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Original Scientific Paper

Methorics of the Precipitation Processes. XXV. Effects of Non-Ionic Surface-Active Agents on Growth and Aggregation of Silver Iodide Sols

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Precipitation kinetics and adsorption behaviour in AgI colloid systems prepared 'in statu nascendi' in the presence of non-ionic surface-active agents of octaphenylethoxylate series were investigated by light scattering method at 20 °C. The rate of precipitation was followed directly by using light scattering photometer with recorder. The adsorption isotherms exhibiting monolayer coverage in the region of maximum flocculation and multilayer adsorption in the stabilization region have been obtained. The mechanism of flocculation and stabilization can be assumed considering several aggregation steps in the dependence of concentration and time.

INTRODUCTION

The effects of concentration and time on the new phase formation and stability of hydrophobic colloids in the presence of non-ionic surface-active agents (NSAA) have been investigated using a light scattering method. This method was chosen as the most sensitive method for following the kinetic features and therefore giving an experimental basis for precipitation kinetics.

Numerous investigations have been performed on the colloid stability caused by the presence of NSAA or ionic detergents[1-8], but the theoretical interpretation of the results achieved in systems prepared by the 'in statu nascendi' method is difficult since both the size and the form of particles change in time and show polydispersity. Steric stabilization caused by polymeric additives has been investigated by many authors.[9-11] Bridging in colloid flocculation by polymers was proposed[12] and accepted as a possible mechanism of interaction[13,14]. In general, steric stabilization was investigated in the 'preformed' colloid systems.[15] Investigating the precipitation kinetics of silver iodide sols by PVA Fleer and Lyklema[16] pointed to the importance of the mixing procedure of sol and polymer. Adsorption isotherms were found to follow the

Langmuir plot at low concentrations of polymers.[17] The monolayer saturation of the surfaces has been obtained for various kinds of polymers.[18,19] The investigations described in this paper were carried out on "non-ideal" polydispersed AgI colloid so to enable comparison with the investigations performed on "ideal" polystirene latex.[20]

As shown in a previous paper,[21] temperature and concentrations of the reacting components influence the processes of flocculation and stabilization of AgI colloid in the presence of NSAA. The aim of the studies presented in this paper was to characterize the early stages of the colloid destabilization and aggregation in the presence of NSAA of different chain lengths. The change in the intensity of scattered light at a fixed angle of observation was the main method of examination. The aggregation phenomena were followed at a scattering angle of 45°, from which the rates of precipitation had been obtained.

EXPERIMENTAL

Materials

The chemicals used (AnalaR grade) were dissolved in twice-distilled water: octaphenylethoxylates (Tritons: $C_8H_{17} — OC_6H_4 — (OCH_2CH_2)_x OH$; $x = 10, 20, 30, 40, 70$) were obtained by courtesy of the Room and Haas Co. and used without further purification; $AgNO_3$ and KI or NaI (»analytically pure« from Merck, Darmstadt) were standardized potentiometrically and by Fajans' method[22]. The relative molecular masses of the Tritons were calculated on the basis of the given empirical formulae.

Precipitation systems of $AgNO_3$ — KI (or NaI) — NSAA were prepared at 293 K by the 'in statu nascendi' method and by the addition of NSAA to the performed AgI colloid. Samples of preformed sols were prepared by mixing the required concentrations of $AgNO_3$ and KI in the usual manner for 15 seconds and then by mixing the resulting colloid with solution of Triton.

Methods

The turbidity was continually recorded (from 30 seconds after mixing all the reacting components to 1 hour) by making conventional light scattering measurements using a Virtis Brice Phoenix photometer, model DU 2000. The initial intensity of the scattered light ($I_{45} = I_r$ at a scattering angle of 45°) was plotted versus the logarithm of time, *t*. Discontinuities in these kinetic curves were observed; in between these discontinuities the plots were linear. The mean time of each process, indicating the change in the rate of precipitation, was determined from these kinetic curves (shown later in Figures 3. and 4.).

The concentrations of Tritons in the adsorption experiments were determined polarographically using the polarograph METROHM type E 506 with the hanging mercury drop electrode to measure the capacities of the electrical double layer. The method has been described in detail elsewhere[23]. Before the polarographic determination the colloid was separated from supernatant by centrifugation on the Beckman ultracentrifuge at 2600 G during 20 minutes.

RESULTS AND DISCUSSION

Previously[21], in the systems of $AgNO_3$ — KI or NaI, in the presence of Tritons, both flocculation and stabilization phenomena were found. Flocculation region is limited by the critical flocculation concentration (c.f.c.) and the critical stabilization concentration (c.s.c.). It has been shown that flocculation and stabilization processes can be treated as aggregation or disaggregation of primary particles. Earlier,[24] the kinetic effects were followed by means of a

Zeiss tyndallometer, offering no possibility for continuous monitoring. This time, some kinetic measurements were made using a universal light scattering photometer with recorder. Thus it was possible to follow most directly the processes of formation of the solid phase from the homogeneous solution. Observing the kinetics of particle growth for preformed and 'in statu nascendi' sols of AgI in the presence of Triton (Figures 1. and 2.), it is possible

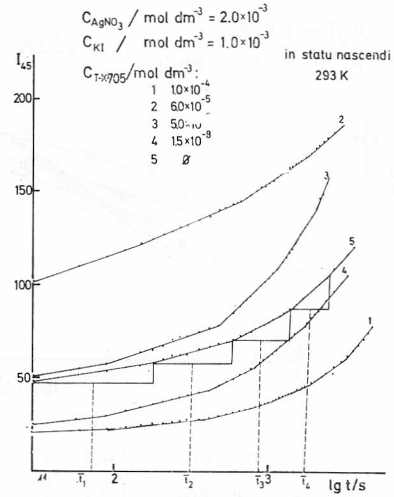


Figure 1. Light scattering — time diagram presenting the kinetics of AgI precipitation in the presence of T-X-705 for 'in statu nascendi' sols.

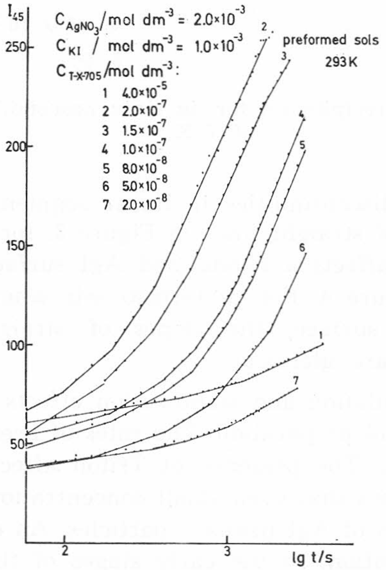
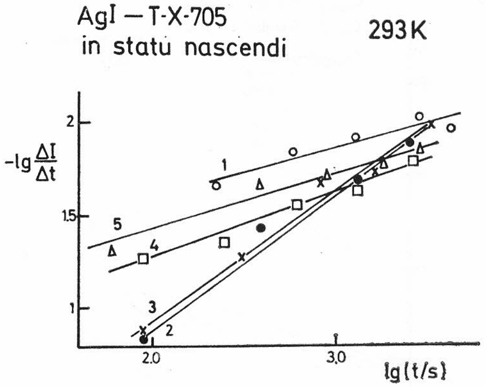


Figure 2. Light scattering — time diagram presenting the kinetics of AgI precipitation in the presence of T-X-705 for preformed sols.

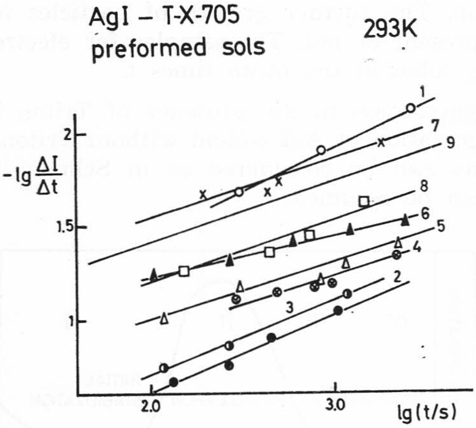
to consider $\Delta I/\Delta t$ as corresponding to the rate of precipitation. Typical kinetic curves were obtained by plotting $\Delta I/\Delta t$ versus time (Figures 3. and 4.) exhibiting hyperbolic plot, or linear plot if $\lg(\Delta I/\Delta t)$ is plotted versus $\lg t$. In these calculations the rate of precipitation $\Delta I/\Delta t$ was obtained, as shown in Figure 1., determining also the average time (t) for each aggregation step. It is obvious that the kind (size and/or number) of particles had been changed and, as a result, the discontinuities in linear segments of time curves were exhibited. The slopes of straight lines in Figure 3. for 'in statu nascendi' sols differ because Triton affects a nondefined AgI surface; the opposite case is presented in small Figure 4. For preformed sols when Triton influences the already defined AgI surface, the slopes of straight lines for different Triton concentrations are identical.



C_{AgNO_3}/mol dm^{-3} = 2.0 × 10^{-3}
C_{KI}/mol dm^{-3} = 1.0 × 10^{-3}
$C_{T\text{-}X\text{-}705}$/mol dm^{-3} = 1. 1.0 × 10^{-4}
2. 6.0 × 10^{-5}
3. 6.0 × 10^{-8}
4. 1.5 × 10^{-8}
5. ∅

Figure 3. The rates of precipitation for 'in statu nascendi' AgI sol in the presence of T-X-705.

Sensitization, flocculation and stabilization effects were exhibited regardless of the manner of sol preparation. The rates of precipitation show that the processes are very fast. The presence of Triton affects the sizes of primary particles. Figure 5. shows that even small concentrations of Triton affect both the size and the growth of AgI primary particles. An electron microscope was used for size determination. In the early stages of the precipitation process, the time dependence of the primary particles growth was shown even at small detergent concentrations. Primary particles exhibited smaller sizes than



C_{AgNO_3} /mol dm^{-3} = 2.0 × 10^{-3}
C_{KI}/mol dm^{-3} = 1.0 × 10^{-3}
$C_{T-X-705}$/mol dm^{-3} = 1. 4.0 × 10^{-5}
2. 2.0 × 10^{-7}
3. 1.5 × 10^{-7}
4. 1.0 × 10^{-7}
5. 8.0 × 10^{-8}
6. 5.0 × 10^{-8}
7. 2.0 × 10^{-8}
8. 1.5 × 10^{-8}
9. ∅

Figure 4. The rates of precipitation for preformed AgI sol and T-X-705 added.

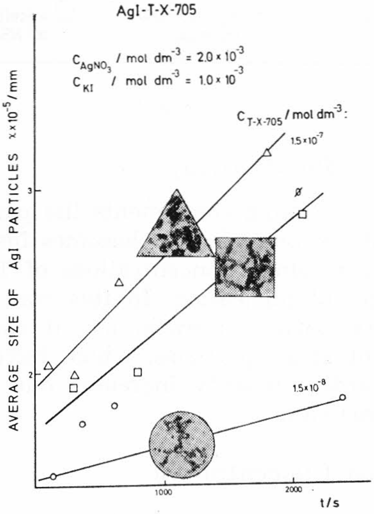
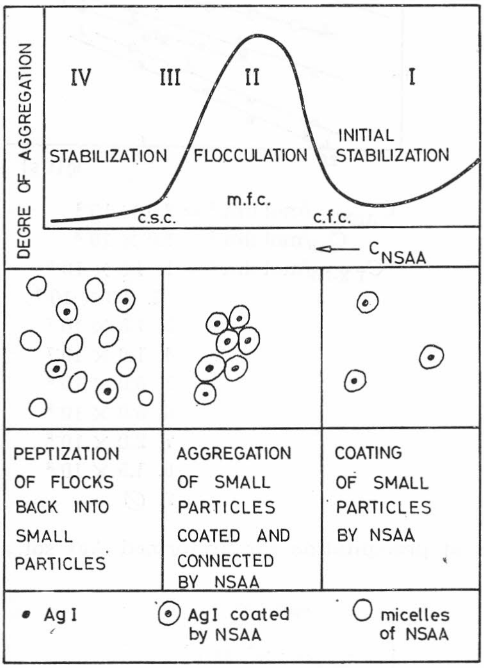


Figure 5. The average size of AgI particles (in the systems prepared 'in statu nascendi' in the presence of T-X-705) versus time. Total magnification in electron micrographs 83 200x.

those without Triton. The further growth of particles is linearly increased whether Triton is present or not. The samples for electron microscopy were taken from reacting tubes at the mean times *t*.

The rates of aggregation in the presence of Triton have shown similar behaviour as in aggregation of AgI colloid without Triton. The mechanism of aggregation processes can be considered as in Scheme 1, in which several aggregation steps can be assumed.



Scheme 1.

(I) Sensitization (Initial Stabilization)

During the mixing of reacting components the particles become protected — stabilized, but the rate of precipitation becomes faster than that of "pure" AgI, which shows that very small concentrations of Triton affect the growth of AgI in the first stages of nucleation. In this way Triton changes further processes of the primary particle growth, i. e. it causes retardation of the aggregation, protection of small particles, which have thus no possibility of further growth. Afterwards, turbidity increases due to slow aggregation of the already stabilized particles.

(II) Critical Flocculation Concentration

The critical change in the rates of aggregation of primary stabilized particles causes a rapid aggregation of smaller particles into large flocs. There is a smaller concentration of NSAA within the methoric layer[25] than in the bulk of the solution and it causes the osmotic pressure to become a driving force for bringing particles together.

(III) Maximum Flocculation Concentration

The rate of precipitation cannot be measured because the processes become too fast.

(IV) Critical Stabilization Concentration

The rate of precipitation decreases. Looking at Figure 3. it can be easily concluded that the rates for the critical conditions (stabilization or flocculation) are very similar. Even the slopes of the straight lines are identical. This shows the influence of NSAA in the same stages of AgI nucleation for both the critical conditions. The peptization of large flocs back into smaller particles occurs as a result of the excess of NSAA concentration within the methoric layer when compared to that in the bulk of the solution.

(V) Stabilization

The AgI primary particles seem to be definitely stabilized, surrounded by NSAA micelles, the rate of precipitation is smaller than for the »pure« AgI system, even for preformed sols (Figure 4.). The aggregation rates become very slow.

By correlating kinetic to adsorption measurements a good agreement was shown. The adsorption isotherms for T-X-100, T-X-305 and T-X-705 were determined and they showed the same type of adsorption. The representative results are presented for T-X-305 in Figures 6. and 7. A repetition of measurements (denoted by triangles and open circles) has shown reproducibility of adsorption data. The results show considerable agreement with the previous work[21] and with the presumption in Scheme 1. The dependence of flocculation and stabilization effects on Triton concentration can be characterized as follows:

— in the maximum flocculation concentration (m.f.c.) the adsorption is 100%,

— up to m.f.c. the Langmuir plot has been obtained indicating the monolayer saturation in both systems, prepared 'in statu nascendi' and preformed sols,

— the preformed sols have shown plateau almost up to c.s.c., where the multilayer adsorption begins,

— the sols 'in statu nascendi' have exhibited the multilayer adsorption in the concentration region of NSAA after reaching m.f.c. Therefore, different mechanisms occur in the concentration regions smaller or greater than m.f.c. Differences in the adsorption isotherms for differently prepared sols can be explained by the size of the available surface. The isotherm, as shown in Figure 7. also has been proved for the polymer adsorption.[26]

These results can be compared with the investigations of Lange[27] of adsorption isotherms indicating the "closepacked area", and with the adsorption layers proposed by Bisio[28], who investigated molecular orientation of aqueous

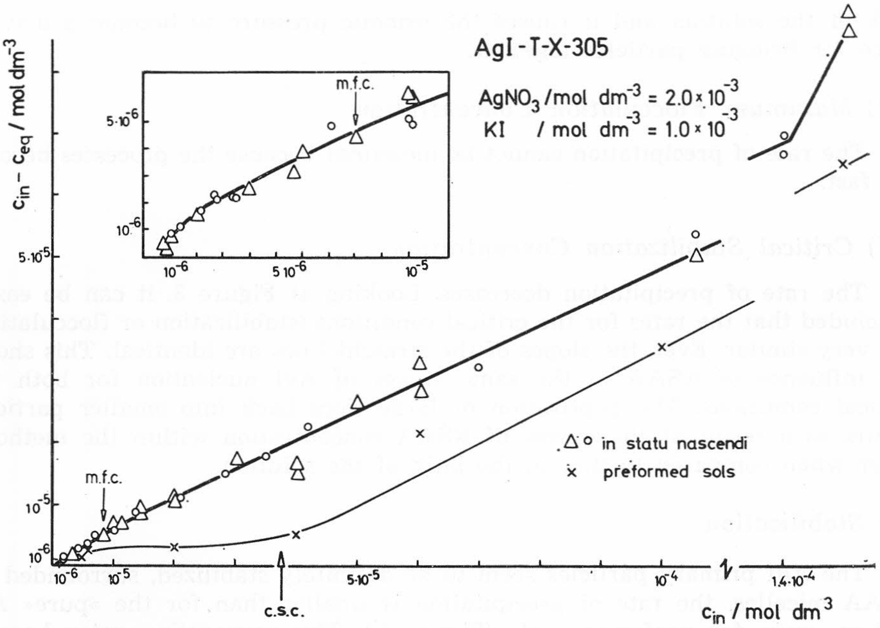


Figure 6. Adsorption isotherms: adsorbed amount of T-X-305 versus its initial concentration. Low coverage has been shown for preformed sols in the concentration region smaller than c.s.c.; in greater concentrations, a multilayer adsorption similar to 'in statu nascendi' sols has been found.

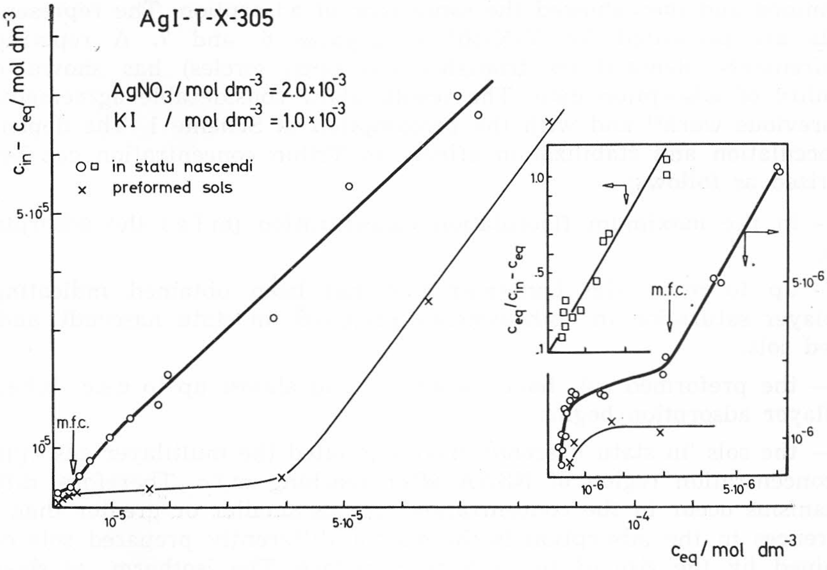


Figure 7. Adsorption isotherms: adsorbed amount of T-X-305 versus its equilibrium concentration. In the small picture, the extended scale and the Langmuir plot are shown. In the region bellow the maximum flocculation, a monolayer coverage has been found. The plateau level is higher for 'in statu nascendi' sols because a greater surface is available.

surfactants on a hydrophobic solid; adsorption layer thickness near c.m.c. of Triton corresponds approximately to the length of the surfactant molecule; just above the c.m.c. the adsorption layer thickness changes to twice this length, indicating the formation of an adsorption bilayer.

Our results show that in the stabilization region the c.m.c. of Triton is usually exceeded. This can be compared to the results of Rosenthal.[29]

Watanabe considered that adsorption of non-ionic surfactants as multilayers occurs at high concentrations.[30] By comparing the results of stereospecific interactions of dyes,[31], macromolecules[32] or polymers[18,33] or non-ionics (this paper) and different colloids, such as AgI[19], silica[34,35], the same mechanism of interaction in the methoric layer can be assumed.

The critical phenomena of flocculation and stabilization for different sol concentrations are presented in Figure 8. It is obvious that an increase in AgI

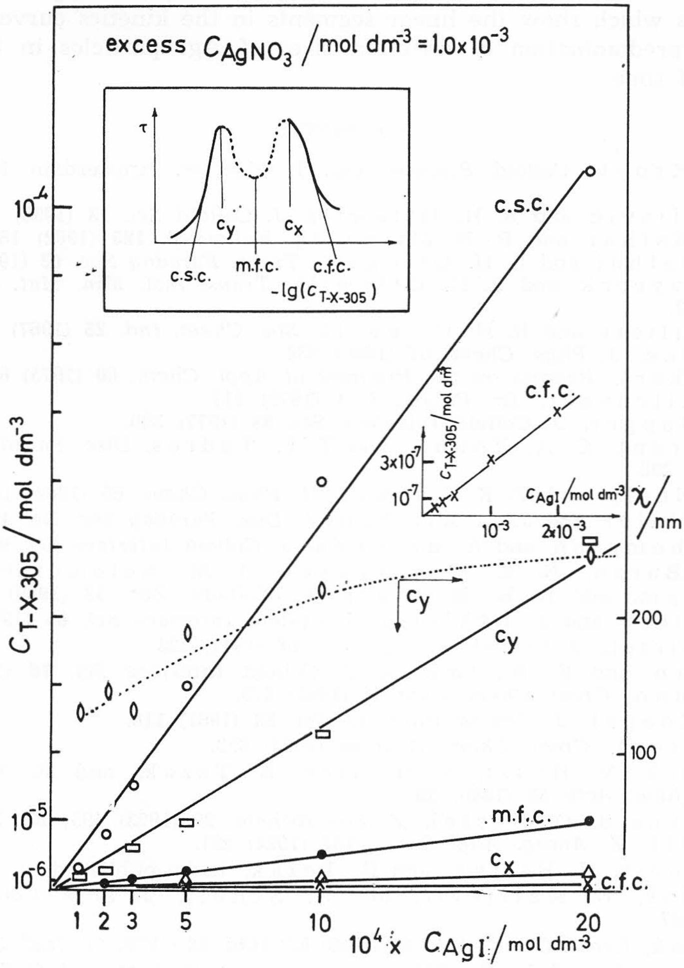


Figure 8. T-X-305 concentration versus AgI sol concentration presenting linearity for all critical conditions.

sol concentration causes the increase of the available AgI colloid surface. The amount of NSAA linearly increases. These effects are in agreement with the results of Lindström[36] who found that the effectiveness of the polymer increases with the molecular mass. In addition, Tamamushi[37] investigated the effects of long chain cations on the negative silver iodide sol.

CONCLUSION

The precipitation phenomena carried out on non-ideal polydisperse AgI colloid have shown that the mechanism of flocculation in the presence of NSAA in the region of flocculation maximum is characterized by a monolayer coverage. The stabilization process is characterized by an increase of adsorption capacities exhibiting the multilayer adsorption in the concentration region of NSAA higher than that causing the maximum flocculation effect.

It can be assumed that these processes can be explained by several aggregation steps which show the linear segments in the kinetics curves characterizing the predomination of different sizes of AgI particles in the related segments of time.

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SAŽETAK

Metorika taložnih procesa. XXV. Utjecaj neionskih površinsko-aktivnih agensa na rast i agregaciju solova srebrnog jodida

Đ. Težak, N. Batina i B. Ćosović

Adsorpcijski kapaciteti i kinetika precipitacije u koloidnim sistemima AgI u prisutnosti neionskih površinski aktivnih agensa oktafeniletoksilatnog niza istraživani su metodom raspršenja svjetla pri 293 K. Brzina precipitacije praćena je neposredno, primjenom fotometra za raspršenje svjetla s pisačem. Adsorpcijske izoterme pokazuju monoslojnu pokrivenost u području maksimuma flokulacije, a višeslojnu u području stabilizacije.

Glede mehanizma flokulacije i stabilizacije, može se pretpostaviti postojanje nekoliko agregacijskih stupnjeva, ovisnih o vremenskim i prostornim (koncentracijskim) parametrima.