and mixed processes were determined. The possibility of the characterization of latter processes was also suggested by the fact that the solubility of AgBr precipitate at 363 K could be achived near the complex solubility limit where crystallization processes had been supposed. In the region of mixed processes partial solubility was found, while in the region of coagulation (near the c. c. c. of K^+-ion) higher temperature caused faster aggregation. By cooling, from the complex solution crystals were formed, while at lower concentrations of KBr only aggregations of distinct primary particles were obtained.

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SAŽETAK

Karakterizacija precipitacionih procesa negativno nabijenog AgBr precipitata pomoću neionskog SAA i promjene temperature

V. Hrust i B. Težak

Praćena je kinetika precipitacije *in statu nascendi* solova u blizini granice kompleksne topljivosti negativno nabijenog precipitata srebro-bromida.

Analizom kritičnih vremena precipitacije utvrđena je pojava različitih procesa rasta, koji se mogu karakterizirati s pomoću neionskog SAA T-X-305 i promjene temperature.

Rezultati ukazuju na dva procesa rasta sekundarnih struktura, ovisno o koncentraciji KBr u suvišku: agregacijski procesi pri nižim i kristalizacijski pri višim koncentracijama kalij-bromida uz samu granicu kompleksne topljivosti.

ODJEL FIZIČKE KEMIJE
INSTITUT ZA KEMIJU
SVEUČILIŠTE U ZAGREBU
41000 ZAGREB

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