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The Colloidal Stability of the Negatively Charged Silver Chloride System in the Presence of a Non-Ionic Surface-Active Agent and Electrolytes*

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The kinetics of the coagulation of negatively charged silver chloride sols in statu nascendi at a temperature of 293 K by K-, Mg-, and La-nitrate in the presence of a non-ionic surface active agent (SAA) T-X-305 was investigated by the light scattering method, using the tyndallometric technique. The concentration region between 1×10^{-4} and 2×10^{-3} mol dm⁻³ AgCl/Cl⁻ with 1×10^{-3} mol dm⁻³ KCl in excess was examined. The colloid stability is presented with the relative rate constants of coagulation (or stability coefficients) and also with the critical times of coagulation, because a linear relationship was found to exist between them. The stability study was completed with adsorption and electrophoretic mobility measurements which revealed a good correlation of all three interfacial parameters.

The experimental results can be summarized as follows:

(i) Non-ionic SAA, T-X-305, could not destabilize the stable negative AgCl sols in the absence of counter ions regardless of the amounts added (below critical micellization concentration c. m. c.).

(ii) Negative AgCl sols both with and without T-X-305 below c. m. c. were found to coagulate by counter ions in a manner which is typical of charged hydrophobic colloids. For both group of systems the linear Schulze-Hardy rule is obeyed. The critical coagulation concentrations (c. c. c.) of counter ions decrease with the increase in T-X-305 concentration below approximately 3×10^{-5} mol dm⁻³ (flocculation) and above this concentration up to 3×10^{-4} mol dm⁻³ T-X-305 (c. m. c.) they linearly increase (stabilization).

(iii) At c. m. c. T-X-305 exhibits the greatest stabilizing effect on negative AgCl sols, which then act as hydrophilic sols, and cannot be coagulated by cations over the same concentration region.

INTRODUCTION

The influence of various kinds of non-ionic surface active agents (SAA) of the polyoxyethylene type on disperse systems such as silver iodide sols¹⁻⁵, arsenic sulphide sols^{4,6}, antimony sulphide sols⁷ and, recently, polystyrene latices^{7,8,9} has been examined. The effect of non-ionic SAA on the stability of systems is manifested by the fact that the concentration of inorganic cations required to produce coagulation in their presence increases with the increase

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of their concentration^{2,4,6,7,9}. However, some authors^{4,6,9} have observed first a decrease in sol stability indicating flocculation and subsequently an increase, as the concentration of non-ionic SAA increases, implying stabilization of sols. Addition of non-ionic SAA results in a regular decrease of the electrophoretic mobility of sol particles^{2,5,6} and in a increase of the amount adsorbed^{2,6,7,9}.

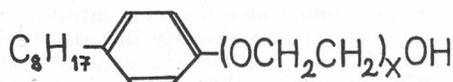
The influence of non-ionic polymers such as polyvinyl alcohols on AgI sols^{10,11}, non-ionic dextrans on AgBr sols¹², dextrans, T-X-100 and gelatin on teflon dispersions¹³ have been reported recently too, and also the effect of stabilization and flocculation in the presence of electrolytes is evident.

In order to obtain further information on the influence of non-ionic SAA on hydrophobic colloids, the stability of negatively charged silver chloride sols in statu nascendi (which means that all components were mixed together simultaneously) and the kinetics of coagulation by potassium, magnesium, and lanthanum nitrate in the presence of T-X-305 (a member of t-octyl-phenoxy-polyethoxy-ethanol series) was investigated using the light scattering method. The coagulation of AgCl sols in statu nascendi by simple electrolytes has already been investigated by Težak et al^{14,15,16}. The stability study was supplemented with electrophoretic-mobility and adsorption measurements and the results obtained by the three methods were correlated. A systematic investigation of the stability and the electrokinetics and adsorption behaviour of AgCl/Cl⁻ sols in the presence of T-X-305 and electrolytes may provide data on the changes in the double layer of colloid particles, i. e. on both the electric repulsion between particles and the steric energetic barrier, which is due to the coating of sol particles with an adsorbed hydrophilic layer.

According to La Mer^{17,18,19} and Težak²⁰ the term flocculation is differentiated from the term coagulation: the former is used for the interactions of hydrophobic sols with large organic molecules such as dyes, detergents, polymers etc., in which their stereoadsorption on particles surface is more important than the coulombic interactions.

EXPERIMENTAL

The aqueous solutions of inorganic components were prepared by dissolving the dry salts (p. a., »Merck«, Darmstadt) in double distilled water and were standardized potentiometrically, except the KNO₃ solution. T-X-305 was obtained from »Rohm & Haas Co.«, Philadelphia, and was not purified further. Its formula is:



where X is about 30.

The AgCl sols were prepared by directly mixing two solutions of equal volumes which were poured 7 times from one tube to another so that the mixing was achieved within 15 seconds. The first solution contained KCl and T-X-305 and the second AgNO₃ and metal nitrate. In one set of experiments the metal nitrate concentration was changed gradually and T-X-305 concentration was constant, and in other was oppositely.

The tyndallometric values (relative intensities of scattered light, I_{rel}) were obtained using a Zeiss tyndallometer connected to a Pulfrich photometer (Jena, DDR). The scattered green light ($\lambda = 530$ nm) was registered at an angle of $\pi/4$ rad to the transmitted beam.

The electrophoretic mobilities u ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) and the particle charge were determined by means of an ultramicroscope with a double capillary cell, which had a circular cross section.

The equilibrium concentrations of T-X-305 ($[\text{T-X-305}]_{\text{eq}}$) were determined by measuring the decrease of the initial T-X-305 concentration ($[\text{T-X-305}]_{\text{in}}$) in the liquid phase using a Pye Unicam SP 1800 ultraviolet spectrophotometer. After equilibration for 24 hours at the temperature of 293 K, the sol was removed by centrifugation for 10 minutes at 10,000 r.p.m. and the absence of a Tyndall beam was examined. The adsorption band at 276 nm was used for calibration. We observed a linear dependence between the absorbance at this λ and T-X-305 concentrations below $1.2 \times 10^{-3} \text{ mol dm}^{-3}$. This manner for determining the adsorbed T-X-305 concentrations ($[\text{T-X-305}]_{\text{ads}}$) cannot be applied for determination of lower concentrations than $10^{-5} \text{ mol dm}^{-3}$ T-X-305.

The critical micellization concentration (c. m. c.) of T-X-305 water solution freshly diluted, as determined by means of refractometry, is about $10^{-4} \text{ mol dm}^{-3}$. This value was shifted to $3 \times 10^{-4} \text{ mol dm}^{-3}$ during the aging of the solutions for seven days. Ray and Nemethy²¹ have obtained with T-X-305 a c.m.c. value of $5.3 \times 10^{-4} \text{ mol dm}^{-3}$, which would correspond to $3.67 \times 10^{-4} \text{ mol dm}^{-3}$, had the data not been corrected to the content of water in the samples, determined by NMR technique. The pH values of T-X-305 water solutions from 3×10^{-6} to $3 \times 10^{-4} \text{ mol dm}^{-3}$ correspondingly decreased from 7.4 to 5.4, as was established by a Beckman pH meter with a calomel and glass electrode.

RESULTS

The tyndallometric curves and the curves of electrophoretic mobilities against the initial T-X-305 molar concentration, as well as the adsorption curve, for $10^{-3} \text{ mol dm}^{-3}$ AgCl with different excess of KCl concentration, are presented in figure 1. The KCl concentration $6 \times 10^{-2} \text{ mol dm}^{-3}$ at which flocculation occurred is in the critical coagulation region of K^+ ions. The flocculation maximum is limited by the critical flocculation concentration (c. f. c.) and by the critical stabilization concentration (c. s. c.), as shown in the lower part of Figure 1. The curve of electrophoretic mobilities (middle part) of these systems show two steps. The negative u values gradually change with increasing T-X-305 concentration to about $3 \times 10^{-5} \text{ mol dm}^{-3}$, remain practically constant to about $10^{-4} \text{ mol dm}^{-3}$, to drop rapidly again to zero at c. m. c. (particles did not move in the electric field of $\sim 27 \text{ V/cm}$). The adsorption isotherm (upper part), c_{ads} versus c_{eq} , of the same systems show an increase of c_{ads} in the concentration region in which mobility decreases, approaching asymptotically a certain saturation value, which is reached at about $3 \times 10^{-5} \text{ mol dm}^{-3}$ T-X-305. The c_{ads} starts to increase sharply above $10^{-4} \text{ mol dm}^{-3}$ T-X-305. The adsorption curves are of the Langmuir type below the c. m. c. of T-X-305, as can be easily demonstrated by linearization. A sudden increase in c_{ads} occurs above the c. m. c. and the adsorption curves are of the »high affinity type«.

In the absence of counter ions (c. i.), however, the flocculation maximum disappears (the systems with $2 \times 10^{-3} \text{ mol dm}^{-3}$ KCl). The electrophoretic mobilities of these systems slightly change with increase in T-X-305 concentration and not reach zero value.

To make a comparison of the experimental results, the colloid stability was estimated both in terms of critical times of precipitation (t_{crit}) defined by Težak and in terms of stability coefficients (W) given by Reerink and Overbeek. The t_{crit} were obtained by extrapolating the steepest portion of the tyndallometric curves (I_{rel} versus $\log t$) to zero tyndallometric value²². The other way of presenting stability was calculating the relative rate constants of coagulation

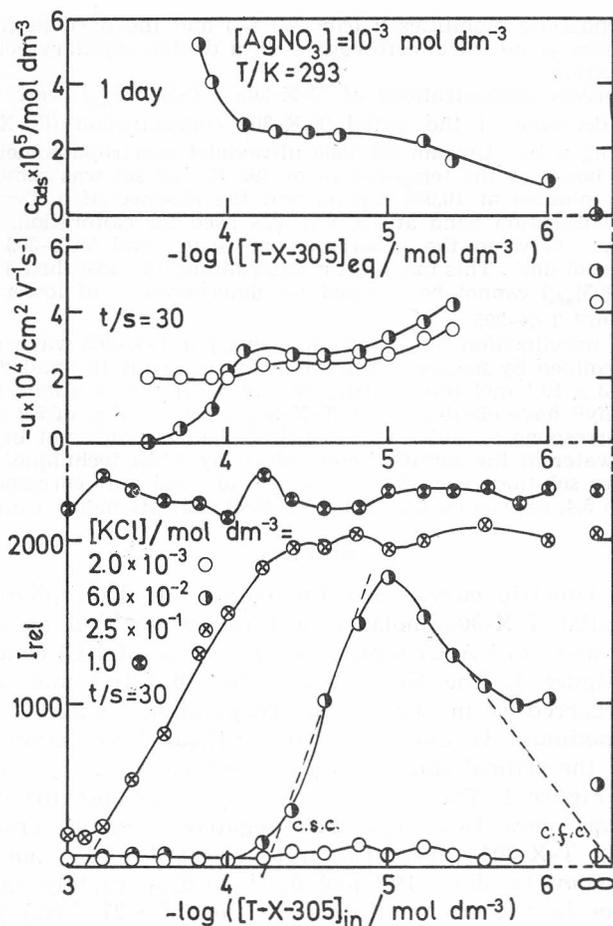


Figure 1. Upper part: Concentration of T-X-305 adsorbed (c_{ads}) plotted against its equilibrium concentration for the system $1 \times 10^{-3} \text{ mol dm}^{-3}$ and $6 \times 10^{-2} \text{ mol dm}^{-3}$ KCl (●). Equilibration time: 1 day.

Middle part: Electrophoretic mobilities (u) measured 30 seconds after mixing the components plotted against the initial T-X-305 concentration for the system $1 \times 10^{-3} \text{ mol dm}^{-3}$ $AgNO_3$ and $6 \times 10^{-2} \text{ mol dm}^{-3}$ KCl (●) and $2 \times 10^{-3} \text{ mol dm}^{-3}$ KCl (○) respectively.

Lower part: Tyndallometric values (I_{rel}) plotted against the initial T-X-305 concentration for the system $1 \times 10^{-3} \text{ mol dm}^{-3}$ $AgNO_3$ and 1.0 (●), 2.5×10^{-1} (⊗), 6×10^{-2} (⊙), 2×10^{-3} (○) mol dm^{-3} KCl respectively.

(k_{rel}) from the initial slopes of tyndallometric curves and further assuming that $W = 1$ for rapid coagulation in the absence of T-X-305²³.

The mode of determination of t_{crit} and k_{rel} is presented in Figure 2. The upper part of figure shows the time-tyndallograms of $AgCl/Cl^-$ sols without T-X-305 and with 6 different $Mg(NO_3)_2$ concentrations, while the lower part presents the same in the presence of the stabilizing T-X-305 concentration: $6 \times 10^{-5} \text{ mol dm}^{-3}$ and 4 different $Mg(NO_3)_2$ concentrations. The t_{crit} of the systems containing high electrolyte concentrations were reduced in the presence

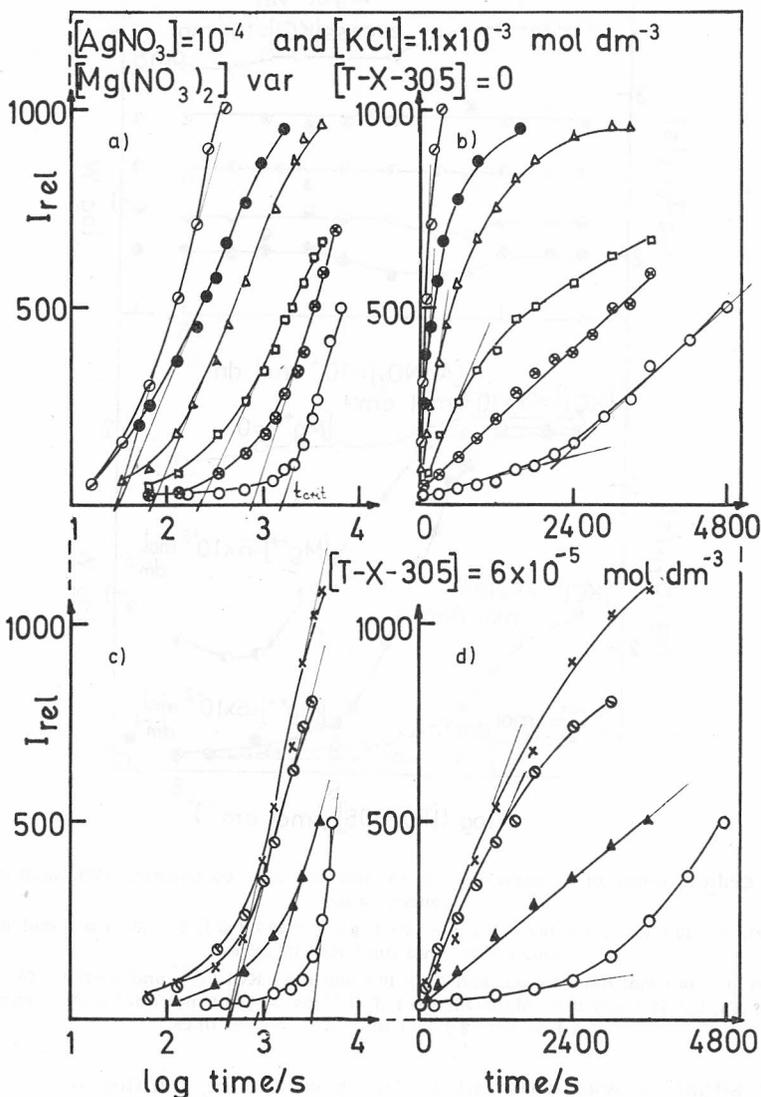


Figure 2. Tyndallometric values (I_{rel}) against time (sec) for the system $10^{-4} \text{ mol dm}^{-3} \text{ AgCl}$, $10^{-3} \text{ mol dm}^{-3} \text{ KCl}$ in excess and different $\text{Mg}(\text{NO}_3)_2$ concentration: 4×10^{-1} (\times), 1×10^{-1} (\bullet), 6×10^{-2} (\odot), 5×10^{-2} (\ominus), 2×10^{-2} (\blacktriangle), 1×10^{-2} (\triangle), 8×10^{-3} (\square), 6×10^{-3} (\oplus), 1×10^{-3} (\circ) mol dm^{-3} . a) and b) without T-X-305, c) and d) with $6 \times 10^{-5} \text{ mol dm}^{-3}$ T-X-305.

of $6 \times 10^{-5} \text{ mol dm}^{-3}$ T-X-305, whereas t_{crit} of the systems with low $\text{Mg}(\text{NO}_3)_2$ concentrations remained unaltered.

The upper part of Figure 3. shows that t_{crit} decrease with AgCl sol concentration and $10^{-3} \text{ mol dm}^{-3} \text{ KCl}$ in excess, but are independent of T-X-305 levels, in the absence of added salts up to $2 \times 10^{-3} \text{ mol dm}^{-3} \text{ AgCl}$.

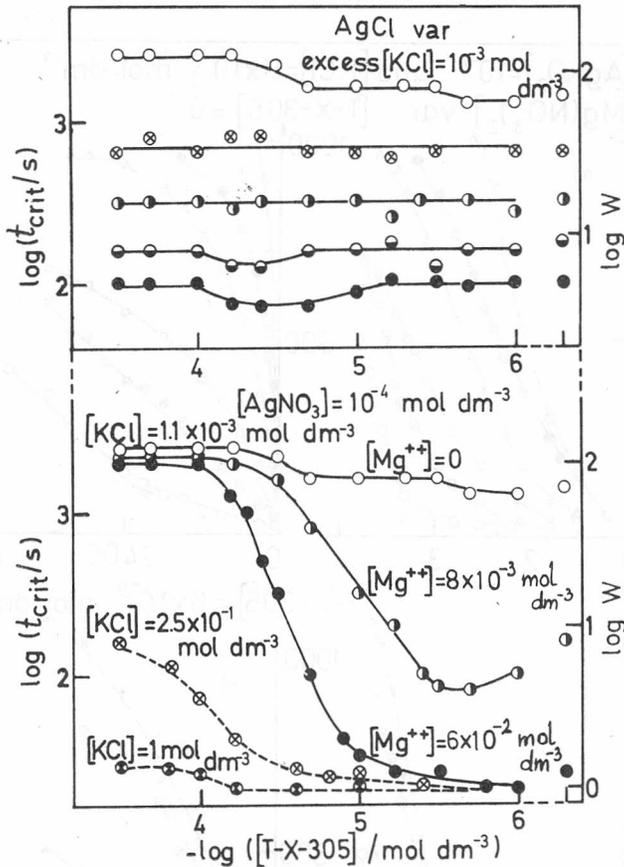


Figure 3. Critical times of precipitation (t_{crit}) and stability coefficients (W) against T-X-305 concentration.

Upper part: 1×10^{-4} (○), 2×10^{-4} (⊗), 6×10^{-4} (⊙), 1×10^{-3} (◡), 2×10^{-3} (●) mol dm^{-3} AgCl and 1×10^{-3} mol dm^{-3} KCl in excess.

Lower part: 1×10^{-4} mol dm^{-3} AgNO₃ and 1.1×10^{-3} mol dm^{-3} KCl (○), and with 8×10^{-3} mol dm^{-3} Mg(NO₃)₂ (⊙), 6×10^{-2} mol dm^{-3} Mg(NO₃)₂ (●), full lines; 1×10^{-4} mol dm^{-3} AgNO₃ and 2.5×10^{-1} (⊗) or 1.0 (⊙) mol dm^{-3} KCl, dotted lines.

The situation was different in the presence of counter ions, e.g. Mg^{++} ions, which can produce a moderate or rapid coagulation. The results for 10^{-4} mol dm^{-3} AgCl and 10^{-3} mol dm^{-3} KCl in excess are given in the lower part of Figure 3. In the presence of 8×10^{-3} mol dm^{-3} Mg(NO₃)₂, a small decrease in t_{crit} was observed at low T-X-305 concentration (flocculation) and an increase in t_{crit} near the c.m.c. region (stabilization). The most appreciable effect of T-X-305 on stability is at electrolyte concentrations somewhat exceeding c.c.c. (critical coagulation concentration), e.g. 6×10^{-2} mol dm^{-3} Mg(NO₃)₂. There is a marked increase in stability at c.m.c., and these systems are about 100 times more stable than those in the absence of T-X-305. When the potential-determining ion (p.d.i.) and counter ion (c.i.) concentrations were increased simultaneously, then again an independence of stability from T-X-305 con-

centration was observed (dotted curves). However such systems undergo a rapid precipitation process.

The ability of the negatively charged silver chloride sols to coagulate with mono-, bi-, and trivalent cations in the presence of a given T-X-305 concentration is presented in Figure 4. The similarity in the counter ion effect which is expressed as a decrease in stability with added electrolytes and the validity of the linear Schulze-Hardy rule, was proved on both systems with and without T-X-305. $\log t_{crit} - \log$ c.c.i. curves have two parts parallel with the abscissa and between them is the concentration range of sharp changes. The c.c.c. defined by Težak¹⁵ is the electrolyte concentration above which the stability starts to decrease sharply. The c.c.c. of all three c.i. are enhanced linearly with rising T-X-305 concentration from about 3×10^{-5} to 3×10^{-4} mol dm⁻³. In lower concentrations T-X-305 acts as a flocculating agent, what is demonstrated with a shift of c.c.c. to lower c.c.i., and can be also seen in Table I. These results are in agreement with the results of other authors^{4,6,9,12,13}. The rapid coagulation rate is independent from the counter ion valency for AgCl sols with and without T-X-305, which only very roughly or not at all applies to AgI sols¹¹. With increasing T-X-305 concentration the $\log t_{crit} - \log$ c.c.i. curves gradually assume the shape of a straight line, in the presence of 3×10^{-4} mol dm⁻³ T-X-305, while t_{crit} become independent

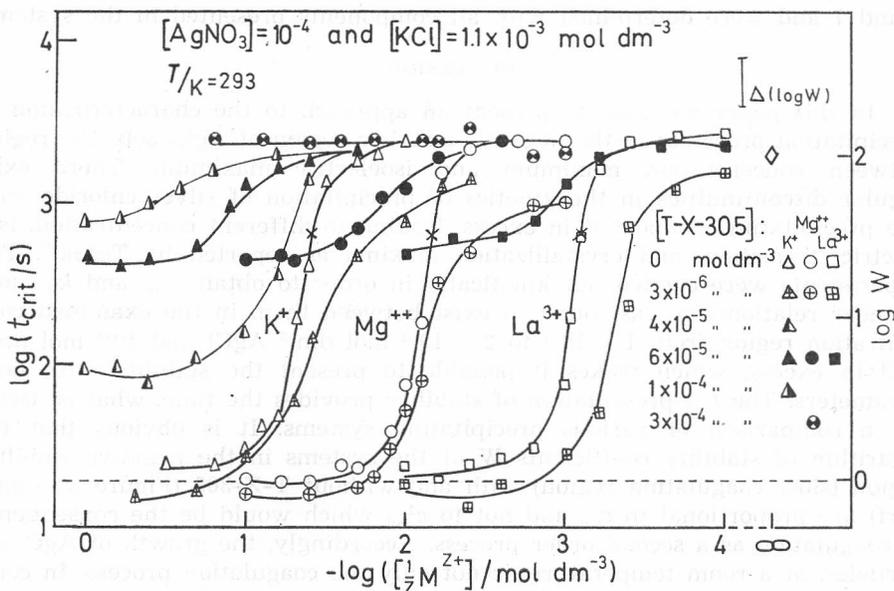


Figure 4. Critical times of precipitation (t_{crit}) and stability coefficients (W) against K-, Mg-, La-nitrate concentration for the system 1×10^{-4} mol dm⁻³ AgCl and 1×10^{-3} KCl in excess and a given T-X-305 concentrations:

- T-X-305 absent: KNO_3 (Δ), $Mg(NO_3)_2$ (\circ), $La(NO_3)_3$ (\square), without salts (\diamond)
 3×10^{-6} mol dm⁻³ T-X-305: KNO_3 (\blacktriangle), $Mg(NO_3)_2$ (\oplus), $La(NO_3)_3$ (\boxplus)
 4×10^{-5} " " " : KNO_3 (\blacktriangle),
 6×10^{-5} " " " : KNO_3 (\blacktriangle), $Mg(NO_3)_2$ (\bullet), $La(NO_3)_3$ (\blacksquare)
 1×10^{-4} " " " : KNO_3 (\blacktriangle),
 3×10^{-4} " " " : $Mg(NO_3)_2$ ($\bullet\oplus$)

TABLE I

[AgCl] = 1×10^{-4} mol dm⁻³excess [KCl] = 1×10^{-3} mol dm⁻³

$\frac{[T-X-305]}{\text{mol dm}^{-3}}$	$\frac{[KNO_3]_{\text{coag}}}{\text{mol dm}^{-3}}$	$\frac{[1/2 Mg(NO_3)_2]_{\text{coag}}}{\text{mol dm}^{-3}}$	$\frac{[1/3 La(NO_3)_3]_{\text{coag}}}{\text{mol dm}^{-3}}$
0	5.0×10^{-2}	7.0×10^{-3}	8.0×10^{-4}
1×10^{-6}	8.0 —	4.0×10^{-3}	
3×10^{-6}	2.0×10^{-2}	4.0×10^{-3}	4.0×10^{-4}
1×10^{-5}	2.0×10^{-2}	1.0×10^{-2}	
3×10^{-5}	4.0×10^{-2}	2.0×10^{-2}	
4×10^{-5}	6.0×10^{-2}	2.5×10^{-2}	
6×10^{-5}	1.5×10^{-1}	2.5×10^{-2}	2.5×10^{-3}
1×10^{-4}	3.0×10^{-1}	5.0×10^{-2}	
3×10^{-4}	no coagulation	no coagulation	

c. c. c. values correspond to $\log t_{\text{crit}}/\text{min} = 1$ and $\log W = 1.5$ respectively.

of c.c.i. These systems undergo a slow coagulation, despite the presence of c.c.i. which exceeds the c.c.c. Similar results have been obtained by Ottewill et al.^{2,7} The pH values in coagulation experiments with $La(NO_3)_3$ had not been adjusted to 4.6 to avoid hydrolysis. The pH values were ranging between 5 and 7 and were determined with all components presented in the systems.

DISCUSSION

In this paper we wish to present an approach to the characterization of precipitation processes in the negative stability region of AgCl sols, the region between concentration maximum and isoelectric maximum. There exist regular discontinuities in the kinetics of precipitation of silver chloride with one precipitating component in excess, leading to different concentration, isoelectric, transition, and crystallization maxima as reported by Težak²⁴. The experiments were carried out kinetically in order to obtain t_{crit} and k_{rel} , and a linear relationship was found to exist between them in the examined concentration region from 1×10^{-4} to 2×10^{-3} mol dm⁻³ AgCl and 10^{-3} mol dm⁻³ KCl in excess, which makes it possible to present the stability with both parameters. The t_{crit} presentation of stability provides the time, what is useful for a comparison of various precipitating systems. It is obvious that the logarithm of stability coefficients W of the systems in the negative stability region (slow coagulation region) with and without T-X-305 (Figure 3., upper part) are proportional to c_{sol} and not to c_{sol}^2 which would be the consequence of coagulation as a second order process. Accordingly, the growth of AgCl sol particles, at a room temperature, is not only the coagulation process. In comparison to the precipitation of AgBr and AgI sols, which show more colloidal characteristics, the precipitation of AgCl is largely characterized by rapid recrystallization. The growth of AgI particles in the negative stability region is a second order process ($\log W \propto c_{\text{sol}}^2$) both for in statu nascendi sols²⁵ and for aged sols².

The experimental results presented in upper part of Figure 3., show that there is neither stabilization nor flocculation at a low electrolyte concentration regardless sol concentration. Similar results have been obtained on teflon

dispersions, and have been reported recently¹³. On the other side, rapid coagulation by electrolytes (c.c.i. > c.c.c.) in the presence of T-X-305 in concentrations higher than c.m.c. does not occur. Similar results have been obtained on AgI sols² and on polystyrene latices⁷. Both groups of systems mentioned above undergo slow precipitation. Comparison of the electrophoretic mobility results with the adsorption behaviour showed, that the adsorption isotherm is reflected in the form of the electrophoretic mobility curve for a given electrolyte concentration. However, the electrophoretic mobility curve was obtained at a given time after mixing the precipitating components (nonequilibrium process) while the results of adsorption were obtained under equilibrium conditions.

Flocculation occurs in the concentration region of non-ionic SAA (T-X-305) between the concentration at which its adsorption begins and the concentration at which it reaches saturation value. The W or t_{crit} are subject to the greatest changes between c.s.c. and c.f.c. Above c.s.c. and below c.f.c. stability does not change at any electrolyte concentration higher or lower than the c.c.c. Only the absolute values of t_{crit} depend on counter ion concentration. Equal t_{crit} (or W) values are obtained in the presence of all three counter ions in concentrations higher than c.c.c. at a given T-X-305 concentration. A high degree of similarity can be observed to the results reported by Ottewill and Walker⁷ on polystyrene latices by reducing electrical repulsion to zero both when using La^{3+} ions in concentrations exceeding the c.c.c. and when lowering the pH to 1.5 ($W = 1.4$ and 1.2 respectively). Adsorption behaviour is in agreement with La Mer's^{17,18,19} concept of polymer adsorption and their conclusion that maximum flocculation will occur if a part of particle surface is covered by a polymer.

According to Težak²⁰, because of the specific adsorbability of uncharged molecules their number is smaller in the methorical layer²⁶ (due to their adsorption) than in the bulk of solution, and this may lead to flocculation. In the case of a higher concentration of molecules, if adsorption has exceeded a certain maximum value, the higher concentration near the particle surface may be considered to be the cause of stabilization.

In the case of coagulation, however, the interaction of ions with the discrete (fixed) charges on the surface²⁷ leads to a critical situation in which, because of the fixed distribution of surface charges, the probability of ion-pair formation in the methorical layer is greater than in the bulk of solution. Thus the mechanism of ion-pair formation¹⁵, and the adsorption of counter ions which have been investigated by Herak and Mirnik^{28,29} provide a basis for the explanation of coagulation process, expressed by the linear Schulze-Hardy rule and also confirmed by the present results, both in the absence of T-X-305 and in its presence in concentrations up to critical micellization concentration. In Figure 5. is presented the linear relationship between valency of the coagulating cations and their critical coagulation concentration (c.c.c. are given in normalities) for 10^{-4} mol dm^{-3} AgCl and 10^{-3} mol dm^{-3} KCl in excess in the presence of some T-X-305 concentrations and without it.

According to DLVO theory the coagulation concentrations of monovalent, divalent, and trivalent binary electrolytes should show the following ratios: $c_1 : c_2 : c_3 = 1 : (1/2)^6 : (1/3)^6 : \dots = 100 : 1.6 : 0.14 : \dots$

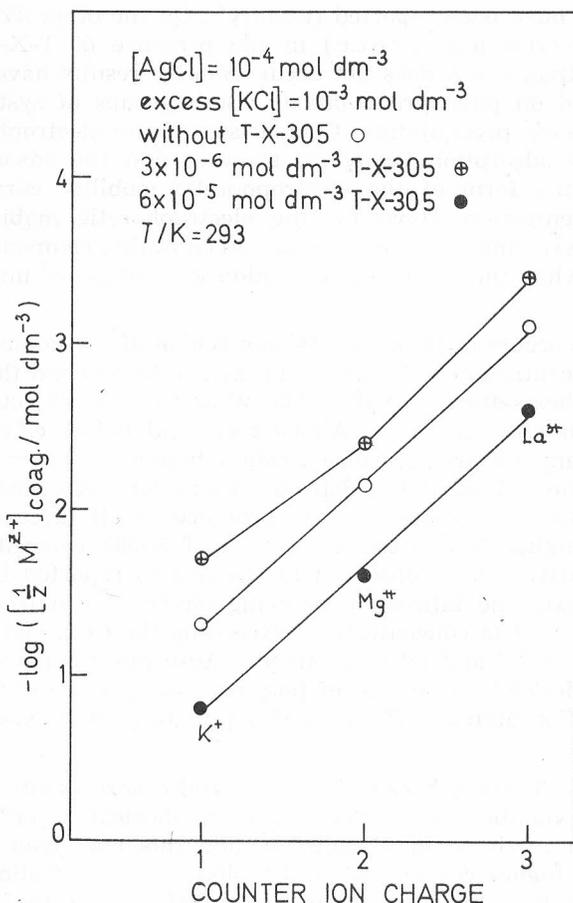


Figure 5. The dependence of critical coagulation concentration of K-, Mg-, La-nitrate on the counter ion charge in the absence of T-X-305 (\circ), in the presence of $3 \times 10^{-6} \text{ mol dm}^{-3}$ T-X-305 (\oplus), and in the presence of $6 \times 10^{-5} \text{ mol dm}^{-3}$ T-X-305 (\bullet). $1 \times 10^{-4} \text{ mol dm}^{-3}$ AgCl and $1 \times 10^{-3} \text{ mol dm}^{-3}$ KCl in excess.

Our results from the Table I. for AgCl sols without T-X-305 give:
 $0.05 : 0.0035 : 0.00026 = 100 : 7 : 0.53$

For AgCl sols in the presence of $3 \times 10^{-6} \text{ mol dm}^{-3}$ T-X-305 (flocculating concentration):

$$0.02 : 0.002 : 0.00013 = 100 : 10 : 0.66$$

And in the presence of $6 \times 10^{-5} \text{ mol dm}^{-3}$ T-X-305 (stabilizing concentration):
 $0.15 : 0.0125 : 0.00083 = 100 : 8.3 : 0.55$.

Obviously the ratios are much smaller than would be predicted from the theory, since the electrolytes used are not those (ideal binary electrolytes) for which the theory was derived.

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REFERENCES

1. K. G. Mathai and R. H. Ottewill, *Kolloid-Z.* **185** (1962) 55.
2. K. G. Mathai and R. H. Ottewill, *Trans. Faraday Soc.* **62** (1966) 750, *ibid* p. 759.
3. K. G. Mathai and R. H. Ottewill, *Kolloid-Z. Z. Polym.* **236** (1970) 147.
4. Yu. M. Glazman, *Discuss. Faraday Soc.* **42** (1966) 255.
5. Yu. M. Glazman and G. M. Kabysh, *Kolloid Zh.* **31** (1969) 27.
6. K. J. Daluja and S. N. Srivastava, *Indian J. Chem.* **7** (1969) 790.
7. R. H. Ottewill and T. Walker, *Kolloid-Z. Z. Polym.* **227** (1968) 108.
8. R. H. Ottewill and T. Walker, *J. Chem. Soc., Faraday Trans I* **70** (1974) 917.
9. S. G. Ash and E. J. Clayfield, *J. Colloid Interface Sci.* **55** (1976) 645.
10. G. J. Fleer and J. Lyklema, *J. Colloid Interface Sci.* **46** (1974) 1.
11. G. J. Fleer and J. Lyklema, *J. Colloid Interface Sci.* **55** (1976) 228.
12. A. D. Lindsay, E. Matijević, and J. P. Kratochvil, *J. Colloid Polymer Sci.* **253** (1975) 581.
13. S. Kratochvil and E. Matijević, *J. Colloid Interface Sci.* **57** (1976) 104.
14. B. Težak, *Arhiv kem.* **20** (1948) 1.
15. B. Težak, *ibid.* **22** (1950) 26.
16. E. Matijević, K. Schulz, and B. Težak, *Croat. Chem. Acta* **28** (1956) 81.
17. R. H. Smellie and V. K. La Mer, *J. Colloid Sci.* **13** (1958) 589.
18. V. K. La Mer and T. W. Healy, *J. Phys. Chem.* **67** (1963) 2417.
19. T. W. Healy and V. K. La Mer, *J. Colloid Sci.* **19** (1964) 323.
20. B. Težak, *Croat. Chem. Acta* **40** (1968) 63.
21. A. Ray and G. Nemethy, *J. Amer. Chem. Soc.* **93** (1971) 6787.
22. B. Težak, E. Matijević, and K. Schulz, *J. Phys. Colloid Chem.* **55** (1951) 1557.
23. H. Reerink and J. Th. G. Overbeek, *Disc. Faraday Soc.* **18** (1954) 74.
24. B. Težak and Dj. Težak, in collaboration with E. Bonetta, D. Dimitrovski, I. Fišer, M. Kramberger, and N. Stubičar, *Croat. Chem. Acta* **45** (1973) 275.
25. N. Kallay and S. Vučković, *Indian J. Chem.* **14 A** (1976) 156.
26. B. Težak, *Arhiv kem.* **21** (1949) 93.
27. M. Mirnik, *Croat. Chem. Acta* **35** (1963) 217.
28. M. J. Herak and M. Mirnik, *Kolloid-Z.* **168** (1960) 139.
29. M. J. Herak and M. Mirnik, *ibid* **179** (1961) 130.

SAŽETAK

Koloidna stabilnost negativno nabijenog argentum klorid sistema u prisustvu neionskog površinski-aktivnog agensa i elektrolita

N. Puzigaća-Stubičar i B. Težak

Istraživana je kinetika koagulacije negativno nabijenih solova srebro-klorida *in statu nascendi* s K-, Mg-, i La-nitratom u prisustvu neionskog površinski aktivnog agensa T-X-305 metodom raspršenja svjetlosti, tindalometrijskom tehnikom na temperaturi 293 K. Ispitano je područje koncentracije sola od 1×10^{-4} do 2×10^{-3} mol dm⁻³ AgCl/Cl⁻ sa 10^{-3} mol dm⁻³ KCl u suvišku. Koloidna stabilnost je prikazana relativnim konstantama brzine koagulacije (odnosno koeficijentima stabilnosti) i također kritičnim vremenima koagulacije, jer je nađeno da postoji linearna ovisnost među njima. Studij stabilnosti kompletiran je mjerenjima adsorpcije i elektroforetske gibljivosti i nađena je povezanost sva tri međupovršinska parametra.

Ekperimentalni rezultati mogu se sumirati kako slijedi: (i) neionski SAA, T-X-305, ne može destabilizirati stabilne negativne AgCl solove u odsutnosti protuiona bez obzira na dodanu količinu (do kritične micelarne koncentracije, c. m.c.); (ii) nega-

ktivni solovi AgCl sa i bez T-X-305 ispod c. m. c. koaguliraju se s protuionima na način tipičan za nabijene hidrofobne koloide. Za obje skupine sistema vrijedi linearno Schulze-Hardyjevo pravilo. Kritične koagulacijske koncentracije (c. c. c.) protuiona smanjuju se s porastom koncentracije T-X-305 do oko 3×10^{-5} mol dm⁻³ (flokulacija), a iznad te koncentracije do oko 3×10^{-4} mol dm⁻³ T-X-305 (c. m. c) one linearno rastu (stabilizacija); (iii) kod c. m. c. T-X-305 pokazuje najveći stabilizacijski efekt na negativne AgCl solove, koji tada djeluju kao hidrofilni solovi i ne mogu biti koagulirani s kationima u istomu koncentracijskom području.

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