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Original Scientific Paper

Methorics of the Precipitation Processes. XX. Silver Salts of Dyes of the Fluorescein Group (Fluorescein, Eosin, and Erythrosin) in Aqueous Medium

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The precipitation systems consisting of aqueous solutions of silver nitrate and the dyes of the fluorescein group (fluorescein, eosin, and erythrosin) have been investigated by means of tyndallometric measurements by systematically varying the concentration of the precipitating components. The general and three-dimensional precipitation diagrams of the »precipitation bodies« show very characteristic features. The silver fluoresceinate shows two regions; the precipitation region and the region of clear systems are divided by a straight line with the slope indicating the formation of Ag_2-fluoresceinate in accordance with the ionic solubility law. The silver eosinate systems show two precipitation regions divided by a narrow region of clear systems. With respect to both the limits of the clear equivalency region and the two precipitation regions, the silver erythrosinate systems are even more specific. An attempt has been made to give an explanation for the negative charges of primary particles in spite of the large excess of silver ion, as well as for the characteristic shape of the »precipitation bodies«.

INTRODUCTION

Although the precipitation systems consisting of silver nitrate and the dyes of the fluorescein group in aqueous medium are frequently used as indicators in analytical chemistry, their physical and chemical characteristics were scarcely investigated. Therefore, it was thought to be of interest to investigate the reaction between silver ions and the following dyes:

(1) uranin (disodium salt of fluorescein);

(2) eosin (disodium salt of tetrabromofluorescein);

(3) erythrosin B (disodium salt of tetraiodofluorescein).

Several authors[1-4,7] have mentioned different silver salts of these dyes and W. Pohl[6] has determined their solubility products. It seemed to be of interest to investigate the interaction between silver ions and these dyes in aqueous solution over a wide range of concentrations by means of tyndallometric and fluorometric measurements and to compare the behaviour of such systems with those of silver halides as well as with systems where the oppositely charged large organic ions are interacting.

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EXPERIMENTAL

The turbidity measurements were performed on a Zeiss tyndallometer in connection with a Pulfrich photometer and a red filter. Fluorometric measurements were made with a set consisting of a photoelectric fluorimeter (B. Lange), model G. A. 42), equipped with a mercury lamp (HGE 42) and a violet filter (for the isolation of spectral band 365 mμ), and a multiflex galvanometer (Lange MGF 4, sensitivity 6.85×10^{-10} A/mm). The *p*H- measurements were made with a Macbeth *p*H-meter — Macbeth Corp. New York, and a glass electrode. The sign of the charges of the particles formed was determined by ultramicroscopic electrophoretic observations. The concentrational limits of sediment formation were determined visually.

Reagents used were of »*AnalaR*« quality and were not purified further: sodium fluoresceinate (Basler Drogerie, Bohny & Cie A.—G., Basel), sodium eosinate (Adsorption Indicator — Hopkin & Williams Ltd.), erythrosin B (National Aniline Division Allied Chemicals & Dye Corporation, New York), silver nitrate (Pliva, Zagreb). The solutions were prepared with bidistilled water.

RESULTS

Silver Fluoresceinate System

Fig. 1 and Fig. 2 illustrate the interaction between silver nitrate and sodium fluoresceinate. Fig. 1 shows a typical precipitation system with the sodium fluoresceinate gradient ranging from 1.0×10^{-1} to 1.0×10^{-5} *M* and the constant silver nitrate concentration of 5.0×10^{-3} *N*. The precipitation phenomena are illustrated by the tyndallometric curve (10 min), the sediment height (mm) in the test-tube (1 hour and 1 day after the preparation of the systems), and the relative intensity of fluorescence of standard systems and systems under examination. The quantity of sediment increases with increasing

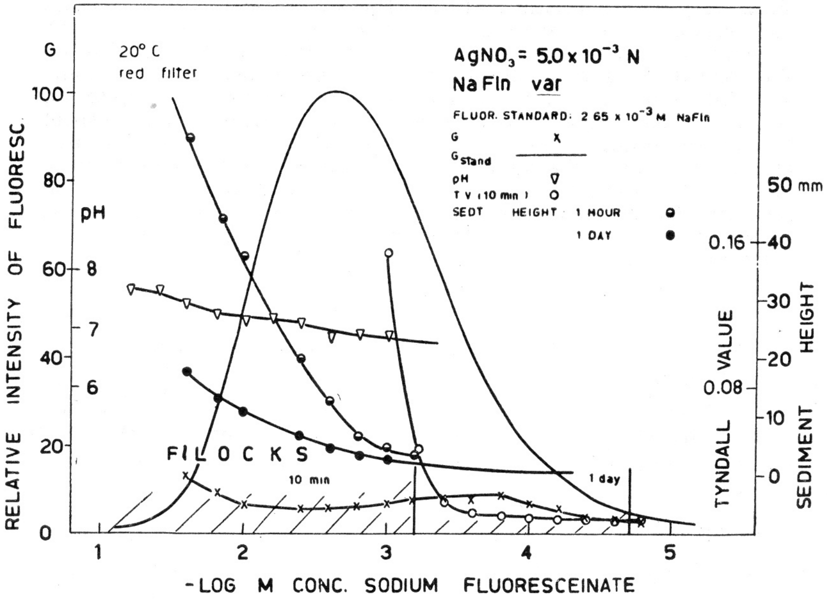

Fig. 1. Relative intensity of fluorescence and sediment height in the system $AgNO_3$ — sodium fluoresceinate as a function of dye concentration.

concentration while the fluorescence disappears at the same time. The shematic picture of the formation of silver salt is given by the general precipitation diagram shown in Fig. 2, where the negative logarithms of the sodium fluoresceinate concentration are plotted against the negative logarithms of silver nitrate concentration. One day after preparation of systems the precipitation values of systems with constant silver nitrate and different concentrations of sodium fluoresceinate give the limit of pink flocky sediment, the particle charges being always negative, even with large excess of silver nitrate.

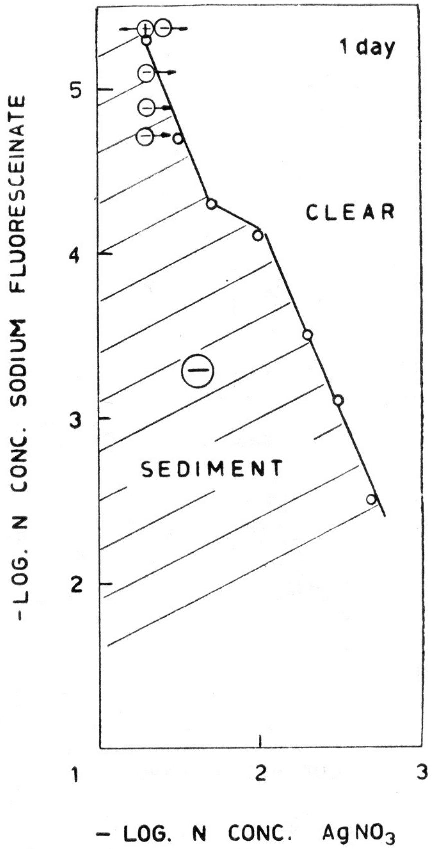

Fig. 2. General precipitation diagram:
axes x: — log. of $AgNO_3$ concentration;
y: — log. of sodium fluoresceinate concentration.

Silver Eosinate System

The system consisting of silver nitrate and sodium eosinate shows little similarity with that of silver nitrate and sodium fluoresceinate. The general picture of the formation of silver salt is shown in Fig. 3, by plotting —log of the sodium eosinate concentration against —log of the silver nitrate concentration. Two kinds of sediment appear divided by the narrow region of clear systems between them. The trend of the region of clear systems follows the equivalency until the concentration 1.0 × 10^{-2} *N* of both components is reached, then the limits of the reddish violet clear systems proceed parallel with the y axis, and the precipitation becomes practically independent of the concentration of sodium eosinate. After mixing the solution of silver nitrate (1.0 × 10^{-2} *N*) with solutions of different concentrations of sodium eosinate (between 1.0 × 10^{-2} and 1.0 × $^{-5}$ *N*) the red flocks precipitated very quickly.

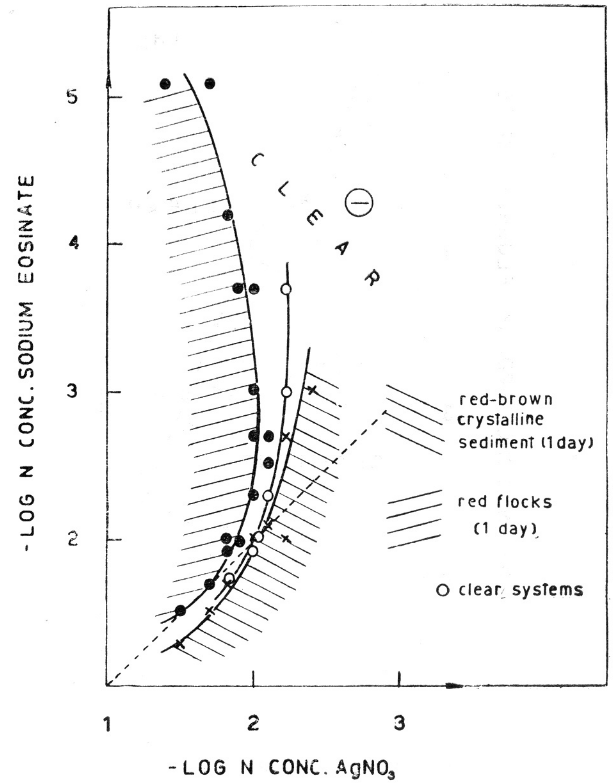

Fig. 3. General precipitation diagram:
axes x: — log. of $AgNO_3$ concentration;
y: — log. of sodium eosinate concentration.

In the excess of sodium eosinate a reddish brown-crystalline precipitate is formed the sedimentation velocity of which is very small. The particle charges of the clear systems as well as of those of both kinds of sediments are negative. *p*H values of these systems were in the range between 4.5 and 6.5.

Silver Erythrosinate System

Precipitation phenomena in the system consisting of silver nitrate and sodium erythrosinate were also investigated by mixing their aqueous solutions and observing the turbidity change after fixed time intervals. Fig. 4 shows the general precipitation diagram, *i. e.* the tyndallometric value as a function of both the silver nitrate concentration (3.0 × 10^{-2} to 3.0 × 10^{-5} *N*) and the sodium erythrosinate concentration (3.0×10^{-1} to 3.0×10^{-6} N). Two different precipitation regions of silver erythrosinate can be clearly seen, one in the excess of silver nitrate, and the other in the excess of sodium erythrosinate, whereas in the equivalency region these systems are clear even 1 or 2 days after their preparation.* The sedimentation limits are also shown. The kind of the sediment depends on the excess of either silver nitrate or sodium erythrosinate in solution. In the excess of silver nitrate reddish violet flocks were observed, the sedimentation velocity of these precipitates being quite high. In the excess of sodium erythrosinate the precipitation proceeds quite differently: the tyndallometric values of such systems increase very slowly giving after about 24 hours tyndallometric curves with very pronounced maxima while in the solution fine gold-yellow silk-like particles are formed simultaneously. After 1 or 2 days these settled on the bottom of the test tube in the form of a gold-yellow layer, the sediments over this layer being red and silk-like.

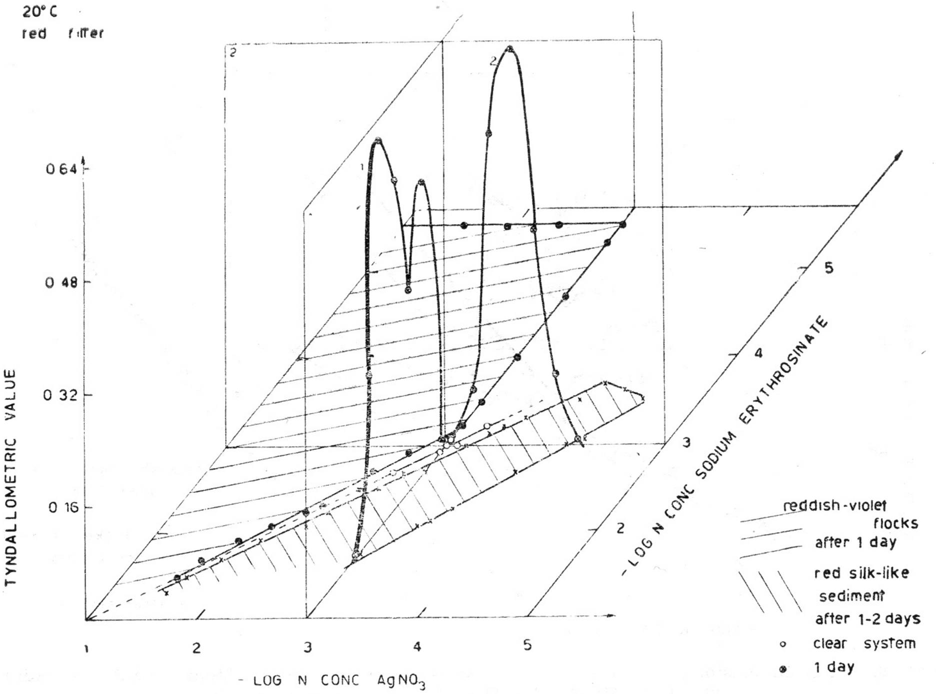

Fig. 4. Three-dimensional diagram: tyndallometric values of the system $AgNO_3$ — sodium erythrosinate.

Fig. 5 corresponds to Fig. 4 showing the sedimentation velocity of silver erythrosinate in the region of excess of silver nitrate. The sediment height

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* The quantitative analysis of the precipitates of silver erythrosinate in the regions of the precipitation maxima has been made, but the results are not quite conclusive. Instead of 2 Ag in the molecule the results of the analysis show 3 Ag for the Ag-erythrosinate prepared in the excess of silver ions, and 2.7 Ag for the Ag-erythrosinate obtained in the excess of erythrosinate ions.

(in mm) in the test tubes has been plotted against the concentration of silver nitrate and sodium erythrosinate (1 minute and 16 hours after the preparation of the systems). While the quantity of sediment depends on the concentration of sodium erythrosinate, the limit seems to be practically the same over a wide range of silver nitrate concentrations.

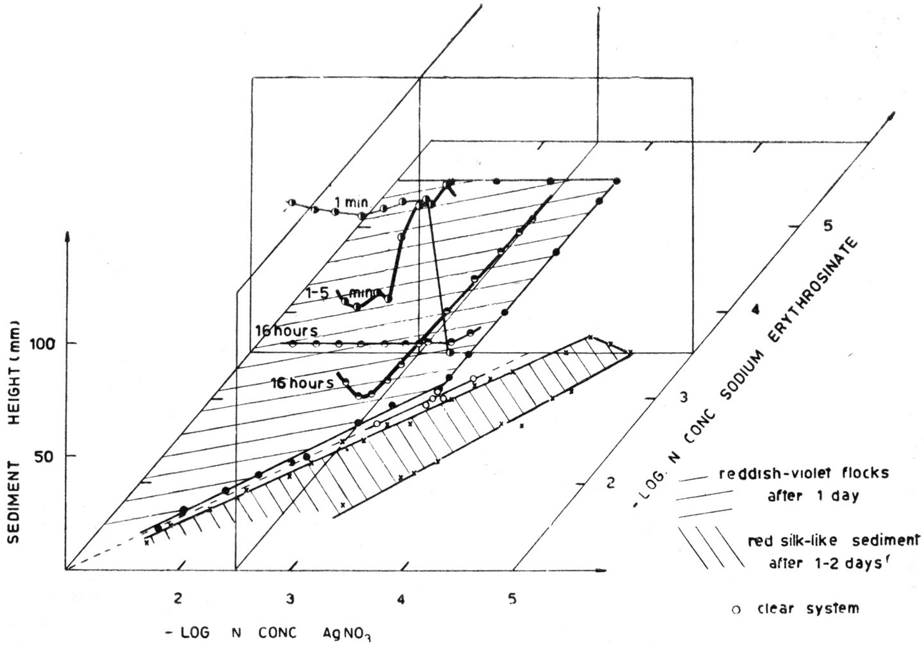

Fig. 5. Three-dimensional diagram: height of sediment in the system $AgNO_3$ — sodium erythrosinate after various times of measurements.

The Fig. 6 gives the ground-plane of the three-dimensional precipitation diagram using the data of Fig. 4 and 5 and representing a shematic picture of the silver erythrosinate sedimentation in the excess of silver nitrate as a function of time. The sedimentation limits for 1 minute, 20 minutes, 1 hour and 1 day are also given. These limits are very steep, being parallel with the axis as well. They remain constant for a large gradient of silver nitrate concentrations (between 1.0×10^{-1} and 1.0×10^{-3} N). With equivalent concentrations of both silver nitrate and sodium erythrosinate (1.0×10^{-3} N) there is a limit between the precipitated and the stable region. At higher concentrations of both components the limit lies close to the straight line marking the equivalency ratio. These systems are intensely coloured (reddish-violet) and some of them are sedimenting only after 2 or more days. By addition of neutral electrolytes [$NaNO_3$, $Mg(NO_3)_2$, $La(NO_3)_3$] it has been shown that the Schulze-Hardy rule (Fig. 7) is followed.

The charges of these systems are negative both in the equivalency region and on its sides. Only in a narrow region with large excess of silver nitrate (Fig. 6) the charges become positive (silver nitrate $1.5 \times 10^{-2}N$; sodium erythrosinate 1.0×10^{-4} *N*). In the region with excess erythrosinate ion there is a wide band of red silk-like precipitating systems parallel with the equivalency line.

*p*H-values of systems consisting of silver erythrosinate amounted to 5.5—7.

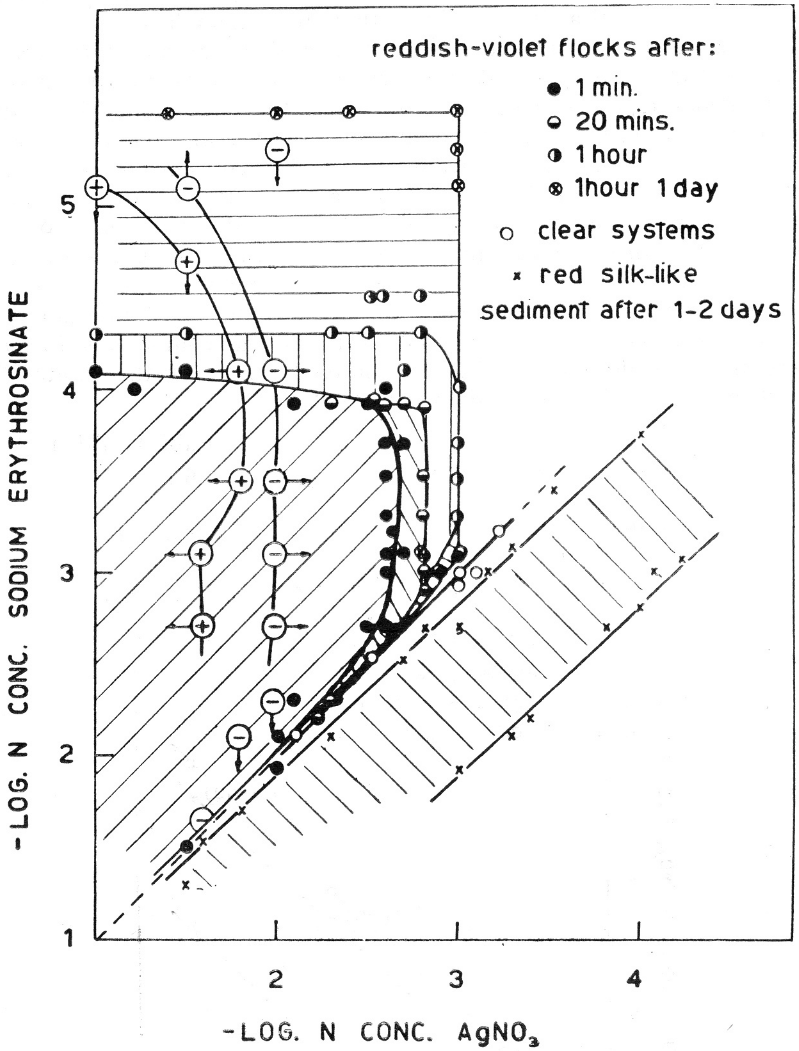

Fig. 6. General precipitation diagram:
axes x: — log. of $AgNO_3$ concentration
y: — log. of sodium erythrosinate concentration.

DISCUSSION

The best overall picture of the differences and similarities between the investigated systems can be obtained by comparing their general precipitation diagrams. While the silver fluoresceinate systems show two regions, one of precipitates and the other of clear solutions, divided by a nearly straight line indicating the composition of the Ag_2-fluoresceinate precipitate in accordance with the ionic solubility law, the systems of silver eosinate and erythrosinate behave in a quite peculiar way. Firstly, a narrow region appeares which follows, more or less, the equivalency relationship of the two precipitating components; secondly, the precipitates in the two regions differ in their physical appearance as well as in the rate of their formation. The systems of silver eosinate seem to be transitional ones between those of silver fluoresceinate and silver erythrosinate. The latter show not only the regularity in dividing the precipitation region by clear systems along the equivalency line, but also the characteristic limits of the precipitation regions; in excess of silver ions these are limited by constant concentrations of silver ions on one side, and constant concentrations of erythrosinate ions on the other; in excess of erythrosinate ions the limit is given by the stretch along the clear equivalent systems. It should also be taken into account that all systems are preferentially negative even in large excess of silver ions owing to the great differences in the size between the large organic anion and the small inorganic cation. These differences as well as the insolubility of the compounds formed are increasing in the order: silver fluoresceinate, eosinate, erythrosinate. This is illustrated by the results obtained by W. Pohl[6]:

	Solubility (*M*/l)
Ag-fluoresceinate	6.1×10^{-4}
Ag-eosinate	1.1×10^{-5}
Ag-erythrosinate	5.8×10^{-6}

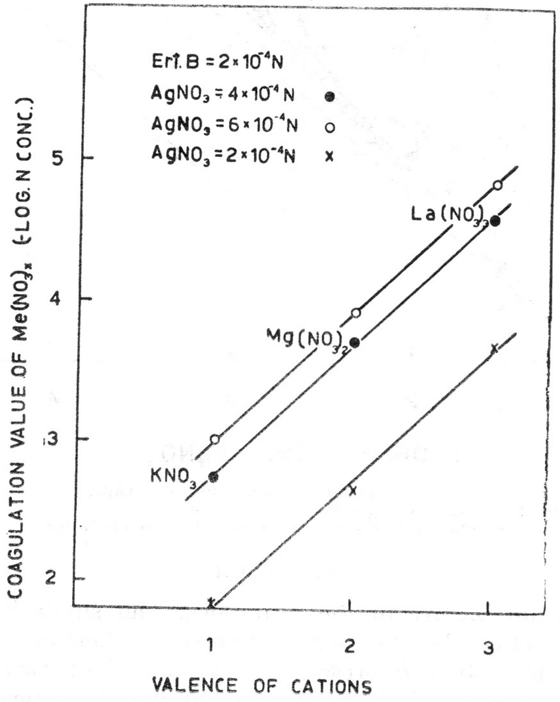

Fig. 7. Coagulation values of KNO_3, $Mg(NO_3)_2$ and $La(NO_3)_3$ in the system $AgNO_3$ — sodium erythrosinate as a function of the valence of cations.

Thus, the velocity of nucleation may be quite different in various regions where the relationship between the concentrations of precipitating ions differ. This mechanism of nucleation and the subsequent growth or stabilization of the primary particles can be taken as an explanation for the formation of the precipitation region in excess of erythrosinate. In the equivalency region such velocity in nuclei formation may be highest with resulting exhaustion of the precipitating substance. Therefore the »equivalent bodies« do not represent systems of isoelectric point, and such stable systems may be coagulated by uni-, bi-, and trivalent cations following the Schulze-Hardy rule (Fig. 7). In excess of silver ions the erythrosinate systems may be limited by the presence of ionic associates or silver erythrosinate molecules in solution and a methorical layer of the agglomerating particles, all this in spite of the charges resulting from dissymetry of the precipitating ions.

If we wish to compare our systems as exemplified by silver erythrosinate to other sparingly soluble silver salts, then, as the most characteristic feature, the fact should be taken that charges of the primary particles are of quite negligeable effect against the other constitutive properties of the precipitating ions. The inverse phenomenon observed (clear systems dividing two precipitation regions) instead of the usual precipitation maximum in equivalency region, may also be used as some proof for such a statement.

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IZVOD

Metorika precipitacionih procesa. XX. Srebrne soli boja fluoresceinske grupe (fluoresceina, eozina, eritrozina) u vodenomu mediju

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Precipitacioni sistemi srebrnog nitrata i boja fluoresceinske grupe (fluoresceina, eozina i eritrozina) u vodenim otopinama ispitivani su tindalometrijski uz sistematsko variranje koncentracija precipitacionih komponenata. Opći i trodimenzionalni precipitacioni diagrami »precipitacionih tijela« pokazuju karakteristična svojstva. Kod srebrnoga fluoresceinata pojavljuju se dva područja; precipitaciono područje i područje bistrih sistema koji su međusobno odijeljeni pravcem. Nagib pravca upućuje na stvaranje Ag_2-fluoresceinata u skladu sa zakonom produkta topljivosti. Srebrni eozinat pokazuje dva precipitaciona područja, odijeljena uskim područjem bistrih sistema. U pogledu granica bistrih i precipitiranih sistema srebrni eritrozinat je još specifičniji. Učinjen je pokušaj za objašnjenje negativnoga naboja čestica usprkos velikoga suviška srebrnih iona, kao i za karakteristična svojstva »precipitacionih tijela«.

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