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Methorics of the Precipitation Processes. XXI. Flocculation and Stabilization Phenomena of Sodium Fluoresceinate on Positive Silver Iodide Sols *in statu nascendi*

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The flocculating and stabilizing action of sodium fluoresceinate on silver iodide sol was investigated by tyndallometric, fluorimetric and electrophoretic measurements. The limits of the precipitation region were determined. The amount of sodium fluoresceinate adsorbed on AgI-particles was calculated from fluorimetric measurement data. The fact that the end-point of fluorimetric titration of the system $AgNO_3$—KI—sodium fluoresceinate takes place at *p*H 5 is in complete agreement with the results of tyndallometric and electrophoretic observations of ours and other author's experiments.

INTRODUCTION

Our investigations on the precipitation of silver halides are related with the known titration methods using Fajans' adsorption indicators[1-5]. The phase changes related to the action of adsorption indicators are generally known in Fajans' interpretation as the Fajans-Paneth rule (1914) and the Hahn rule (1923). The new indicators in the sense of Fajans' theory were investigated and used by many anthors[6-8]. Pungor and Schulek[9,10] proposed a new classification of indicators according to the mechanism of their action.

Some dyes of the fluoresceine series were found to be very useful for the investigation of the precipitation of silver iodide.

The flocculation and stabilization of strychnine[11] and quinine[12] has been investigated recently.

EXPERIMENTAL

Methods

The systems were prepared by using technique *in statu nascendi* described earlier[13]. Tyndallometric values were measured by means of a Pulfrich photometer in connection with a Zeiss tyndallometer. The relative intensity of fluorescence was measured by means of a UV-set consisting of a B. Lange photoelectric fluorimeter model G. A. 42, a Hg-lamp HQE 42, a violet filter for isolation of the spectral band at 365 nm, and a Multiflex galvanometer MGF 4 (maximal sensitivity $6.85 \times \times 10^{-10}$ A/mm).

An aqueous solution of sodium fluoresceinate having the highest fluorescence (set to $G = 100$) was used as the fluorimetric standard solution.

The particle charges were determined by ultramicroscopic electrophoresis.

The potentiometric measurements were performed on a Fisher Sci. Co. type S Potentiometer with a silver-silver iodide electrode[14].

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The concentrations of systems were expressed as negative logarithms. The symbol NaFln is used for sodium fluoresceinate.

Materials

All the chemicals used were of »AnalaR« grade: sodium fluoresceinate — Basler Drogerie Bohny & Cie A. G., silver nitrate and sodium iodide — Merck, Darmstadt. The solutions were prepared with bidistilled water.

RESULTS

In order to observe the interaction of the precipitation components: silver nitrate and sodium iodide in the presence of sodium fluoresceinate it was necessary to divide the Fajans titration into separate steps, *e. g.* to examine the phase changes during the process of precipitation. The systems were prepared so that the concentrations of two components were constant, and the concentration of the third was systematically varied.

The flocculating and stabilizing action of fluoresceinate on silver iodide sols *in statu nascendi* is shown in Fig. 1 A—C. The tyndallometric curves show the dependence of the precipitation of silver iodide sol, which takes place in the form of orange flocks, on the excess of silver nitrate and the concentration of indicator dye. With concentrations of silver iodide sol 1.0×10^{-3}, 5.0×10^{-4}, 2.0×10^{-4} *N* the concentration of silver nitrate was varied from 10^{-4} to 10^{-2} *N*. Three regions characterized the concentrational relationship of the interacting components and the kind of precipitated particles, and could be seen on the diagrams: (1) the region without precipitation effects in the range of low fluoresceinate concentration; (2) the flocculation region, and (3) the stabilization region or region of reversal of charge. The limits which determined flocculation maxima were found to be from 6×10^{-6} to 6×10^{-5} *M* of sodium fluoresceinate for the beginning of flocculation, and from 10^{-4} to 3×10^{-4} *M* of sodium fluoresceinate for the beginning of stabilization in the system of 1.0×10^{-3} *N* silver iodide. If the concentration of silver iodide is 5.0×10^{-4} *N* (Fig. 1 B), the corresponding flocculation values are from 10^{-6} to 5×10^{-6} *M*, and stabilization values from 3×10^{-5} to 10^{-4} *M* of sodium fluoresceinate. For 2.0×10^{-4} *N* silver iodide sol concentration the flocculation values are 5×10^{-6} *M*, and stabilization values from 2×10^{-5} to 10^{-4} *M* of sodium fluoresceinate. It may be seen that the stabilization and flocculation values depend on the excess of silver nitrate. If the excess of silver nitrate increases, more fluoresceinate is necessary to give the precipitation effects.

Generally, it may be seen that the flocculation is more expressed as the concentration of silver iodide sol and the excess of silver nitrate increase. The tyndallometric values show (Fig. 1 C) that the flocculation effects disappear if the concentration of silver iodide sol is 2.0×10^{-4} *N*, and the excess of silver nitrate 1.0×10^{-4} *N*.

The measurements of electrophoretic mobility show that the change of positive particle charge occurs in the moment when the silver iodide sol in the presence of fluoresceinate begins to flocculate or in the region of flocculation maximum.

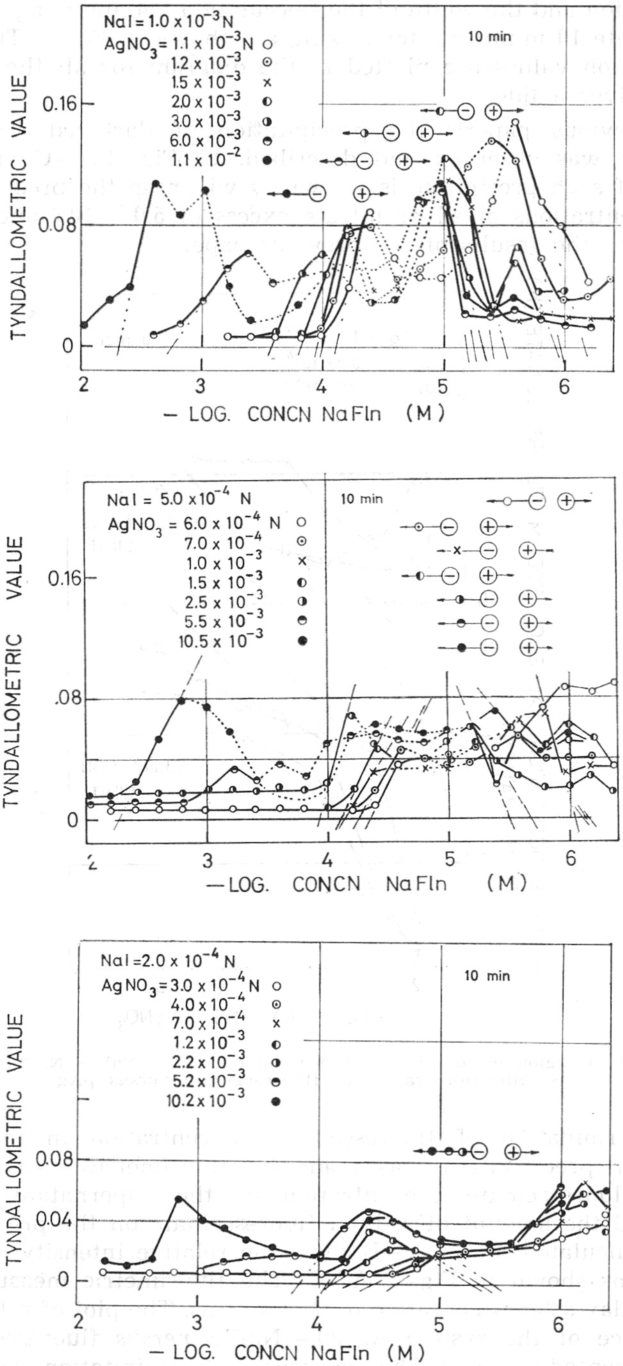

Fig. 1 A—C. The precipitation action of sodium fluoresceinate in the system $AgNO_3$ (in excess) — NaI — NaFln (10-minutes diagrams). Dotted lines indicate the precipitated systems, for which the tyndallometric values are not real.

The position and the width of the flocculation maximum against the excess of silver nitrate 10 minutes after mixing are shown in Fig. 2. The flocculation and stabilization values are plotted in the diagram for all the three concentrations of silver iodide.

In a previous paper[15] the precipitation of dark-red flocks of silver fluoresceinate was observed and described. In Fig. 1 A—C and Fig. 2 the appearance of such precipitate is shown by widening the precipitation region for the concentrations of silver nitrate excess of 5.0×10^{-3} and 1.0×10^{-2} *N*, thus extending the results of the previous paper.

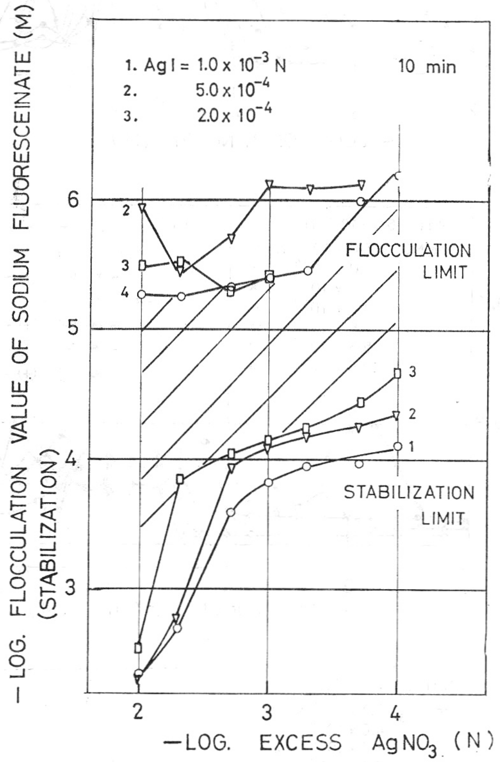

Fig. 2. Precipitation region in the system $AgNO_3$ (in excess) — NaI — NaFln. Flocculation and stabilization values of fluoresceinate *versus* pAg.

The determination of fluoresceinate concentration in the supernatant solution after precipitation was made by fluorimetric measurements. The change of fluoresceinate concentration of the supernatant solution was measured and the amount of sodium fluoresceinate on the precipitated silver iodide was calculated. Fig. 3 A—B show the relative intensity of fluorescence of the systems shown in Fig. 1 A—C. The fluorimetric measurements were performed 1 day after preparation of the systems. The plot of relative intensity of fluorescence of the system $AgNO_3$—NaFln *versus* fluoresceinate concentration is presented in Fig. 4. The appearence of precipitation was not observed in this system, and the fluorescence was measured in the clear solutions. Comparison of the intensity of fluorescence for the systems with and without

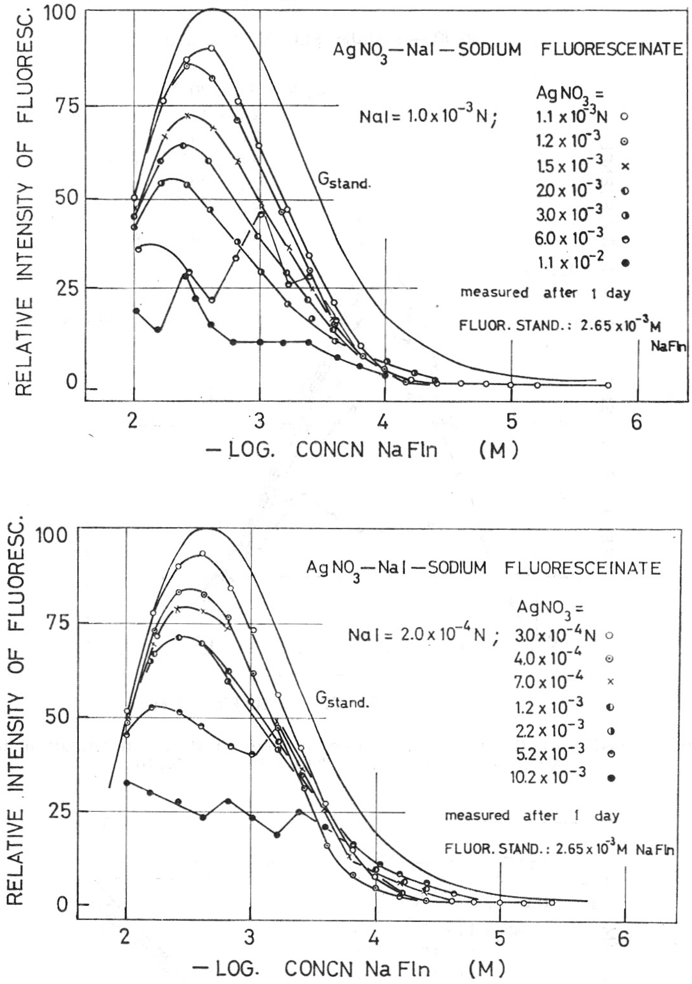

Fig. 3 A—B. Relative intensity of fluorescence in dependence on dye concentration in the system $AgNO_3$ (in excess) — NaI — NaFln. G_{stand} is the fluorescence of standard solution (2.65×10^{-3} *M* NaFln).

sodium iodide (Fig. 3 A—B) indicates a difference between these curves (the silver nitrate concentration is the same in both cases). The intensity of fluorescence is smaller when: (a) sodium iodide is present in the system; (b) the concentration of silver iodide is greater, and (c) the excess of silver nitrate increases. The small diminution of maxima in the system consisting of silver nitrate and sodium fluoresceinate is due to the formation of non-fluorescent silver fluoresceinate in the solution[15]. The amount of fluoresceinate adsorbed on the surface of silver iodide is calculated from the difference between the fluorescence of standard solution and of the system measured, and the values are plotted *versus* the concentration of fluoresceinate in the system before mixing the components. The logarithm of the amount of fluoresceinate adsorbed on silver iodide, calculated from relative

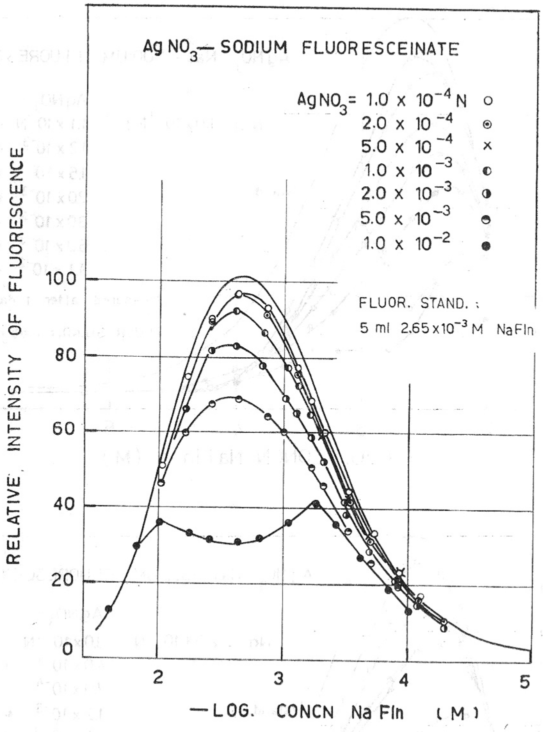

Fig. 4. Relative intensity of fluorescence in dependence on dye concentration in the system $AgNO_3$—NaFln. $G_{stand} = 2.65 \times 10^{-3}$ *M* NaFln.

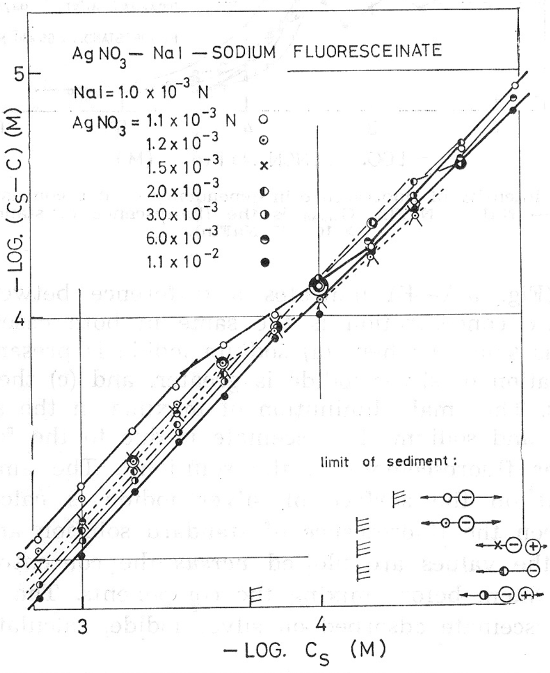

Fig. 5. Plot of the amount of fluoresceinate adsorbed on AgI ($c_6 - c$) *versus* fluoressceinate concentration c_s (c = concentration of fluoresceinate in supernatant solution).

intensity of fluorescence, to the logarithm of initial fluoresceinate concentrations shows a linear relationship (Fig. 5).

The fluorimetric titration (Fig. 6) in the system consisting of silver nitrate, sodium iodide and sodium fluoresceinate is performed by parallel tyndallometric, potentiometric and fluorimetric measurements for two different concentrations of the silver iodide sol (1.0×10^{-3} and 1.0×10^{-2} *N*) and 1.0×10^{-3} *M* of sodium fluoresceinate. The change of the fluorescence intensity occurs, regardless of the concentration of silver iodide sol, at *p*Ag 5. This point has the meaning of the titration end-point.

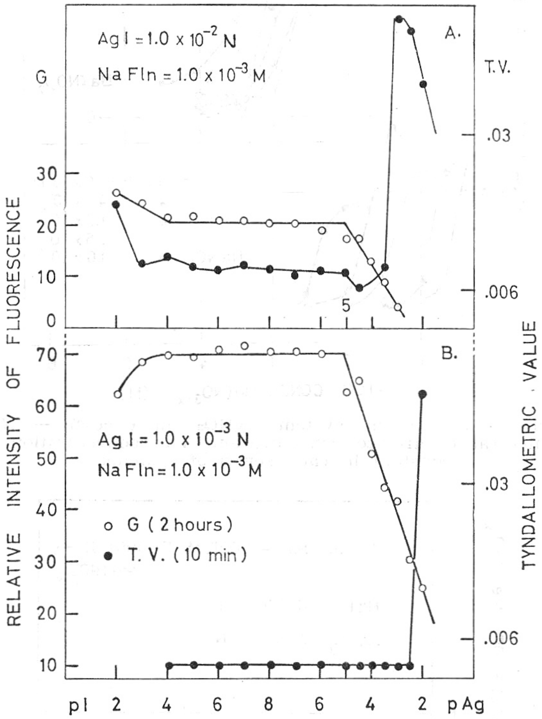

Fig. 6. Change of the relative intensity of fluorescence and of the turbidity in the system $AgNO_3$—NaI—NaFln in dependence on *p*Ag and *p*I, respectively.

The reversal of charge of silver iodide sol in the presence of stabilizing concentration of sodium fluoresceinate is proved by ultramicroscopic electrophoretic observations which show the change of charge in the flocculation maximum.

The positive systems of silver iodide stabilized by negative fluoresceinate ions have been coagulated in the presence of neutral electrolytes $Na(NO_3)$, $Ba(NO_3)_2$ and $La(NO_3)_3$. The results are presented in Fig. 7 for the positive sol consisting of 1.0×10^{-3} *N* sodium iodide and 2.0×10^{-3} *N* excess of silver nitrate. The concentrations of fluoresceinate and neutral electrolyte are proportional. The coagulation values of neutral electrolytes in the presence of fluoresceinate show a linear relationship (Fig. 8) and are in agreement with the Schulze-Hardy rule.

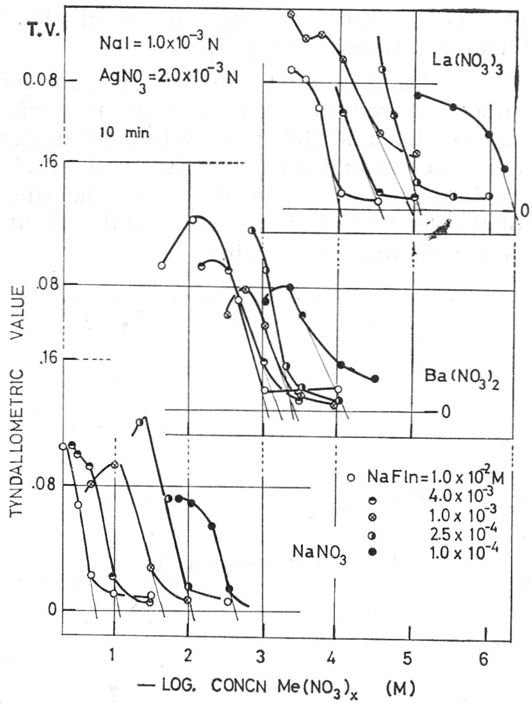

Fig. 7. Tyndallometric values in the system $AgNO_3$ (in excess) — NaI—NaFln—Me(($x = 1, 2, 3$) *versus* neutral electrolyte concentration. The concentration of fluorescein constant in each series of systems.

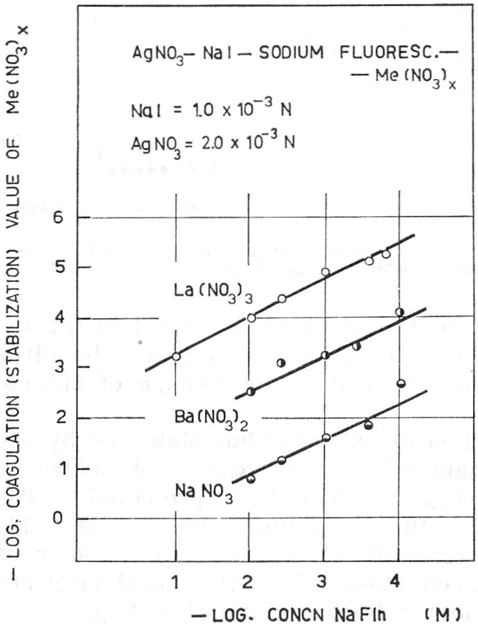

Fig. 8. The coagulation values of neutral electrolytes in the system of Fig. 7.

DISCUSSION

Fajans' theory of adsorption indicators involves adsorption of dyes on a surface of opposite charge as well as the formation of a dye — silver salt.

Pungor and Schulek[9] proposed the acid — base mechanism of surface-precipitation indicators. The main process is the formation of the indicator-dye silver salt on the surface of silver halide particles, due to the fact that the solubility product on the surface is exceeded before that in the bulk solution.

Our conception of the mechanism of the action of adsorption indicators of the Fajans' type is more complex and is based on the investigation of precipitation phenomena. It involves the following: the stereospecific adsorption of fluoresceinate, the flocculation of silver iodide, the reversal of charge and the stabilization, the precipitation of silver fluoresceinate on the surface of silver iodide and in the bulk solution, *i. e.* the coprecipitation of various ionic species. This approach can explain all the phenomena shown systematically on the diagrams presented in this paper, *i. e.* the relationship between the adsorbed amount of sodium fluoresceinate and precipitation effects of silver iodide in the presence of sodium fluoresceinate. Comparing the flocculation values of fluoresceinate with coagulation values of small organic ions[16], it can be seen that the flocculation values of fluoresceinate are in the region of small concentrations of 6×10^{-7} to 6×10^{-6} *M*. These values are smaller even than the coagulation value of tetravalent thorium or citrate ion. The coagulation in the presence of inorganic cations involves the ion-pair formation at the surface of the colloid [17], while the flocculation[18] in the presence of large organic ions is caused by stereoadsorption. When the flocculation value is exceeded, the concentration of fluoresceinate on the colloid surface increases and is accompanied with reversal of charge, *i. e.* stabilization, which was proved by ultramicroscopic electrophoretic measurements. The coagulation of such silver iodide in the presence of neutral electrolytes is in agreement with the Schulze-Hardy rule.

The fluorimetric titration in the system consisting of sodium iodide, silver nitrate and sodium fluoresceinate determines the end-point of titration at *p*Ag 5. This fact is in good agreement with the observations of Kolthoff and Lingane[19] of the adsorption of silver- and iodide ions on freshly precipitated silver iodide. Such silver iodide has the isoelectric point at *p*Ag 5.7. These facts are also in agreement with the observations of Mirnik and Flajšman[20] on the electrophoretic mobility of aged silver iodide. The zero-point of electrophoretic mobility for four-hours aged systems was found to be at *p*Ag 5.3, and was moved to *p*Ag 4.3 after aging of four days.

The calculated values of the amount of fluoresceinate adsorbed on AgI (AgI = 1.0×10^{-3} *N*) during the flocculation and stabilization processes when plotted *versus* the initial concentration of fluoresceinate are on a straight line. The values of the adsorbed amount of fluoresceinate [$\log (c_s - c)$] at *p*Ag 4.0 and the initial concentration of fluoresceinate from 10^{-5} to 6×10^{-5} *M* amount to about 80%. The change of the slope indicates a change from the flocculation to the stabilization region. In the stabilization region between 6.0×10^{-5} and 2.5×10^{-4} *M* of fluoresceinate the adsorbed amount was found to vary from 80 to 50%. When the concentration of fluoresceinate exceeds 2.5×10^{-4} *M* only 50% of fluoresceinate was adsorbed on the surface of AgI-particles regardless of the further fluoresceinate concentration increase.

Under these conditions the maximum of adsorption was reached. With increasing excess of silver nitrate (pAg 3.3) 98% of fluoresceinate disappeared from the solution during the process of flocculation. As the concentration of fluoresceinate in this precipitation system increased, the adsorbed amount decreased to the constant value of 70% (at 2.5×10^{-1} M NaFln).

If the excess of silver nitrate becomes 10^{-2} N, the values of adsorbed fluoresceinate during the process of flocculation (in the maximum) amount 100%; with increased concentration of fluoresceinate the adsorbed amount is about 85%; with further increase of fluoresceinate concentration the amount is 100% as a result of precipitation of silver fluoresceinate.

CONCLUSION

The adsorption and precipitation phenomena in the systems consisting of silver nitrate, sodium iodide and sodium fluoresceinate were investigated by means of tyndallometric, fluorimetric and electrophoretic measurements.

The flocculation and stabilization of silver iodide in the presence of fluoresceinate are due to specific adsorption on the silver iodide particles. The results show the relationship between the precipitation phenomena and increasing concentration of fluoresceinate and silver iodide sol. The end-point of fluorometric titration at pAg 5 is in good agreement with the results of tyndallometric and electrophoretic observations and with the results of other authors.

Fluoresceinate concentration was determined by fluorimetric measurements and the amount of fluoresceinate adsorbed on AgI-particles during the process of flocculation and stabilization was calculated.

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IZVOD

Metorika precipitacionih procesa. XXI. Flokulacioni i stabilizacioni efekti natrium fluoresceinata na solove pozitivnog argentum jodida *in statu nascendi*

Đ. Težak i B. Težak

Flokulaciono i stabilizaciono djelovanje natrium-fluoresceinata na solove argentum jodida bilo je ispitivano pomoću tindalometrijskih, fluorometrijskih i elektroforetskih mjerenja. Određene su granice precipitacionog područja i izračunate adsorbirane količine fluoresceinata na česticama argentum-jodida. Činjenica da završna tačka fluorometrijske titracije ispitivanog sistema leži kod pAg 5 pokazuje dobro slaganje rezultata tindalometrijskih i elektroforetskih mjerenja s ispitivanjima drugih autora.

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