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Methorics of the Precipitation Processes. XXIV. Flocculation Phenomena of Non-Ionic Surface-Active Agents on Silver Iodide Sols

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An explanation concerning the flocculation and stabilization action of non-ionic surface-active agents (NSAA) T-X-305 and T-X-705 on the negatively and positively charged silver iodide stable sols was attempted by means of tyndallometric and microscopic investigations.

The flocculation phenomena were found to occur in the concentrational region of 10^{-7} to 10^{-4} mol dm^{-3} of triton. The influence of temperature, time, and sol concentration on the kinetics of the formation of colloid particles was also examined. The mechanism of flocculation processes was suggested by assuming that the flocculation and stabilization of AgI colloid in the presence of NSAA is a heterogeneous precipitation characterized by the critical concentrational and temporal parameters.

INTRODUCTION

The interaction of ionic and non-ionic surface-active agents, polyelectrolytes, polymers etc, and silver halides, silica, hydroxides and other colloids has been already investigated by a number of authors[1–16].

The investigations presented in this paper were performed in the systems $AgNO_3$ — NaI (KI) — T-X-305 (T-X-705) in order to distinguish the role of coulombic forces from stereospecific adsorption (which is responsible for flocculation processes). The problem of flocculation is discussed according to the concepts of B. Težak[17–19] and V. K. La Mer[20,21].

B. Težak distinguished the coagulation from flocculation as the phenomena caused by different chemical and physical forces:

— the coagulation by electrolytes as a coulombic interactions and ion-pair formation within the methoric layer;

— the flocculation by dyes, macromolecules, polymers, polyelectrolytes, and generally by surface-active agents as a stereospecific interaction.

EXPERIMENTAL

The systems were prepared by the technique »in statu nascendi«[22]. Turbidity measurements were performed on the Zeiss tyndallometer in connection with Pulfrich photometer. Particle size determination was made from calibration curve applying

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Co. No. 223 from the Laboratory of Physical Chemistry.

DQ_T-method[23], by counting particles in the field of the light microscope, and from electron micrographs. The micrographs were made on the Zeiss ultramicroscope Philips EM 300.

Materials. — All the materials used in the experiments were analytically pure: silver nitrate and sodium (or potassium) iodide — from Merck, Darmstadt, standardized potentiometrically; tritons from octylphenoxyethanol series ($C_8H_{17}-C_6H_4-(OCH_2CH_2)_n$; for T-X-305 n = 30, for T-X-705 n = 70) were given by courtesy of Rohm and Haas Co, Philadelphia. In all the experiments the bidistilled water was used.

RESULTS AND DISCUSSION

The concentrational and temporal dependence of the occurence and growth of solid phase from aqueous solutions in a system of $AgNO_3$, NaI or KI (with

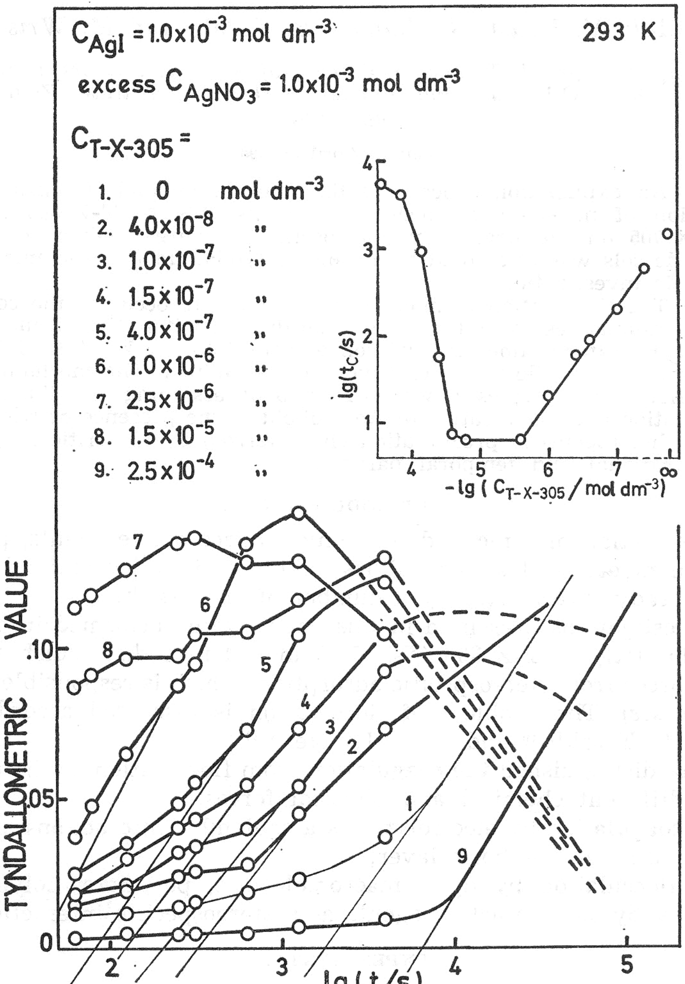


Figure 1. Time tyndallograms of $AgNO_3$ — KI — T-X-305 precipitation system.

Critical times of precipitation (t_c) denoted by drawing the tangent to the steepest part of »tyndallometric value — time curves«, and plotted as a function of T-X-305 concentration (small picture).

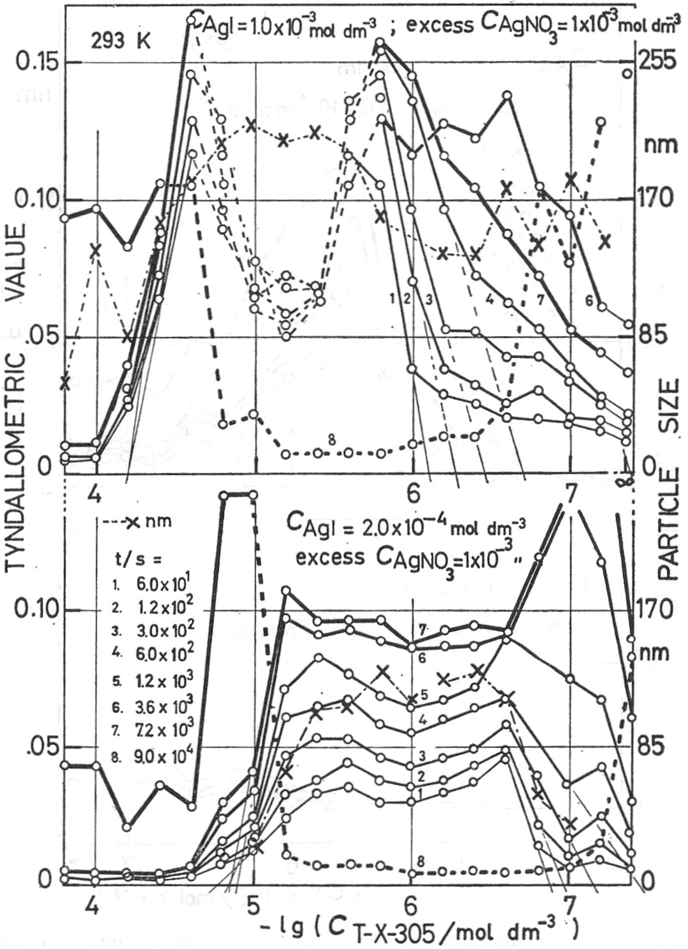


Figure 2. Concentration tyndallograms for two different concentrations of positively charged AgI sol. Particle sizes calculated by DQ_T method. Temperature 293 K.

the excess of either AgNO$_3$ or NaI) in the presence of non-ionic surface-active agents (NSAA) T-X-305 or T-X-705, was investigated at 293, 313 and 333 K. The NSAA was chosen in order to avoid the influence of electrostatic forces. The precipitation of AgI in the presence of NSAA was investigated as a function of time after mixing the precipitation components (1, 2, 4, 5, 10, 20, 60 and 1500 minutes), of temperature, of the sol concentration, and of the excess of constitutive ions Ag$^+$ or I$^-$. The results characterising the rate of particle growth are presented on the time diagram (Figure 1.) by plotting the tyndallometric values for systems of AgI in the presence of and without NSAA as a function of time.

The critical times of precipitation (t_c) were obtained by drawing the tangent to the time-curves. The decrease of the critical times of precipitation of the AgI colloid systems was caused by the addition of low concentrations of T-X-305. It has been observed that unstability grows towards the concen-

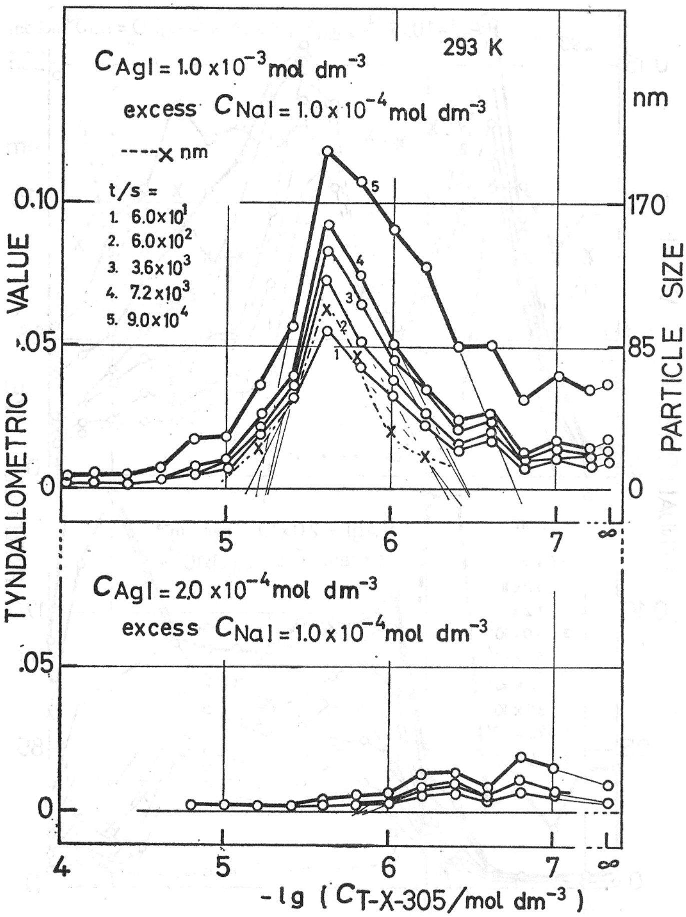


Figure 3. Concentration tyndallograms for two different concentrations of negatively charged AgI sol. Particle sizes calculated by DQ_T method.

tration 2.5 × 10^{-6} mol dm^{-3} T-X-305, and then with further addition of triton t_c increase, which corresponds to the stabilization of colloid system.

The flocculation maximum is characterized by the smallest t_c (small picture in Figure 1), by the greatest rate of flocculation, and it is limited by the critical concentration of flocculation *(c.f.c.)* and the critical concentration of stabilization *(c.s.c.)*.

The precipitation phenomena in the region of flocculation maximum correspond to the refiltration rates of colloidal dispersions flocculated by polyelectrolytes or polymers obtained by La Mer and coworkers[20], who found that the form of all refiltration curves is governed by the maximum value for the refiltration rate or the minimum value of filtration time. That means that the flocculation turbidity maximum is characterized by minimum in critical times of precipitation.

The critical values of *c.f.c.* and *c.s.c.* were determined by drawing the tangent to the turbidity — concentration curves. The crossections of the tangent

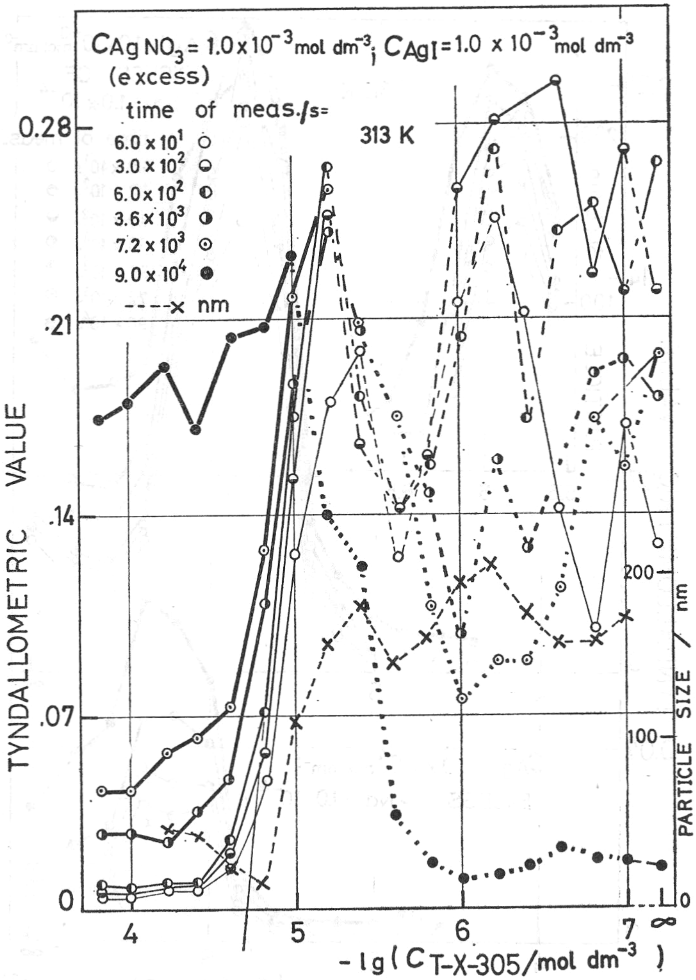


Figure 4. Concentration tyndallograms for positively charged AgI sol. Particle sizes calculated by DQ_T method. Temperature 313 K.

and abscissa presented in Figures 2, 3, 4, 5 show that the *c.s.c.* are very constant in the times of measuring 1 minute to 1 hour, and even 1 day after mixing the precipitation components.

In Figure 2 the turbidity measurements are presented in the system of AgI 10^{-3} and 2×10^{-4} mol dm^{-3} and the excess of $AgNO_3$ 10^{-3} mol dm^{-3} at 293 K. The analogous precipitation phenomena are shown in Figure 3 for AgI colloid negativelly charged, since the excess of NaI is 10^{-4} mol dm^{-3}. The *c.f.c.* and *c.s.c.* are tabulated in Table I.

Particle sizes calculated by DQ_T method give the average size value of polydispersed aggregates. It is obvious that the average particle size corresponds to the phenomena in the flocculation and stabilization region, being greater for AgI 10^{-3} mol dm^{-3} than for the smaller sol concentrations. Generally,

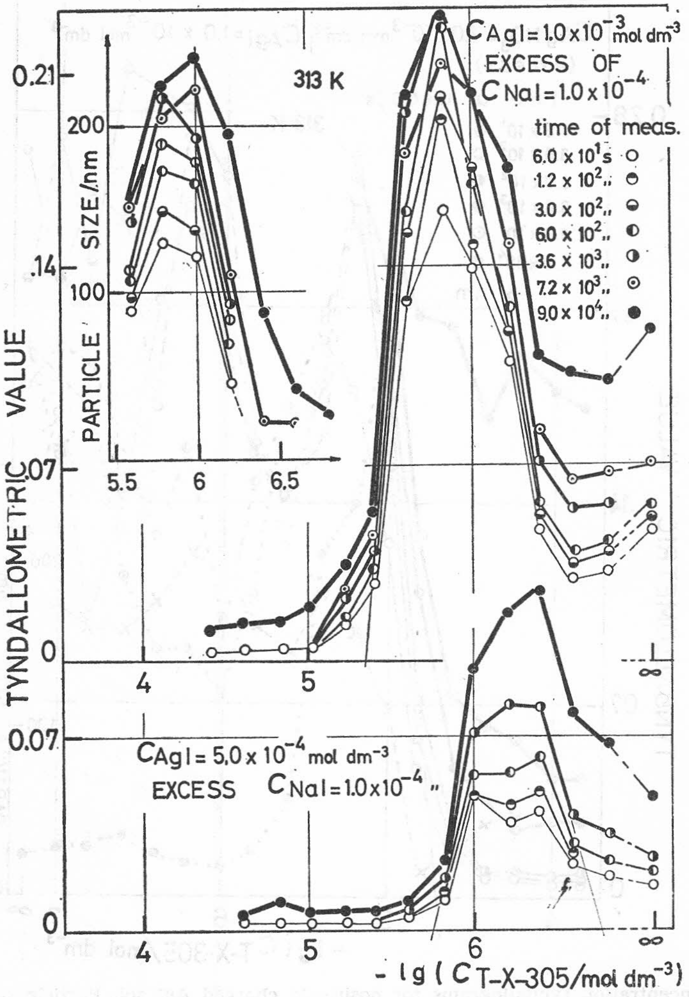


Figure 5. Concentration tyndallograms and particle size determination by DQ_T method for negatively charged AgI sol at 313 K.

TABLE I

sol	c_{sol}/(mol dm^{-3})	c.f.c./(mol dm^{-3})	c.s.c./(mol dm^{-3})
AgI/Ag^+	10^{-3}	5×10^{-7}	6×10^{-5}
AgI/Ag^+	2×10^{-3}	10^{-7}	10^{-5}
AgI/I^-	10^{-3}	3×10^{-7}	6×10^{-6}
AgI/I^-	2×10^{-4}	2×10^{-7}	10^{-6}

the flocculation phenomena are greater for the positively charged sol with the particle size maximum value at about 200 nm, than for the negatively charged sol with the particle size maximum value at about 100 nm.

Raising the temperature to 313 K (Figures 4, 5) results in the shift of *c.f.c.* and *c.s.c.* towards smaller concentrations of T-X-305; the rate of flocculation as well as the particle size are increased.

The small diagram in Figure 5 presents the temporal dependence of particle sizes in the region of flocculation maximum where the particle sizes show the maximum value of 120 nm in 1 minute, and 240 nm 1 day after mixing the precipitation components.

In Figure 6 the temperature influence on the different sol concentrations is shown. The flocculation and stabilization limits are shifted towards smaller concentrations of T-X-305, if the temperature is higher and the sol concentration smaller. The shift in the critical concentrations of triton is expressed in the stabilization region.

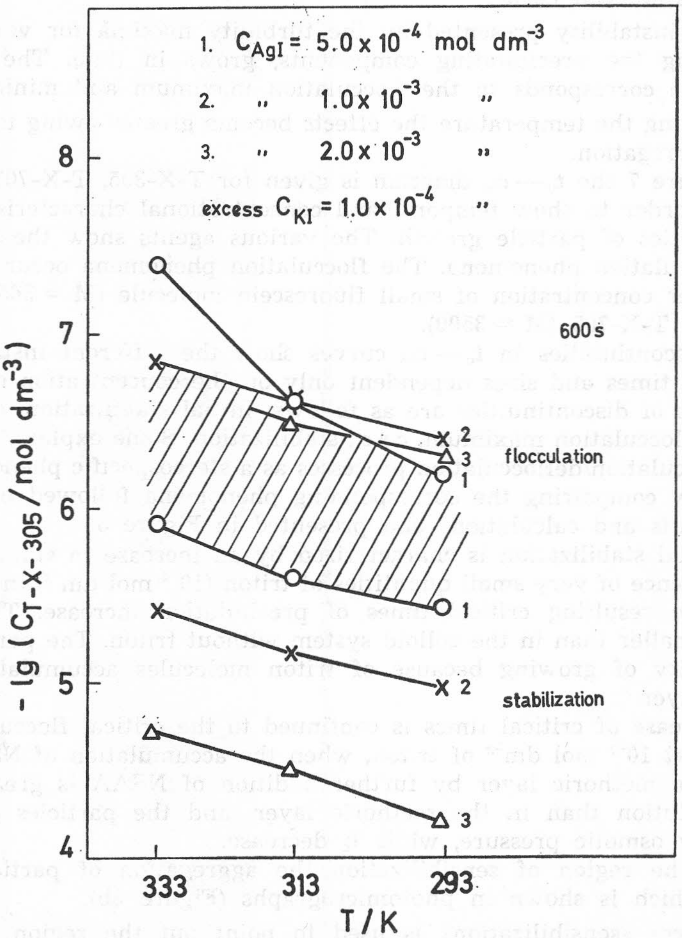


Figure 6. Critical flocculation and stabilization values versus temperature for different concentrations of negatively charged AgI sol.

From the data presented several characteristics of the action of NSAA T-X-305 are shown:

1. Flocculation effects are greater for positively than for negatively charged AgI colloid, because the positively charged AgI is less stable than the negatively. The kinetics of growth is a genotypic factor playing role in the embryonation and micelle formation of AgI colloid and it is quite different in excess of Ag^+ or I^- ions, so that the growth of AgI in the presence of NSAA must also be in connection with the kinetics phenomena in the system without NSAA.

2. Flocculation phenomena are very much dependent on the sol concentration, they are better expressed for AgI 10^{-3} than for 2×10^{-4} mol dm^{-3}. If the concentration of colloid is smaller, the smaller is the concentration of NSAA needed for flocculation and stabilization interaction, so that the characterization of flocculation process may be assumed as a stereospecific adsorption, where the certain critical mass of sol-adsorbent has to be available in order the flocculation can occur.

3. The instability presented by the turbidity maxima for various times after mixing the precipitating components, grows in time. The maximum particle size corresponds to the flocculation maximum and minimum in t_c.

By raising the temperature the effects become greater owing to the faster particle aggregation.

In Figure 7 the $t_c — c_{in}$ diagram is given for T-X-305, T-X-705 and fluorescein in order to show temporal and concentrational characteristic regions of the kinetics of particle growth. The various agents show the similarities in the flocculation phenomena. The flocculation phenomena occur in the ten times higher concentration of small fluorescein molecule ($M = 365$), than for T-X-305 or T-X-705 ($M = 3500$).

The discontinuities in $t_c — c_{in}$ curves show the different instability and varieties of times and sizes dependent only on the concentration of T-X-705. The regions of discontinuities are as follows: initial stabilization, *c.f.c.*, sensibilization, flocculation maximum, *c.s.c.*, stabilization. Some explanation of each step in flocculation/deflocculation processes as a stereospecific phenomena may be given by compairing the corresponding phenomena followed by different measurements and calculations and presented in Figure 8:

— Initial stabilization is characterized by an increase in stability caused by the presence of very small quantities of triton (10^{-8} mol dm^{-3}) in the colloid system. The resulting critical times of precipitation increase. The particle sizes are smaller than in the colloid system without triton. The particles have no possibility of growing because of triton molecules accumulation in the methoric layer.

— Increase of critical times is continued to the critical flocculation concentration at 10^{-7} mol dm^{-3} of triton, when the accumulation of NSAA molecules in the methoric layer by further addition of NSAA is greater in the bulk of solution than in the methoric layer, and the particles are driven together by osmotic pressure, while t_c decrease.

— In the region of sensibilization the aggregation of particles is the greatest, which is shown in photomicrographs (Figure 8b).

The term »sensibilization« is used to point out the region where the NSAA caused the greatest degree of aggregation of hydrophobic colloid, and

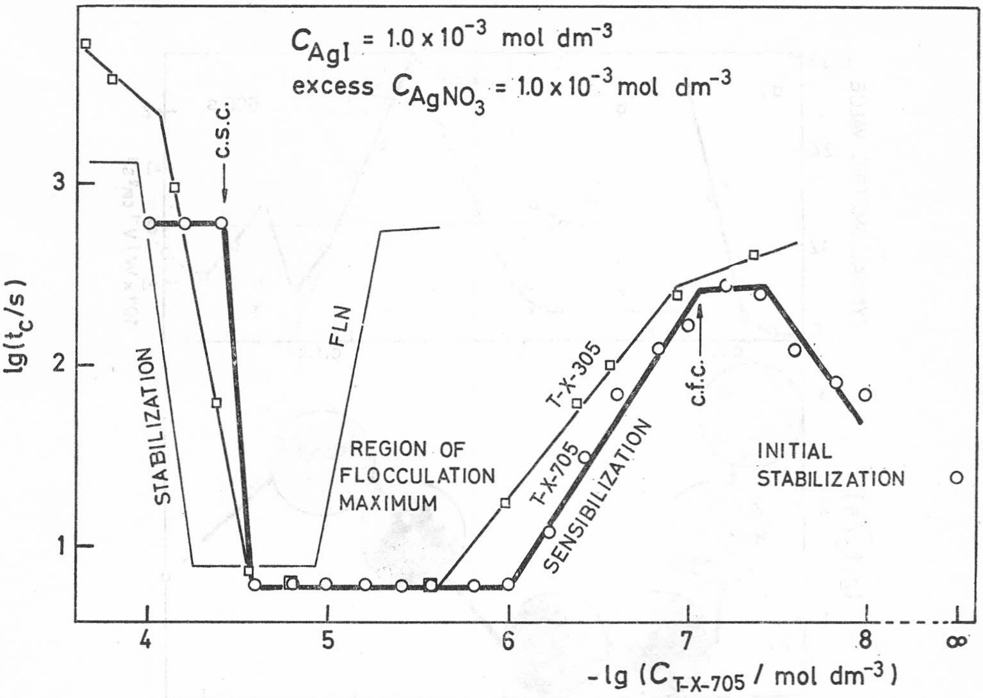


Figure 7. Critical times of precipitation plotted versus concentration of T-X-705, T-X-305 or sodium fluoresceinate.

to distinguish the concentrational difference between the region of increasing flocculation processes from initial stabilization in the smaller concentrations, and the region of flocculation maximum in higher concentrations of NSAA. It is the concentrational region between the greatest (*c.f.c.*) and the smallest (flocculation maximum) critical times of precipitation.

— In the region of flocculation maximum the photomicrographs show the loosely packed aggregation structure, because the rate of aggregation is the highest. At the same time the NSAA molecules are penetrating within the methoric layer, making the structure of aggregates very porose, and by further addition of NSAA, the concentration of NSAA is greater in the methoric layer than in the bulk of solution, so that the colloid particles coated by NSAA are disaggregated, i. e. the stabilization effect of NSAA takes place.

The aggregation/disaggregation stages during the flocculation/stabilization process are shown in light (Figure 8b) and electron micrographs (Figures 9 and 10).

The photomicrographs in Figure 8b show that the size of primary aggregates (p.a.) is almost the same along the whole flocculation and stabilization region and that the primary aggregates are aggregated to the secondary aggregates (s.a.) within the flocculation maximum. The sizes of primary aggregates were calculated from electron photomicrographs and by DQ_T method

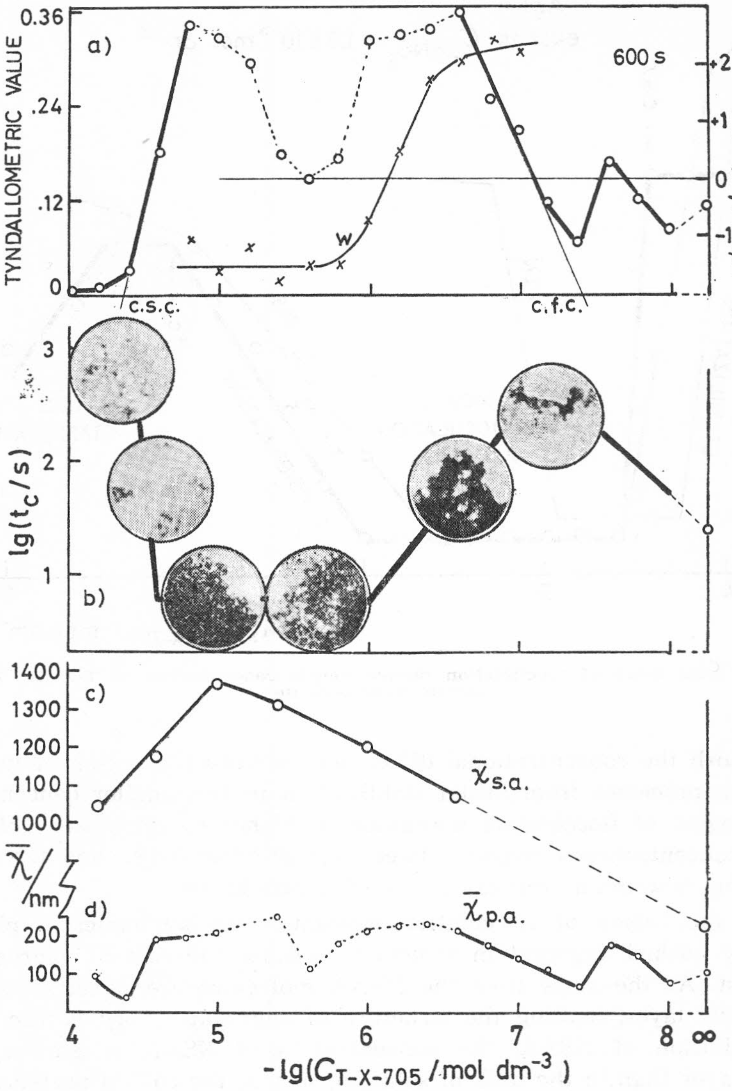


Figure 8. Presentation of the precipitation processes in the flocculation maximum of positively charged AgI sol ($c_{AgI} = 1.0 \times 10^{-3}$ mol dm^{-3}, excess $c_{AgNO_3} = 1.0 \times 10^{-3}$ mol dm^{-3}):

a) by measuring tyndallometric values and electrophoretic mobility (ultramicroscopic electrophoresis);

b) by determination of critical times and presenting the aggregation processes in sensibilization, flocculation and stabilization region by light micrographs (total magnification 480 x), and by plotting the particle sizes versus concentration of T-X-705;

c) the sizes of secondary aggregates by counting particles in the field of light microscope, and

d) the sizes of primary aggregates calculated by DQ_T method describe the maximum corresponding to the tyndallometric maximum and t_c minimum.

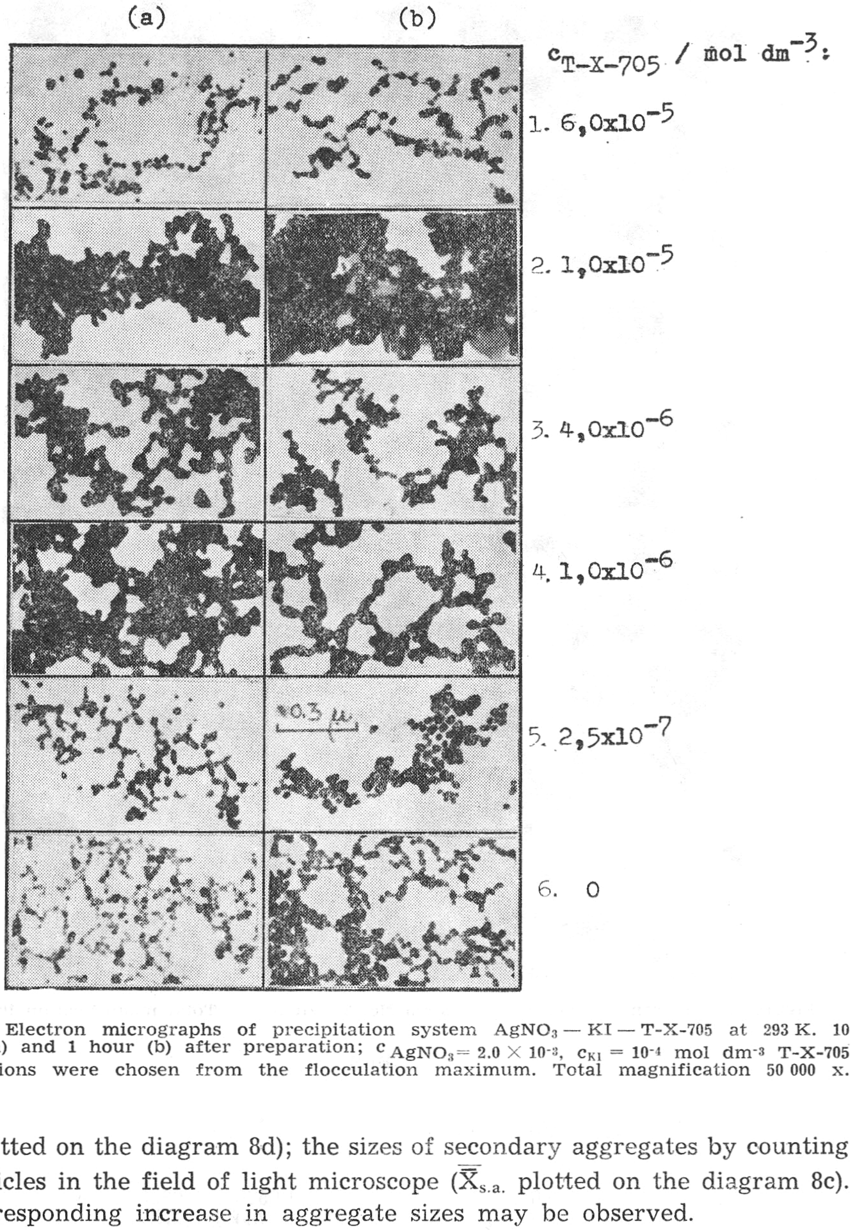


Figure 9. Electron micrographs of precipitation system $AgNO_3$ — KI — T-X-705 at 293 K. 10 minutes (a) and 1 hour (b) after preparation; $c_{AgNO_3} = 2.0 \times 10^{-3}$, $c_{KI} = 10^{-4}$ mol dm^{-3} T-X-705 concentrations were chosen from the flocculation maximum. Total magnification 50 000 x.

($\overline{X}_{p.a.}$ plotted on the diagram 8d); the sizes of secondary aggregates by counting the particles in the field of light microscope ($\overline{\overline{X}}_{s.a.}$ plotted on the diagram 8c). The corresponding increase in aggregate sizes may be observed.

The results of counting particles in the field of light microscope are shown in Table II (results graphically presented in Figure 8c):

The samples for electron microscope were taken in the characteristic flocculation and stabilization region (Figure 9, total magnification 50 000 x) and in the flocculation maximum in detail (Figure 10, total magnification 100 000 x). It is shown that the particles in the whole region of flocculation

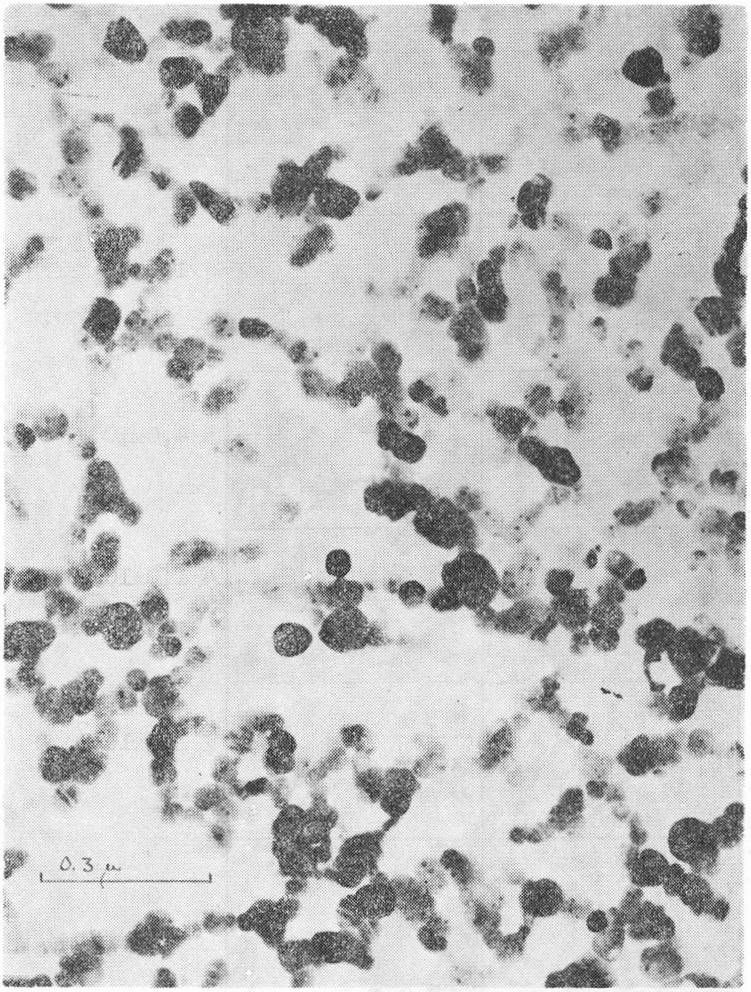


Figure 10. Electron micrograph of system No. 3, (Figure 9). Total magnification 100 000 x.

TABLE II

$c_{\text{T-X-705}}$/(mol dm^{-3})	$\bar{X}_{\text{s.a.}}$/ ± C
6.0×10^{-5}	1.0520 ± 0.0326
2.5×10^{-5}	1.1780 ± 0.0257
1.0×10^{-5}	1.3760 ± 0.0283
4.0×10^{-6}	1.3157 ± 0.0281
1.0×10^{-6}	1.1957 ± 0.0239
2.5×10^{-7}	1.0367 ± 0.0101
∅	0.7260 ± 0.0248

n = 50 countings
$\bar{X}$ = mean particle size
C = unreliability of measurements

maximum have got almost the same average size, only they are more or less aggregated. Generally it may be concluded that the processes of precipitation from solutions, i. e. sensibilization, flocculation, stabilization can be considered as a series of aggregation stages characterized by the definite size of particles. The flocculation process may be schematically presented in stages as it is tabulated in Table III.

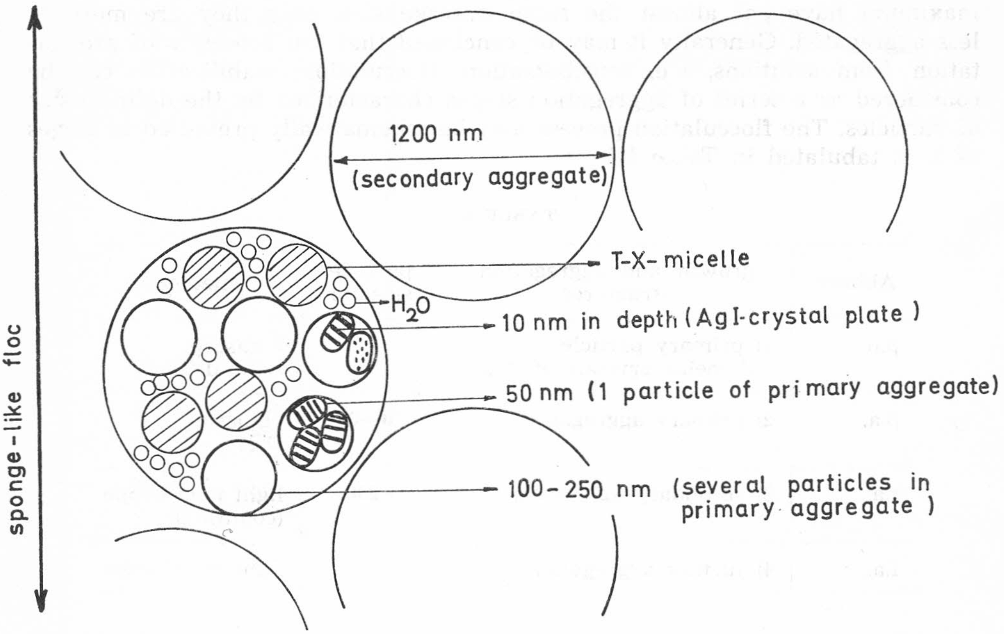
TABLE III

Abbrev.	growth and aggregation structures	particle size/nm	method
p.p.	1) primary particles (lamelar crystals of AgI)		elmiscop Laue diffr.
p.a.	2) primary aggregates	20—80	elmiscop DQ_T
s.a.	3) secondary aggregates	1 200	light microscope (counting)
f.a.	4) further aggregation		light microscope

All the growth and aggregation steps show the tendency of forming monodispersed particles in the presence of triton. The particles in aggregates with triton are somewhat larger than in the AgI colloid without triton. The electron micrographs in Figure 9, where the systems without and with triton taken from the flocculation maximum are presented, show that the primary particles go through the stages of aggregation and are of the similar size in all the systems with triton 10 minutes and 1 hour after mixing the precipitation components, while the size of flocs varies. The sizes of primary aggregates analyzed by DQ_T method have got the average values in the region of flocculation maximum 20—80 nm. The accordance of these results with the electron microscope observations (see Figure 10) is quite satisfactory. The sizes of big sponge-like secondary aggregates correspond to the maximum in the flocculation curve but the size of primary particles and aggregates remain almost the same in the flocculation maximum.

The electron micrograph (Figure 10) shows the lamelar orientation of the monocrystals of AgI primary particles coated by NSAA. The crystals show the reflection of light under the Bragg conditions as well as the Laue diffraction, but do not show that the crystals may grow together in the presence of T-X-705. The crystals are ordered in ellyptically shaped primary aggregates (20—80 nm) like a net of micelles of triton in which the AgI crystals are lamelarly structured without a possibility of further crystal growth or closer approach of crystal plates as it is possible in AgI colloid without triton.

Further aggregation towards the secondary aggregates (1 200 nm) leeds to the further steps of aggregation in the sponge-like flocs. Consecutive aggregation in the flocculation maximum as it may be concluded from Figure 10 can be presented as in Scheme.



Scheme: CONSECUTIVE AGGREGATION IN FLOCCULATION MAXIMUM

The qualitative characteristics of AgI in the presence and without NSAA were observed by centrifugation. The system flocculated by triton and centrifuged for 2 hours (30 000 r.p.m.) showed the very smooth loosely packed light flocs, since the centrifugation of AgI colloid without triton gave the AgI oil drop on the bottom of the test-tube.

CONCLUSION

The processes of precipitation of AgI colloid in the presence of or without NSAA are faster by raising the temperature and the sol concentration, causing the increase of particle sizes. The flocculation process is explained as a stereospecific adsorption interaction of NSAA with colloid, in which the primary particles of AgI showing the crystalline structure, become coated with NSAA molecules and micelles and form the aggregates of definite size during the stabilization and flocculation processes. The maximum aggregation degree is observed in the region of sensibilization and in the flocculation maximum. The particles are disaggregated during the stabilization process.

The mechanism of sensibilization, flocculation and stabilization may be explained by aggregation and disaggregation of primary particles coated by NSAA, according to Težak's mechanism for coagulation and peptization of colloid particles published many years ago[24]. The point is in tendency of equilizing of osmotic pressures and the diffusion of NSAA between the bulk of solution and the methoric layer of colloid particles. When the concentration of NSAA is greater in the bulk of solution than in the methoric layer, the colloid particles are driven together and flocculate. In the case of smaller concentration of NSAA in the bulk of solution than in the methoric layer, the particles begin to deflocculate and we observe the stabilization. The size of primary particles is always almost the same regardless of the different concentration of NSAA, since the size of aggregates differs showing the turbidity maximum in the flocculation region and the corresponding minimum in critical times of precipitation, concluding that these effects are due to the aggregation of primary particles coated with triton molecules.

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SAŽETAK

Metorika precipitacijskih procesa. XXIV. Flokulacijske pojave neionskih površinsko-aktivnih agensa na argentum-jodid solovima

Đ. Težak, V. Hrust, S. Heimer, B. Težak i M. Wrischer

Prikazano je objašnjenje flokulacijskog i stabilizacijskog djelovanja neionskih površinski aktivnih agensa, tritona T-X-305 i T-X-705, na negativno i pozitivno nabijene solove srebro-jodida s pomoću tindalometrijskih i mikroskopskih mjerenja na 293, 313 i 333 K.

Nađene su flokulacijske pojave u području 10^{-8} do 10^{-4} mol dm^{-3} tritona. Ispitivan je utjecaj koncentracije sola, vremena mjerenja i temperature na kinetiku formiranja koloidnih čestica.

Predložen je mehanizam flokulacijskih procesa, uz pretpostavku da je flokulacija i stabilizacija AgI koloida u nazočnosti površinski aktivnih agensa uzrokovana agregacijama ili dezagregacijama primarnih čestica određenih veličina, a te su veličine karakterizirane kritičnim koncentracijskim i vremenskim parametrima.

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