coördinated complex, in no way related to barium chloride metaphosphate. This is emphasized by the behavior of these two apparently similar compounds toward cold dilute acids. Barium fluorophosphate is readily soluble; the chloride metaphosphate is not.

Bengtsson[14] found that an X-ray powder photograph of one form of barium fluorophosphate prepared by Lange's method closely resembled that of barium sulfate. On this evidence he assumed the two substances to be isomorphous. This infers that the oxygen and fluorine atoms have a similar tetrahedral arrangement about the phosphorus atom as the oxygen atoms have about the sulfur atom in $BaSO_4$, a not unlikely arrangement in view of the similarity in size of the oxygen and fluorine ions. A powder photograph of barium fluorophosphate prepared by Lange's method was made, spacings and intensities being available on microfilm.[6] The obvious differences between it and that of barium chloride metaphosphate show a more fundamental difference than would be expected if these two substances differed merely by the substitution of chlorine for fluorine in the PO_4 tetrahedron.

The crystal structures of only two metaphosphates have been determined. Pauling and Sherman[15] showed that aluminum metaphosphate contains ions of the composition $P_4O_{12}^{4-}$ grouped in a ring. This grouping has recently been confirmed by an X-ray analysis of ammonium tetrametaphosphate.[16] It is indeed regrettable that the barium chloride metaphosphate crystals were not suitable for a structure analysis, since metaphosphates as a rule are difficult to crystallize, their glassy or rubbery state being generally attributed to rings or chains of the empirical composition $(PO_3)_n$ analogous to the metasilicates.

(14) E. Bengtsson, *Arkiv Kemi. Mineral Geol.*, **156**, No. 7 (1941).

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(16) C. Romers, J. A. A. Ketelaar and C. H. MacGillavry, *Nature*, **164**, 960 (1949).

MELBOURNE, AUSTRALIA RECEIVED MAY 19, 1950

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ZAGREB]

Coagulation Effects of Thorium Nitrate on Aqueous Sols of Silver Halides in *Statu Nascendi*. I. The Coagulation Curve and the Coagulation Value of Thorium Nitrate

BY B. TEŽAK, E. MATIJEVIĆ AND K. SCHULZ

The effect of thorium nitrate in various concentrations on systems of silver nitrate–hydrobromic acid, and silver nitrate–potassium bromide in aqueous solution, respectively, have been investigated by means of tyndallometrical measurements. By systematic dilution of thorium nitrate, the coagulation curve shows four distinct regions, two stabilization regions and two coagulation regions. For the diluted, negatively charged silver bromide sols in *statu nascendi* (5×10^{-4} N $AgNO_3$–2×10^{-3} N HBr) the first limit of coagulation–stabilization (0.02 N) represents the critical concentration of coagulation where the coagulating ion is nitrate ion, while the stabilizing action is caused by the thorium complexes of positive sign in adsorbed state. Under otherwise same conditions (2×10^{-4} N $AgNO_3$–4×10^{-4} N HBr and 4×10^{-3} N $Th(NO_3)_4$) the coagulation concentration is shifted from 2×10^{-2} N of potassium nitrate to 6×10^{-4} N of potassium sulfate. The second limit of stabilization–coagulation ($\sim 1 \times 10^{-3}$ N $Th(NO_3)_4$) is very much influenced by the initial concentration of the thorium nitrate solution and the acidity of the medium. The third limit of coagulation–stabilization ($\sim 3 \times 10^{-5}$ and $\sim 3 \times 10^{-6}$ N $Th(NO_3)_4$) gives the coagulation values of thorium complexes (probably trivalent and tetravalent, respectively) on the negatively charged silver bromide sol.

In accordance with the Schulze–Hardy rule, owing to its high electric charge, the effect of thorium ion on negatively charged sols is characterized by a small coagulation value. In many cases, however, this strong coagulating power is overshadowed either by the stabilization effect caused by the adsorption of this multivalent ion and the subsequent reversal of the original negatively charged sol into a positive one, or by the formation of variously charged complexes between thorium ion and other components of the system (*e.g.*, ionic parts of the protolytic reactions of water, various anions, etc.). Such examples were found by Gorochowsky and Protass,[1] Bosch and Haemers,[2] Gillis and Eeckhout,[3] Kruyt and Troelstra,[4] and others for coagulation of silver halide sols. The cited investigations gave evidence also that the state of the thorium ion in aqueous solution is far from a simple one, its reactions depending on the concentration and the "age" of the solution of thorium salt, and on the nature of other ionic components, especially those of anionic character. All these factors control the stabilizing effects. As the physical chemistry of aqueous solutions of ions of higher valency is the object of numerous newer investigations,[5] it would be worthwhile to give some results obtained by the tyndallometrical observations of the precipitation of silver halides in presence of thorium nitrate. Especially, it might be of interest to attempt to answer some open questions on this field using the experimental procedure already applied on the similar coagulating systems with ions of lower valency.[6]

(1) G. N. Gorochowsky and J. R. Protass, *Z. physik. Chem.*, **A174**, 122 (1935).

(2) F. Bosch and H. Haemers, *Natuurw. Tijdschr. Belg.*, **18**, 90 (1936).

(3) J. Gillis and J. Eeckhout, *ibid.*, **19**, 49 (1937).

(4) H. R. Kruyt and S. A. Troelstra, *Kolloid-Beihefte*, **54**, 262 (1943).

(5) M. Kasha and G. E. Sheline, Natl. Nuclear Energy Ser., Div. IV, Transuranium Elements, Pt. I (1949), p. 180; M. Kasha, *ibid.*, p. 295; J. C. Hindman and D. P. Ames, *ibid.*, p. 348; J. C. Hindman, *ibid.*, pp. 370, 388, 405. J. Sutton, *J. Chem. Soc.*, S 275 (1949); R. H. Betts and R. K. Michels, *ibid.*, S 286 (1949); E. Glueckauf, H. A. C. McKay and A. R. Mathieson, *ibid.*, S 299 (1949).

(6) B. Težak, *Kolloid-Z.*, **68**, 60 (1934); *Z. physik. Chem.*, **A175**, 219 (1935); *ibid.*, **A191**, 270 (1942); *Arhiv kem.*, **19**, 19 (1947); B. Težak and E. Matijević, *ibid.*, **19**, 29 (1947); B. Težak, E. Matijević and K. Schulz, *ibid.*, **20**, 1 (1948).

Experimental

We used water solutions of the two precipitating components, and mixed them always in the same manner. In each experimental series the one component contained thorium nitrate the concentration of which was varied systematically, and the constant amount of hydrobromic acid, or potassium bromide with or without nitric acid; the other component was a silver nitrate solution of constant concentration. Since the bromide ion was always kept in a fair excess to the silver ion, the concentration of the sol was determined in each of experimental series by the silver ion concentration. The usual procedure of preparing the reacting components was as follows: the first component was prepared by taking a known quantity of thorium nitrate stock solution, adding to it the necessary amount of hydrobromic acid (or solution of potassium bromide and nitric acid), and filling up to 5 ml. with water. The other component consisted of 5 ml. of silver nitrate solution of known concentration (2×10^{-4}, 4×10^{-4} or 1×10^{-3} *N*). For the sake of convenience the concentration data are given for the total volume of the reaction mixture (10 ml.). All the precipitations and measurements were performed at 20°. In certain time intervals the intensity of the Tyndall-beam was measured directly in the test-tubes of *ca.* 15 mm. diameter by means of a Zeiss tyndallometer connected to a Pulfrich photometer.

The tyndallometric values reported in this series of papers were obtained 10 minutes after mixing the reacting components. A green light filter was used, and the results expressed in Sauer's constants (Trübungswerte[7]). As it will be shown elsewhere the time of 10 minutes after mixing has revealed itself through graphical analysis of the kinetics of the coagulation of silver bromide sols in *statu nascendi* as the most suitable for the characterization of instability of the systems observed.

Figure 1 gives the tyndallometric values of the system: 5×10^{-4} *N* silver nitrate–2×10^{-3} *N* hydrobromic acid, where the concentration of thorium nitrate was varied from one sample to the other. Thorium nitrate was diluted from stock solution of 0.20 *N* (for systems between 0.1 to 0.001 *N*), and 0.002 *N* (for systems which were diluted more than 8×10^{-4} *N*). The first critical concentration between coagulation region 1 and stabilization region 2 is due to the coagulating power of the nitrate ion while the sol is obviously positively charged by thorium ions adsorbed on the primarily negative sol particles. Therefore, the critical concentration of coagulation can be changed by anions according to the rule of Schulze and Hardy. In fact, the experimental series with nitrate and sulfate are illustrated by Fig. 2, and were performed under similar conditions as the results of Fig. 1, keeping the concentration of thorium nitrate constant (4×10^{-3} *N*), and varying the concentration of potassium nitrate and sulfate, respectively.

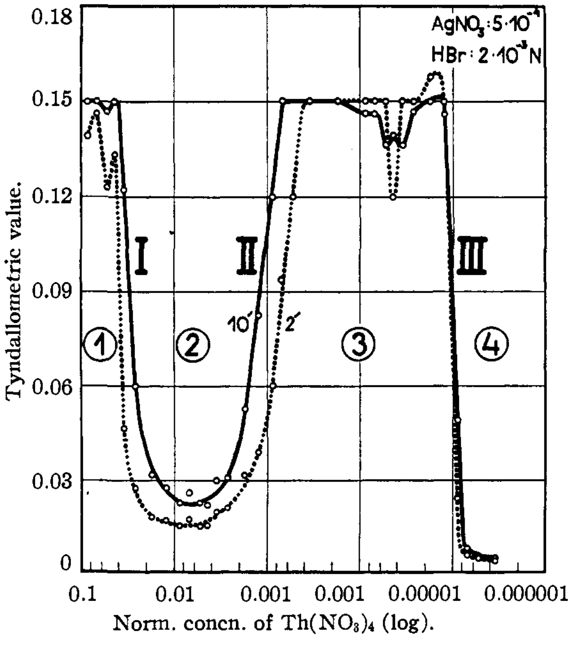

Fig. 1.—Coagulation curve showing the effect of thorium nitrate on silver bromide sol in *statu nascendi*, 10 minutes after mixing the reacting components.

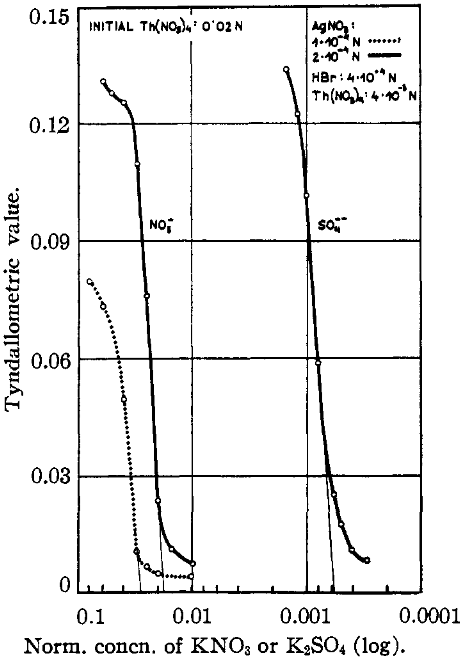

Fig. 2.—Coagulation effects of potassium nitrate and sulfate, respectively, on the silver bromide sol in presence of thorium nitrate.

The coagulation values of both nitrate and sulfate ions showed characteristic variations when the thorium nitrate concentration was varied. These effects, and those which were observed in respect to the other limit between the stabilization region 2 and coagulation region 3 (0.002 *N* thorium nitrate) will be the subject of Part II. Here our

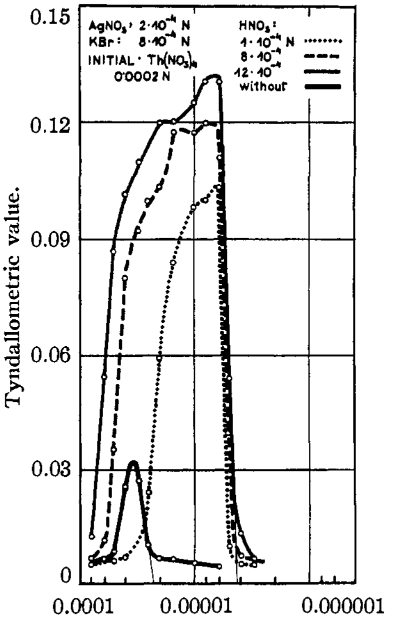

Fig. 3.—Effect of nitric acid on the appearance of the coagulation maximum.

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[7] H. Sauer, *Z. techn. Physik*, **12**, 148 (1931); B. Težak, *Kolloid-Z.*, **74**, 16 (1936).

intention is to give data concerning the third limit between coagulation region 3 and stabilization region 4. Thus the very noticeable influence of the acidity on the appearance of the coagulation maximum of our region 3 is shown in Fig. 3. As can be seen, the effect of the concentration of nitric acid on the critical concentration of coagulation of thorium nitrate is rather small; only the difference in the behavior of neutral and acid systems is pronounced. By continuing the linear part of the coagulation curve which gives our coagulation–stabilization limit, a section point with the abscissas is obtained marking in a fair way the corresponding coagulation value: 2 × 10^{-5} and 4 × 10^{-6} N of thorium nitrate for neutral and acidified coagulating systems, respectively.

In Fig. 4 there are three silver nitrate–potassium bromide systems. The concentration of silver nitrate was varied from 1 × 10^{-4} to 5 × 10^{-4} N with consequent increase of the coagulation value from 2 × 10^{-5} on 4 × 10^{-5} N thorium nitrate.

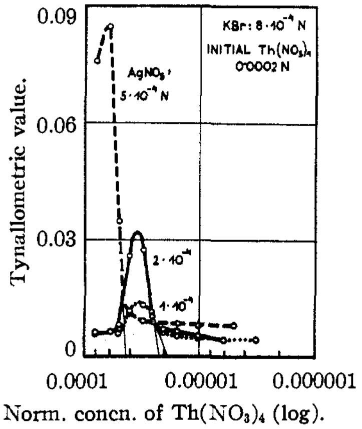

Fig. 4.—Effect of the sol concentration in neutral media on the critical coagulation–stabilization limit.

The effect of various concentrations of potassium bromide on the coagulation value of the thorium nitrate in systems of 2 × 10^{-4} N silver nitrate–8 × 10^{-4} N nitric acid–thorium nitrate, is shown in Fig. 5. With greater concentration of potassium bromide there is a decrease of the coagulation value which may be read from the diagram.

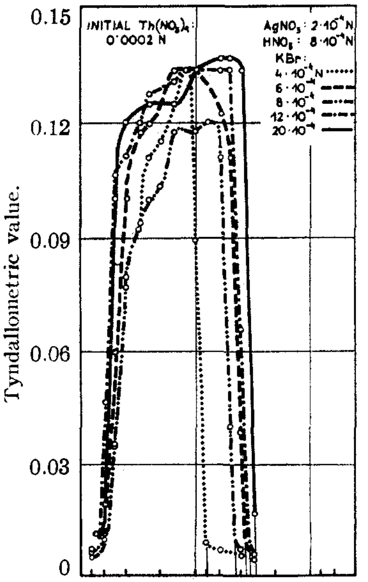

Fig. 5.—Effect of the concentration of potassium bromide on the appearance of the coagulation maximum.

The influence of systematic variations of the concentration of the stabilizing ion for various concentrations of silver bromide sol on the coagulation value of thorium nitrate is summarized on Fig. 6. The variable is here the concentration of hydrobromic acid on the abscissa, while the ordinates are coagulation values of thorium nitrate for precipitating systems in concentration of 1 × 10^{-4}, 5 × 10^{-4} and 1 × 10^{-3} N silver nitrate, respectively.

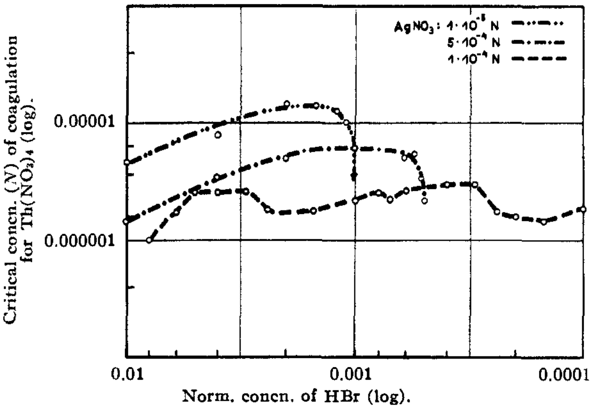

Fig. 6.—Effect of the concentration of hydrobromic acid (as stabilizing electrolyte) on the coagulation value of thorium nitrate for silver bromide sols of various concentrations.

For the sol concentration of 1 × 10^{-4} M silver bromide the majority of coagulation values falls between 7 × 10^{-6} and 3 × 10^{-6} N. For higher sol concentrations the curves show a characteristic feature with a distinct maximum of coagulation value and with a sudden fall in the region of small concentrations of the stabilizing ion. The order is also apparent: with increasing concentration of the sol the coagulation value increases.

Discussion

The general appearance of the coagulation curve for silver bromide sol in *statu nascendi* in presence of thorium nitrate is nearly the same as that for silver iodide.[1] As a first approximation the explanation is a simple one: The interaction of the primary particles of the silver bromide, which are negatively charged owing the adsorption of bromide ions (which are in constant excess to the silver ions in solution), with various complex thorium ions gives the usual phenomena of the reversal of charge and alternating stabilization and coagulation effects. The region 1 of the coagulation is caused by the coagulating action of the nitrate ion which, as the accompanying ion (Nebenion) of the thorium ion, is in critical concentration of coagulation of about 1 × 10^{-2} N with respect to the distribution of the positive charges on the sol particles. Consequently, by keeping the same concentration of thorium salt, the critical concentration of coagulation for sulfate ion is about 1 × 10^{-3} N in accordance with the rule of Schulze and Hardy. The region 2 is, therefore, the stabilization region with positively charged primary particles. The extension of this region is a result of various complex factors which determine the adsorption of the positively charged thorium complexes on the primarily negative sol particles. For instance, the sol concentration, the relation between the precipitating silver and bromide ions, the acidity of the media, the initial concentration of the solution of thorium nitrate, among many others, are such factors. The coagulation region 3 is primarily a direct result of the coagulating action of the multivalent thorium ion on the original negatively charged sol. It is apparent that the stabilization effect of thorium ions is much more pronounced in nearly neutral media, while the relatively small concentration of acid distinctly lowers this stabilization.

The coagulation–stabilization limit III between the regions 3 and 4 gives us, finally, the coagulation value of the multivalent thorium complexes. It seems that there are many reasons to assume that the coagulation value in neutral media (systems with potassium bromide) is about 3×10^{-5} *N*, while in acidified media is about 4×10^{-6} *N*. This difference may be interpreted by the assumption that the coagulation is accomplished with the trivalent and tetravalent thorium complex ions, respectively. In the first case this ion might be $Th(H_2O)_3OH^{3+}$ and in the second $Th(H_2O)_4^{4+}$.

Figure 6 shows the effect of the variation of concentration of the stabilization ion (hydrobromic acid) on the coagulation value of thorium nitrate. It is interesting to note: (1) that the coagulation value except in the range of relatively small excesses of bromide ion shows steady decrease with increasing concentration of hydrobromic acid, and (2) that with increase of the concentration of the sol the coagulation value also increases. The first effect is similar to that which was found for trivalent ions, where with decreasing concentration of the stabilizing ion the coagulation value increased. However, the feature of the whole curve is not the same as for typical trivalent ion. The difference is noticeable in the region of small concentration of stabilizing ion, where with decreasing concentration of this ion the coagulation value of thorium ion decreases. The second effect is opposite to that found with coagulating ions of lower valency.[8] In general, with mono-, bi- and trivalent coagulating ions proportionately more electrolyte is required for coagulation of a diluted sol than for a concentrated one. With tetravalent ions the reverse order is probably due to the prevailing influence of the ratio between the total amount of the stabilization ion adsorbed on the wall of the colloidal particles and the total amount of the tetravalent coagulating ions available in the solution. It may be noted that it was impossible to obtain consistent results with sols of 1×10^{-4} *M* silver nitrate, where this adsorption effects should be lower. However, there is some evidence that true coagulation value of tetravalent thorium ion is 4 or 3×10^{-6} *N*. In this connection it may be noted that by using a linear relationship between the ionic radius, r_i, the valency, z, and the critical concentration of coagulation (coagulation value) as previously described,[9] *viz.*

$$(2r_i + 4.77)z = -5.96 \log {}_cC$$

or

$$(r_i + 2.38)z = -2.98 \log {}_cC$$

where for $z = 4$, and coagulation value, ${}_cC = 4.17 \times 10^{-6}$ *N*, the value of r_i would be 1.63 Å. corresponding approximately to the ionic radius of hydrated thorium ion.

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(8) B. Težak, E. Matijević and K. Schulz, *Arhiv kem.*, **20**, 1 (1948).

(9) B. Težak, *Z. physik. Chem.*, **A191**, 270 (1942); B. Težak and E. Matijević, *Arhiv kem.*, **19**, 29 (1947).

ZAGREB, YUGOSLAVIA RECEIVED SEPTEMBER 27, 1950

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ZAGREB]

Coagulation Effects of Thorium Nitrate on Aqueous Sols of Silver Halides in *Statu Nascendi*. II. The Factors of Stabilization and the Effects of "Aging" of Thorium Nitrate Solution

BY B. TEŽAK, E. MATIJEVIĆ AND K. SCHULZ

The effect of various concentrations of the thorium nitrate solution on the coagulation of the silver bromide sol in *statu nascendi* of various concentrations, was investigated.

For such sols various effects on the critical limits in the central stabilization region, and especially, the relationships between the coagulation value of potassium sulfate and the concentration of hydrobromic acid or thorium nitrate, respectively, the influence of the acidity of the media, and the effect of "aging" of the thorium nitrate aqueous solutions, were observed.

It was found that with decreasing concentration of hydrobromic acid under constant concentration of thorium nitrate the coagulation value of sulfate ion decreases in a typical manner. The similar decrease of coagulation value was also found with decreasing concentration of thorium nitrate solution. By "aging" of the thorium nitrate solutions a characteristic shift of the stabilization–coagulation limit toward lower concentrations was found.

The phenomena observed have been explained by the assumption that in aqueous solutions there exist thorium complexes of different valencies which manifest themselves in typical coagulation values. Thus, for negatively charged silver bromide sol it was found that the coagulation value for bivalent complex is $\sim 4 \times 10^{-4}$ *N*, for trivalent $\sim 3 \times 10^{-5}$ *N*, and for tetravalent complex $\sim 3 \times 10^{-6}$ *N* of thorium nitrate solution.

The phenomena presented in Part I show that the relationship between the stability of the silver bromide sol and the concentration regions of the thorium nitrate solution can simultaneously indicate the state in the boundary region of the coagulating sol particles as well as the change of the ionic structure of the dominating ions in the solution. It seems that the method applied might be convenient for investigations in both directions as an additional proof of the conclusion reached through electrokinetic, transference, spectrometric, cryoscopic and other measurements. To exemplify the possibilities some results are given which are related to the stabilization factors of the thorium nitrate in aqueous solution on silver bromide sol in *statu nascendi*.

Experimental

The same technique was used as previously. The experiments aimed at obtaining some information about the conditions: (1) of the coagulation–stabilization limit I between regions 1 and 2; (2) of the stabilization–coagulation limit II between regions 2 and 3; and (3) of the influence of dilution and of the structure of the solution of