CCA-428

543.243:547.942:546.571.51
Original Scientific Paper

Methorics of the Precipitation Processes. XXI. Flocculation and Stabilization Effect of Quinine Sulphate on Silver Iodide Hydrosol *In Statu Nascendi*

N. Galešić and B. Težak*

Laboratory of Physical Chemistry, Faculty of Science,
University of Zagreb, Croatia, Yugoslavia

Received April 29, 1966

The action of quinine sulphate on the precipitation of silver iodide in aqueous medium is investigated. Using the tyndallometric technique it is found that for quinine sulphate the critical concentrations of flocculation increase from approximately 2×10^{-6} to 1.3×10^{-5} *N*, and the critical concentrations of stabilization from approximately 4×10^{-5} to 3×10^{-4} *N*, and are dependent on both the increase in the silver iodide concentration (from 1×10^{-4} to 1×10^{-3} *M*) and the sodium iodide excess (from 1×10^{-6} to 1×10^{-2} *M*). In the region of stabilization, quinine sulphate reverses the negative sol to a positive one. Its action on the positive sols is also stabilizing. Univalent and divalent quinine exhibit approximately equal behaviour in their interaction with silver iodide sol. The results of the observed phenomena indicate that the adsorption ability of quinine sulphate is of primary and its ionic—coulombic action of secondary importance.

The flocculation and stabilization action of large organic ions on silver halide sols *in statu nascendi* have been investigated by several authors[1-3]. It appears that, as well as coulombic forces, adsorption forces play an important role in the process of precipitation[2]. We have attempted to re-examine this problem. For the large organic ion, we chose the univalent quinine cation from quinine sulphate — $C_{20}H_{24}N_2O_2) \cdot H_2SO_4 \cdot 2H_2O$, and the divalent quinine cation from quinine bisulphate — $C_{20}H_{24}N_2O_2 \cdot H_2SO_4 \cdot 7H_2O$. The stabilization action of quinine salts on silver halide sols has been established by Herculano de Carvalho[4].

EXPERIMENTAL

The measurements were performed by a tyndallometric method[5]. The values obtained using the green filter are presented in the figures. Additionally, the determinations of the sign of the charge of colloidal particles, *p*H, and relative intensity of fluorescence were performed. For tyndallometric measurements the *Zeiss* tyndallometer in connection with a *Pulfrich* photometer were used. Fluorometric measurements were made with a set consisting of a photoelectric fluorimeter (*B. Lange*, model G. A. 42), equipped with a mercury lamp (HQE 42), and a violet filter (for the isolation of the spectral band at 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*

---

* Taken in part from M. Sc. thesis submitted to the University of Zagreb, Zagreb, Yugoslavia.

** Contribution No. 130 of the Laboratory of Physical Chemistry.

pH-meter — Macbeth Corp. New York, and a glass electrode. The sign of the charges of the particles formed was determined by ultramicroscopic electrophoretic observations.

RESULTS

The action of quinine sulphate on negative silver iodide sols was observed in the concentration gradient of quinine sulphate from about 5×10^{-7} to 2.5×10^{-3} *N*. The silver iodide concentration was varied from 1×10^{-4} to 1×10^{-3} *M*, and the concentration of the excess sodium iodide from 1×10^{-6} to 1×10^{-2} *M*.

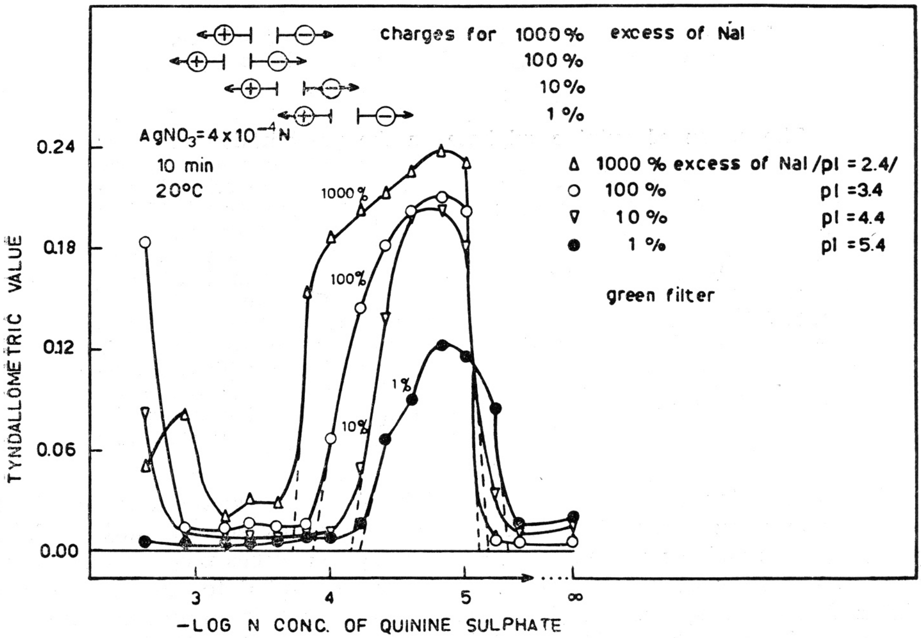

Fig. 1. Typical 10 min. concentration tyndallograms of the system $AgNO_3$-NaI-quinine sulphate in excess sodium iodide.

The tyndallometric curves in Fig. 1 depict some regions of quinine sulphate activity: the region illustrating no visible effect, the region of flocculation, the region of stabilization in which the sign of the sol charge is reversed, and the region illustrating a coagulation effect of the sulphate ion (above about 1×10^{-3} *N* quinine sulphate). In dependence of the concentration of silver iodide sol and the sodium iodide excess, the critical concentrations of flocculation (c. c. f.) of quinine sulphate changed from about 2×10^{-6} to 1.3×10^{-5} *N*, and the critical concentrations of stabilization (c. c. s.) from about 4×10^{-5} to 3×10^{-4} *N* (Fig. 2). In Fig. 2 it is seen that generally, by increasing the sol concentration greater concentrations of quinine sulphate are necessary for the flocculation and stabilization of the sol; a similar effect is observed for increased concentrations of sodium iodide excess. At very high concentrations of sodium iodide excess (over 1×10^{-2} *M*) the matter is complicated by the fact that the complex solubility of silver iodide in sodium iodide is more pronounced[6].

The change of the sign of the charge of the sol from negative to positive, followed by electrophoretic observations in the region of stabilization by quinine sulphate (Fig. 1), was confirmed by the coagulation by nitrate and sulphate in that region (Fig. 3).

It is known that positive sols are less stable than negative ones — their turbidity grows more rapidly. In this case the effect of quinine sulphate is only one of stabilization (Fig. 4). The examination of the coagulation action of nitrate and sulphate on the systems of constant sol concentration (2×10^{-4} *M*), various excess concentrations of silver nitrate and of quinine sulphate concentrations show that with increasing concentrations of quinine sulphate, more of nitrate and sulphate is needed for coagulation (Fig. 5); a plot of their critical concentrations of coagulation (c. c. c.) *versus* quinine sulphate concentration is linear for a constant concentration of silver nitrate excess.

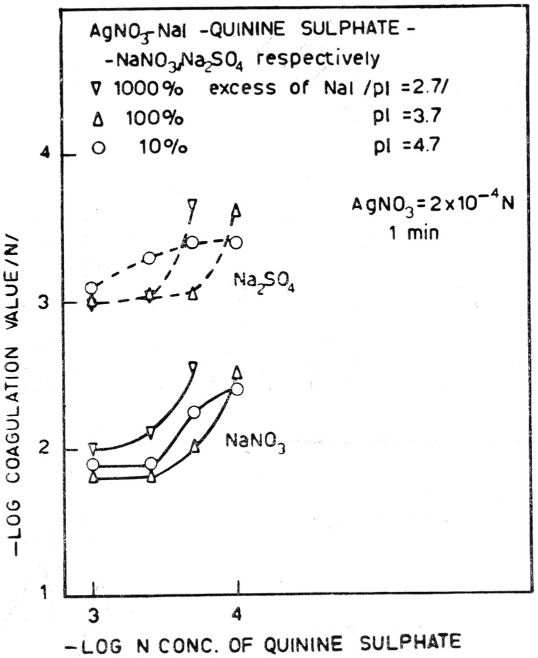

Fig. 2. Dependence of the critical concentrations of flocculation (c. c. f.) and critical concentrations of stabilization (c. c. s.) of quinine sulphate on sol concentration and excess sodium iodide.

The positive silver iodide sol in the presence of quinine sulphate, a few hours after mixing, becomes yellow-brown in colour. In the same time, the *p*H decreases for the higher quinine sulphate concentrations (greater than about 1×10^{-5} *N*), while the intensity of fluorescence increases. The aqueous solution of quinine sulphate is neutral, and of quinine bisulphate is acid (for 1×10^{-2} *N*, the *p*H is about 3.3), which on dilution becomes neutral. The *p*H--values, measured one day after mixing of the systems depicted in Fig. 4, are: 6.5 for 1×10^{-6} *N*, 6.0 for 1×10^{-5} *N*, and 5.0 for 1×10^{-4} *N* quinine sulphate. By further increasing the quinine sulphate concentrations, the *p*H slightly

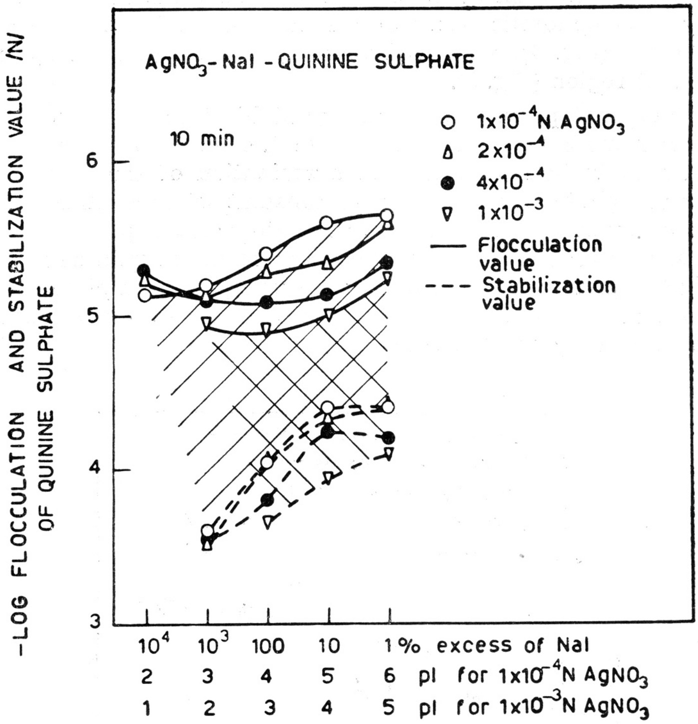

Fig. 3. The coagulation effect of nitrate and sulphate on primary negative silver iodide sol in dependence on quinine sulphate concentration and excess sodium iodide. The concentrations of quinine sulphate are greater than the c. c. s.' s.

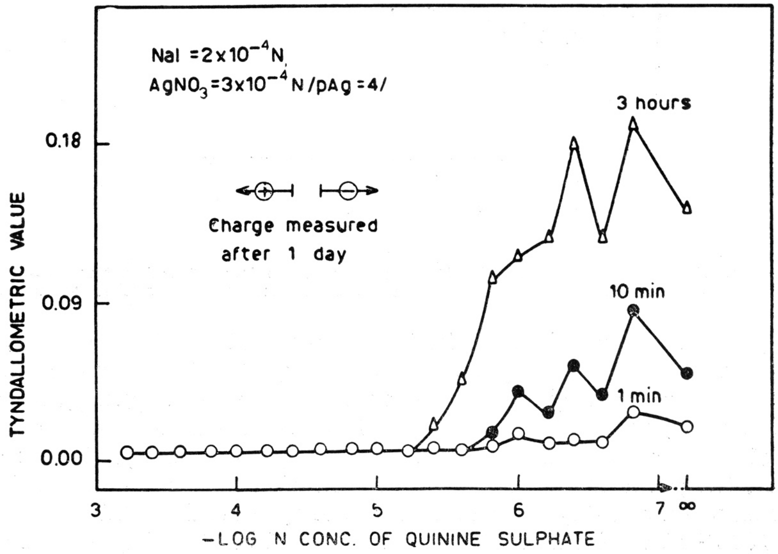

Fig. 4. Stabilization effect of quinine sulphate on positive silver iodide sol.

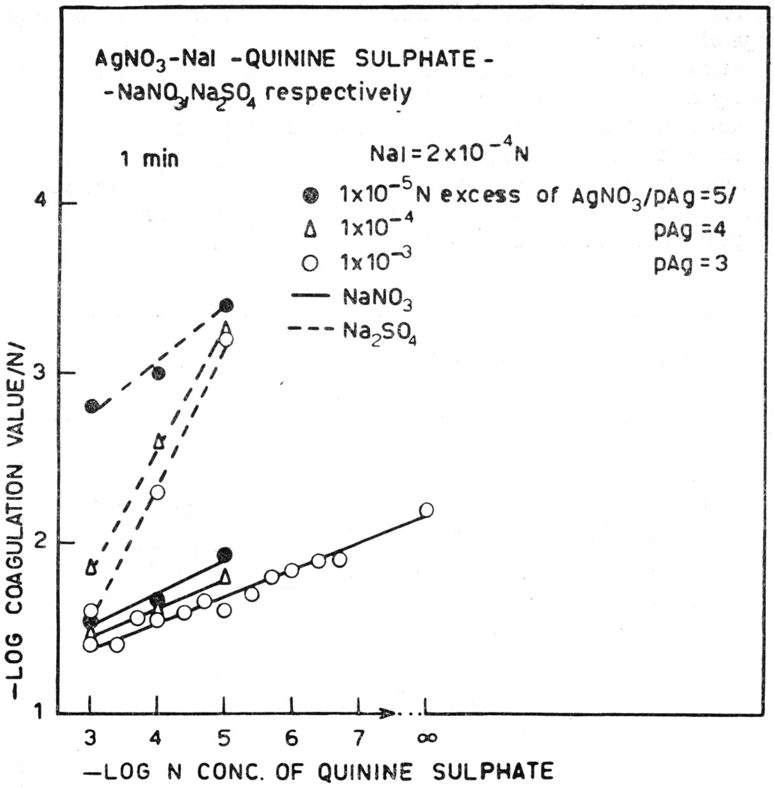

Fig. 5. Coagulation effect of nitrate and sulphate on positive silver iodide sol, in dependence on quinine sulphate concentration and excess silver nitrate.

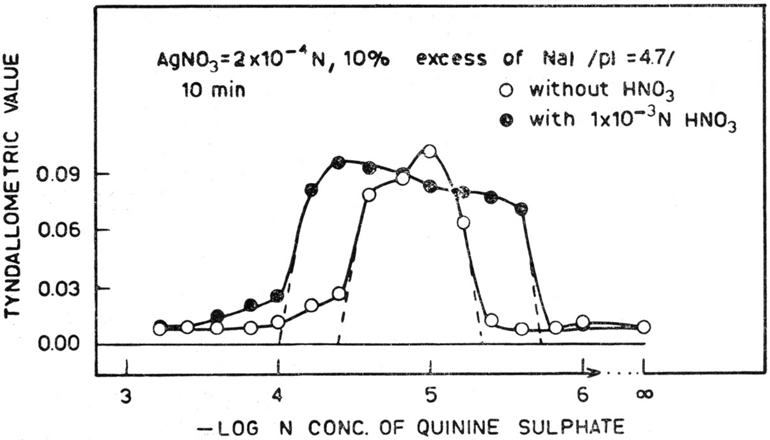

Fig. 6. Comparison of the effect of quinine sulphate with and without nitric acid (1×10^{-3} M HNO_3 in the total volume).

increased; for 6×10^{-4} *N* it was 5.3. The systems of quinine sulphate (over the entire range of concentration) and silver idodide sol in a excess of sodium iodide exhibit practically neutral *p*H. Quinine bisulphate, as well as quinine sulphate, produces only a stabilization to the positive sol. Its stabilizing action on 2×10^{-4} *M* silver iodide sol with an excess of 1×10^{-4} *M* silver nitrate takes place at concentrations greater than 6×10^{-4} *N* (10 minutes after mixing). In the range of quinine bisulphate concentration from 6×10^{-3} to 1×10^{-5} *N* the *p*H increased from 3.5 to 6.0. For further decreasing concentration of quinine bisulphate the *p*H stayed practically in the neutral region (about 6.3).

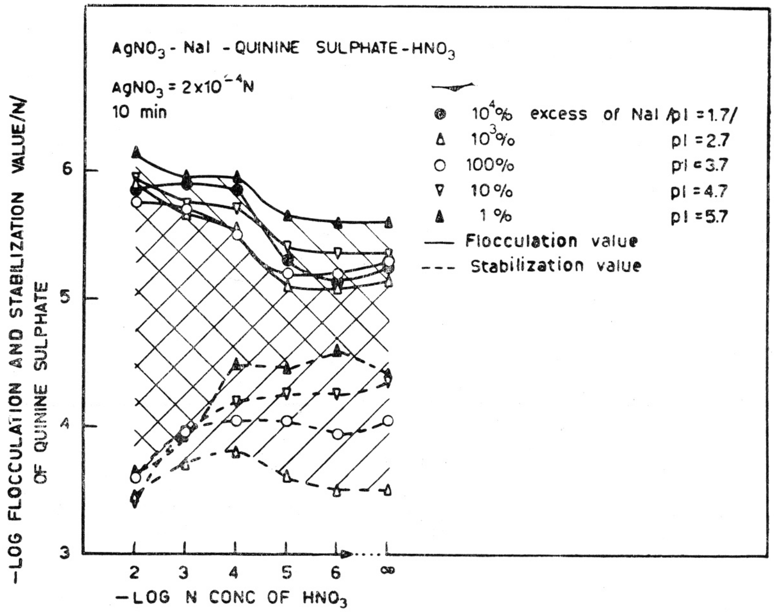

Fig. 7. Dependence of the c. c. f. and c. c. s. of quinine sulphate on nitric acid concentration and excess sodium iodide.

As is known, if an acid is added to a solution of quinine sulphate, the transition from a univalent to a divalent quinine cation takes place. In Figs. 6 to 8 it can be seen that the c. c. f. of quinine sulphate decreases, and the c. c. s. increases by addition of nitric acid. Systems in Fig. 7 were prepared in such a manner that constant concentrations of nitric acid (1×10^{-2}, 1×10^{-3}, 1×10^{-4}, 1×10^{-5}, and 1×10^{-6} *M* in the total volume) were maintained throughout the entire range og quinine sulphate concentrations. The c. c. f. decreases with an increase in nitric acid concentration from 1×10^{-5} to 1×10^{-4} *M*. This corresponds to a change in *p*H from approximately 5 to 4, as determined by *p*H-meter measurements. The c. c. s. increases with an increase in nitric acid concentration from 1×10^{-4} to over 1×10^{-3} *M*, and this corresponds approximately to a change of *p*H from 4 to less than 3. It is found from analogous experiments with quinine bisulphate that its c. c. f.'s are approximately in the neutral region, and its c. c. s.'s at approximately *p*H 4; as mentioned above, the changes in the c. c. f.'s and c. c. s.'s by a change of *p*H take place out of theese *p*H — values.

The *p*H-values corresponding to the systems presented in Fig. 8 are as follows: for case (1) the systems are neutral, for cases (2) to (4), the *p*H increases from 4 to neutral, and for cases (5) and (6) it is approximately 3 and 2, respectively. Univalent and divalent quinine ions exhibit approximately the same c. c. f.'s and c. c. s.'s (the curves 1, 2 and 4), within experimental error if the concentrations of quinine are the same, disregarding their charges.

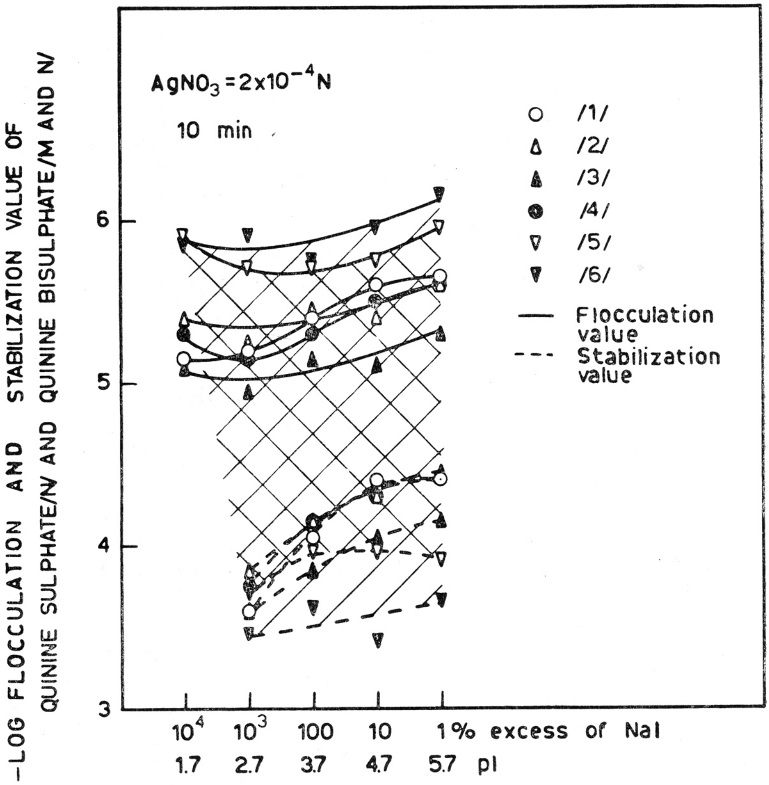

Fig. 8. Comparison of c. c. f.' s and c. c. s.' s of quinine sulphate, quinine bisulphate, and quinine sulphate acidified with nitric acid in different ways, in dependence on excess sodium iodide. (1) Systems with quinine sulphate (*N*); (2) systems with quinine bisulphate (*M*); (3) the same systems as in (2) but quinine bisulphate expressed in normal concentrations (*N*); (4) stock solution of quinine sulphate (1×10^{-2} *N*) acidified with nitric acid to give approximately the same *p*H-value as for the analogous concentrations of quinine bisulphate; (5) systems with quinine sulphate and 1×10^{-3} *M* nitric acid throughout the entire range of quinine sulphate concentrations; (6) the same systems as in (5), but with 1×10^{-2} *M* nitric acid.

Solutions of quinine sulphate have a faint violet, and of quinine bisulphate or acidified quinine sulphate a strong blue fluorescence. We attempted to make use of this phenomenon to estimate the adsorbed quinine sulphate on the sol, but for most cases, the relative intensities of fluorescence of solutions of pure quinine sulphate (bisulphate) and the corresponding clear solutions over the silver iodide sediment were indistinguishable, *i. e.*, it was within the limits of experimental error, and so this method proved unsuccessful.

DISCUSSION

If the term »coagulation« is used for the agglomeration processes caused mainly by coulombic interactions of ions, *i. e.* by formation of ion-pairs in the methoric region, and the term »flocculation« for aggregation processes caused by stereospecific adsorption forces (that is, similar to the proposal of La Mer *et al*[7].), then the activity of quinine sulphate is an intermediate one. Because the stereospecific adsorption of quinine sulphate in the systems in question is of major importance, the term »flocculation« is used.

The regions of flocculation and stabilization action of quinine sulphate (Fig. 1) are analogous to the previously described regions of the action of thorium nitrate on silver bromide sol[8, 9]. Matijević *et al.*[10] coagulated silver iodide sol (of which the primary positive sign of the charge was reversed by 9-tungstophosphoric acid) by means of K-, Ba-, Al-, and Th- ions. The increase in the critical concentrations of stabilization by an increase in positive and negative silver bromide sol concentrations was established by the action of different ionic and nonionic polymers[3]. Univalent and divalent strychnine ions exhibit also approximately equal critical values[11].

Our results indicate that the decrease in c. c. s. by sufficient addition of nitric acid, *i. e.*, by a sufficient decrease in *p*H, is due probably to the change in the quinine adsorption to the negative silver iodide sol, and not to the fact that at the same time univalent quinine is converted to divalent.

The change in *p*H, in the intensity of fluorescence, and in the colour of the systems by the action of quinine sulphate on the positive silver iodide sols is probably due to the formation of silver-quinine complexes. Frausto da Silva[12] established, by means of potentiometric titration with potassium hydroxide, the existence of various silver-quinine complexes in solutions of quinine bisulphate and silver nitrate ($C_{Ag} : S_Q = 1,10$ and 20; where Q represents quinine). He found that in the neutral solutions the predominant species was Ag_2Q_2, and suggested that this species was responsible for the stabilization of silver halogenides in the presence of quinine salts (established already by Herculano de Carvalho[4]).

The much lower c.c.f. of quinine sulphate than the corresponding c.c.c. of simple univalent inorganic cations, ability of sol stabilization, and the approximately equal behaviour of univalent and divalent species indicate that the adsorption ability of quinine sulphate plays the essential role, and that its ionic-coulombic action is overshadowed.

The fluorescence measurements, although not rendering supporting data, indicate that only a very small quantity of quinine is adsorbed on the silver iodide sol.

REFERENCES

1. J. Herak and B. Težak, *Arhiv kem.* **22** (1950) 49.
2. E. Matijević and R. H. Ottewill, *J. Colloid Sci.* **13** (1958) 242.
3. S. Kratohvil, B. Težak, and J. P. Kratohvil, *J. Colloid Sci.* **19** (1964) 373.
4. A. Herculano de Carvalho, *Comunicacao a Academia das Ciencias, Portugal* (November, 1932, and July, 1933), Cit. in Ref. 12.
5. B. Težak, E. Matijević, and K. Schulz, *J. Phys. & Colloid Chem.* **55** (1951) 1557.
6. K. Schulz and B. Težak, *Arhiv kem.* **23** (1951) 200.
7. K. La Mer and T. Healy, *J. Phys. Chem.* **67** (1963) 2417.
8. E. Matijević and B. Težak, *Arhiv kem.* **22** (1950) 62.

9. B. Težak, E. Matijević, and K. Schulz, *J. Am. Chem. Soc.* **73** (1951) 1602, 1605.
10. E. Matijević, D. Broadhurst, and M. Kerker, *J. Phys. Chem.* **63** (1959) 1552.
11. H. Freundlich, Z. *Physik. Chem.* **79** (1912) 407; Wo. Ostwald, *Kolloid-Z.* **26** (1920) 69. Cit. from Ref. 1.
12. J. J. R. Frausto da Silva, *Rev. Port. Quim.* **4** (1962) 119.

IZVOD

Metorika precipitacionih procesa. XXI. Flokulaciono i stabilizaciono djelovanje kinin-sulfata na hidrosol argentum-jodida

In statu nascendi

N. Galešić i B. Težak

Ispitivano je djelovanje kinin-sulfata na precipitaciju argentum-jodida u vodenom mediju. Tindalometrijskom tehnikom je nađeno da se kritične flokulacione vrijednosti kinin-sulfata kreću između približno 2×10^{-6} do $1{,}3 \times 10^{-5}\,N$, a kritične stabilizacione vrijednosti između približno 4×10^{-5} do $3 \times 10^{-4}\,N$, u zavisnosti o promjeni koncentracija argentum-jodida od 1×10^{-4} do $1 \times 10^{-3}\,M$, a suviška natrium-jodida od 1×10^{-6} do $1 \times 10^{-2}\,M$. U koncentracijama u kojima djeluje stabilizaciono, kinin-sulfat prenabija primarno negativni sol u pozitivni. Na pozitivnom solu kinin-sulfat djeluje stabilizaciono. Jednovalentni i dvovalentni kinin u interakciji sa argentum-jodidom pokazuju približno podjednako djelovanje. Rezultati upućuju da kod promatranih pojava adsorpciona sposobnost kinin-sulfata igra bitnu, a ionsko-kulonska sporednu ulogu.

FIZIČKO-KEMIJSKI INSTITUT
PRIRODOSLOVNO-MATEMATIČKI FAKULTET
ZAGREB

Primljeno 29. travnja 1966.