marily 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.*

$$(2r_i + 4.77)z = -5.96 \log_c C$$

or

$$(r_i + 2.38)z = -2.98 \log_c C$$

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.

(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).

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[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

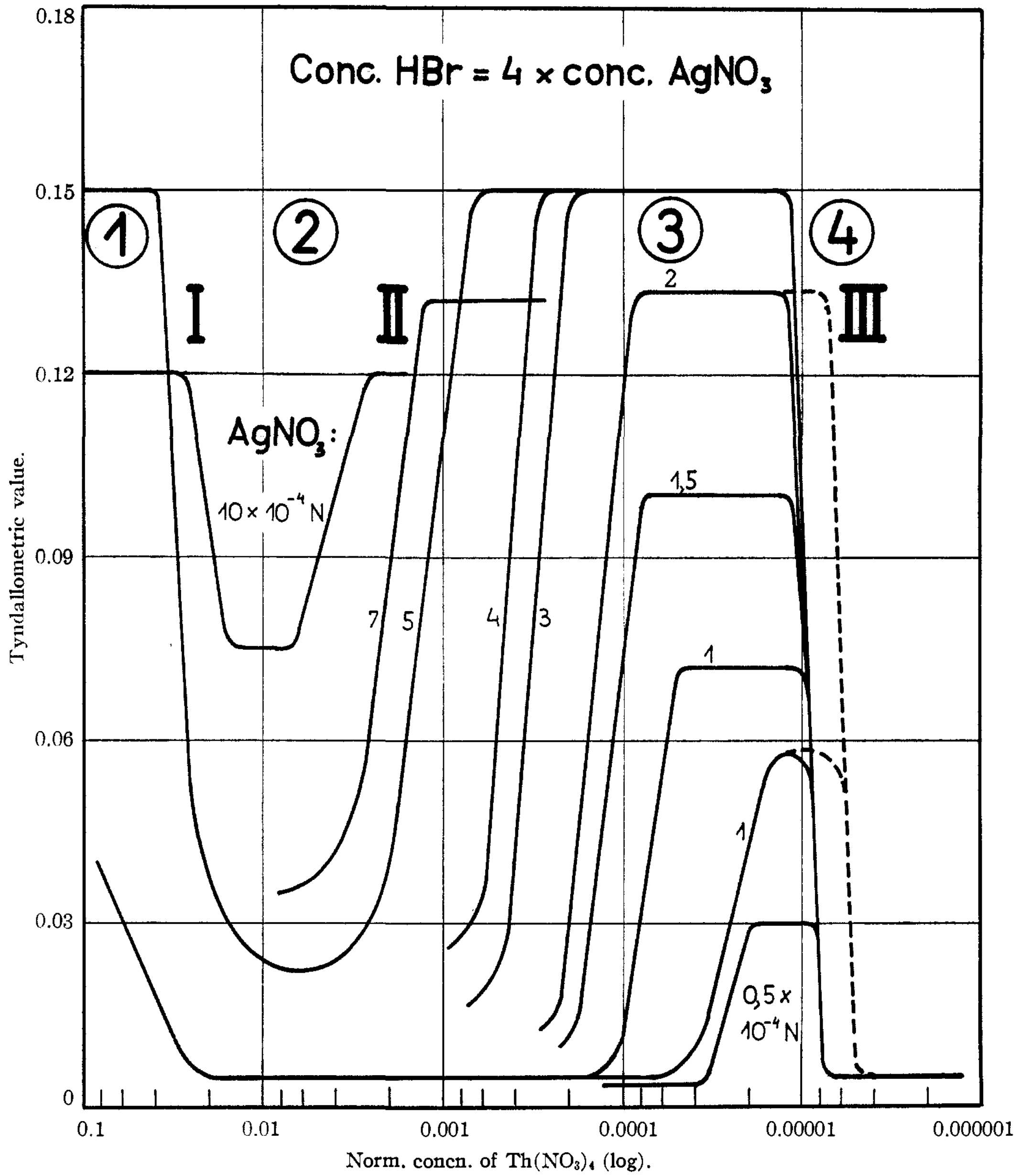

Fig. 1.—Coagulation curves showing the effect of the concentration of thorium nitrate on various concentrations of silver bromide sols in *statu nascendi*, 10 minutes after mixing the reacting components.

the thorium nitrate on the appearance of the coagulation maximum between the limits II and III, denoted as region 3 in Fig. 1 of the Part I and this communication.

As shown in Part I the limit I represents the coagulating effect of the nitrate ion against positively charged sol. This positive charge was due to the reversal of the sign of charge of the primarily negatively charged colloidal particles. As can be seen on Fig. 1 the increase of the sol concentration decreases the coagulation value of nitrate ion. As the critical concentration of coagulation with potassium sulfate lies in the middle of the stabilization region 2, such systems are very convenient for the investigation of the influence: (1) of the variation of the concentration of the stabilizing ion, and (2) of the variation of thorium nitrate concentration.

When the concentration of thorium nitrate is kept constant there is a characteristic relationship between various concentrations of hydrobromic acid and the coagulation value of potassium sulfate (Fig. 2). With decreasing concentration of hydrobromic acid the coagulation value decreases in a way similar to that with monovalent coagulating ions.

The relationship between various concentrations of thorium nitrate and the coagulation value of potassium sulfate is shown in Fig. 3. After being constant in a narrow region of relatively high concentration of thorium nitrate, the coagulation value of sulfate ion decreases with decreasing concentration of thorium nitrate. The reasonable cause is the decrease of the number of thorium ions adsorbed on the walls of the primary particles.

With increasing concentration of the sol, the stability region 2 becomes steadily narrower. In Fig. 4 this shift of 10 minutes coagulation curves is shown once more for the systems of silver nitrate–hydrobromic acid–thorium nitrate, where the concentrational relation between silver nitrate and hydrobromic acid in the initial precipitating mixture was 1:4. If the concentrations of silver nitrate solutions (or the sol concentrations) of Fig. 4 are taken as abscissas on a new diagram, and the concentrations of thorium nitrate which correspond to one fixed tyndallometric value, say 0.06 (denoted as black points), as ordinates, a nearly linear relationship is obtained. Figure 5 shows such relationships not only for systems where the ratio between silver nitrate and hydrobromic acid was 1:4, but also for ratios 1:2 and 1:8. As was mentioned in Part I, the influence of the acidity is very pronounced, and Fig. 6 may give an illustration of this effect.

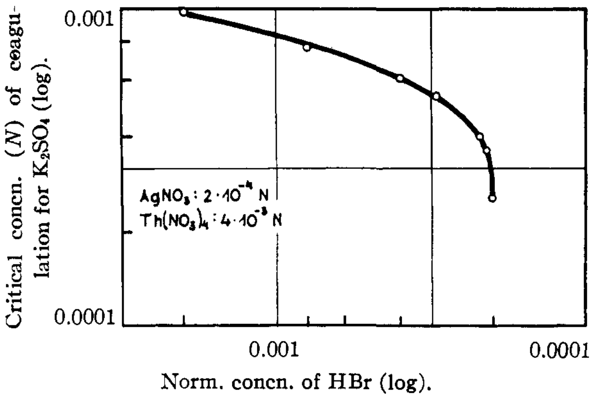

Fig. 2.—Effect of the concentration of hydrobromic acid on the coagulation value of potassium sulfate in presence of thorium nitrate.

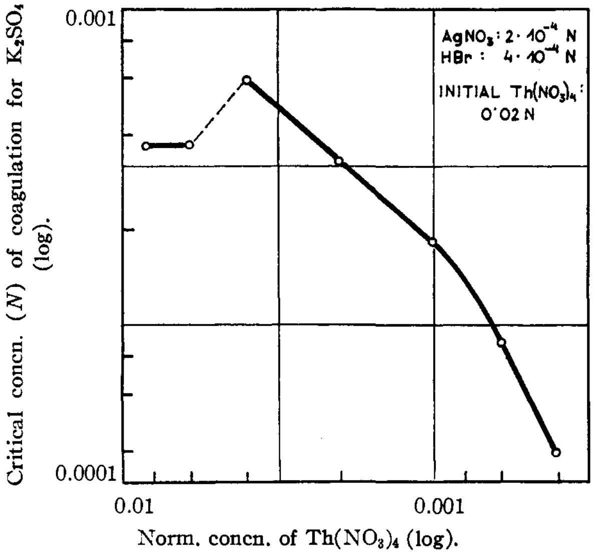

Fig. 3.—Effect of the concentration of thorium nitrate on the coagulation value of potassium sulfate.

Not only the acidity of the medium but also the ionic state of the thorium nitrate solution is indicated in a very sharp manner with our coagulating systems. Figure 7 shows the tyndallometric values of the systems of 2 × 10^{-4} N silver nitrate-8 × 10^{-4} potassium bromide-1.2 × 10^{-3} N nitric acid with varying concentration of thorium nitrate. As usual, all tyndallometric values were read 10 minutes after mixing the reacting components, the only differences of the systems being in the preparation of the solutions of thorium nitrate. When for the preparation of our concentration gradient in separate test-tubes the initial concentration of the stock solution amounted to 2 × 10^{-2} N, the stabilization-coagulation limit II was at about ten times higher concentration of thorium nitrate than in an analogous series where the concentration of the stock solution was 2 × 10^{-4} N thorium nitrate. With respect to the time factor it may be mentioned that it usually took about 30 minutes to prepare the whole set of samples by diluting the corresponding volume of the stock solution of thorium nitrate with water, the solution of potassium bromide and the nitric acid, before mixing it with silver nitrate solution.

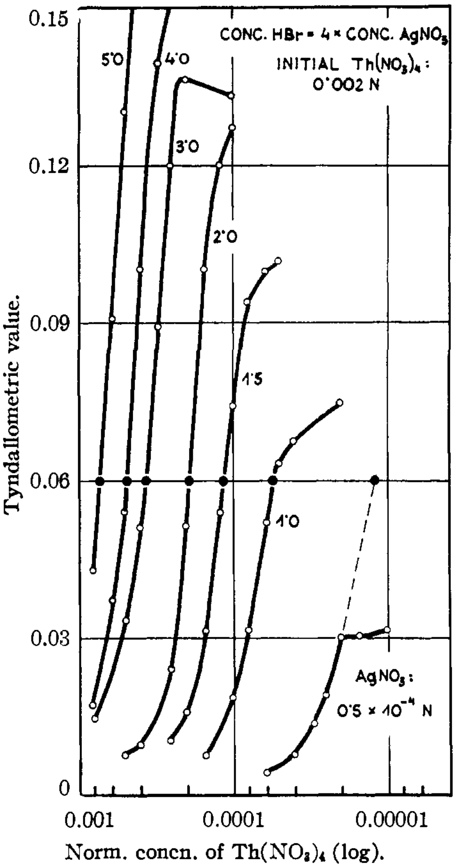

Fig. 4.—Effect of the concentration of the sol on the tyndallometric values of the systems with various concentrations of thorium nitrate, 10 minutes after mixing the reacting components.

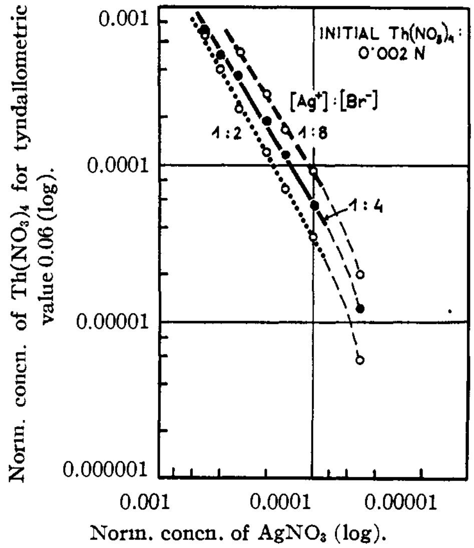

Fig. 5.—Relationships between the concentration of the thorium nitrate for systems of the same tyndallometric value and the concentration of the sol where the ratios Ag$^+$:Br$^-$ amounted to 1:2, 1:4 and 1:8, respectively.

For obtaining an insight in the mechanism of this interesting influence of the initial concentration of thorium nitrate solution, the samples were prepared so that the necessary volumes of thorium nitrate stock solution of 2 × 10^{-2} N were diluted with water to 4.0 ml., and allowed to stand for a period indicated in Fig. 7. Again, 0.60 ml. of 2 × 10^{-2} N nitric acid and 0.40 ml. of 2 × 10^{-2} N potassium bromide solution were added to each sample to fill it up to the volume of 5.0 ml. immediately before mixing it with 5.0 ml. of 4 × 10^{-4} N silver nitrate solution. In this way the aqueous thorium nitrate solution was "aged" through the time indicated in connection with various curves of our Fig. 7.

A similar series of systems of 2 × 10^{-4} N silver nitrate–4 × 10^{-3} N hydrobromic acid with varying concentration of thorium nitrate solutions is given in Fig. 8. The samples were prepared in a similar manner by "aging" of 4.8 ml.

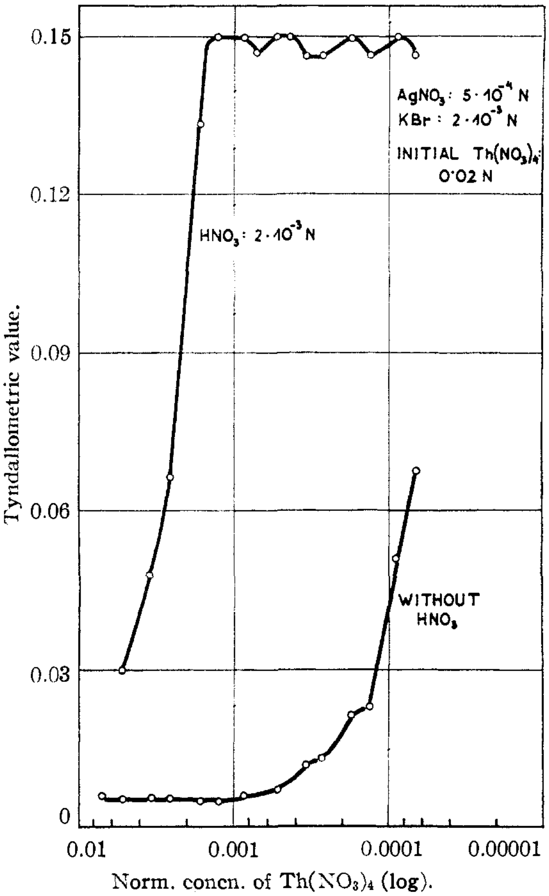

Fig. 6.—Effect of the acidity on the stabilization–coagulation limit (systems prepared from thorium nitrate stock solution of 0.02 N).

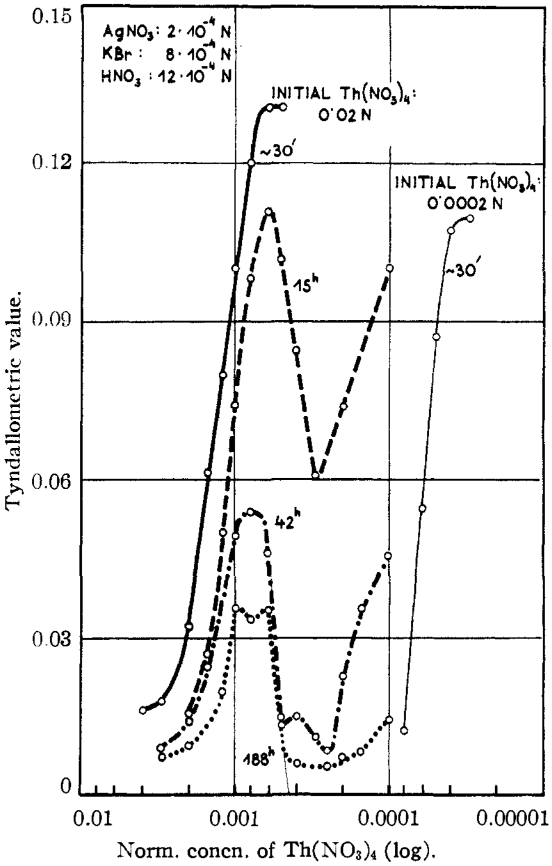

Fig. 7.—Effects of initial concentration and of "aging" of the aqueous thorium nitrate solutions on the precipitation of the silver bromide sols ($AgNO_3$–KBr–HNO_3), 10 minutes after mixing the reacting components.

of the gradually diluted stock solution 2 × 10^{-2} N thorium nitrate through various time periods, and adding 0.2 ml. of 0.2 N hydrobromic acid just before mixing with silver nitrate solution.

In both series of experiments there is a significant maximum in the region of 8 × 10^{-4} N thorium nitrate concentration indicating a new critical concentration limit of about 4 × 10^{-4} N thorium nitrate by a falling slope of the tyndallometric values.

The electrophoretic observations showed that the sol particles throughout the range of thorium nitrate concentrations down to those of the limit III (critical concentration of coagulation for thorium ion) are usually positively charged. However, this last maximum from which the region 3 was composed contained also neutral or sometimes negatively charged particles, while on the very limit III between regions 3 and 4 the sols were regularly negative.

With respect to the variation of the hydrogen ion concentration with falling concentration of thorium nitrate the steady but slow increase was observed in concentrations from 2 × 10^{-2} N, where pH was about 3.2, down to 2 × 10^{-4} N of thorium nitrate, where pH was about 4.2; in the region between 3 × 10^{-4} and 3 × 10^{-5} N the change was sometimes irregular with greater rate in pH-variation showing an increase from pH 4 to pH 6.2, with little change after further dilution.

Discussion

The stabilization–coagulation effects observed are primarily connected with the boundary state of the silver bromide sols. On the other hand, all the changes of the state of thorium ions or their complexes in the solution must also have an influence. In the majority of cases the positive thorium complexes are fixed on the primary particles giving a positive charge to the walls of the primarily negative particles. In such circumstances, the coagulation of these positive sols is accomplished with the anionic component of the ionic system present.

In Fig. 2 it may be seen from the relationship between the coagulation value of potassium sulfate and the excess of the bromide ions (keeping the concentration of thorium nitrate constant), that the adsorption of bromide ions is a prerequisite for the fixation of thorium complexes. The coagulation value of potassium sulfate shows also a pronounced decrease with decreasing concentration of thorium nitrate. That may be explained by assuming a proportionately decreasing density of the positive charges on the walls as a consequence of the decreasing adsorption of the thorium complexes. The same explanation in principle may be proposed for the increasing concentration limit II of thorium nitrate with increasing concentration of the sol (Figs. 4 and 5); the sol of higher concentration adsorbs greater amount of thorium complexes lowering their relative density on the walls. With the effect of acidity, and of the initial concentration of the thorium nitrate stock solutions, as well as with the "aging" of the thorium nitrate solutions on the region 3, we are entering in the field where the character of the complex thorium ions plays a decisive role. Kruyt and Troelstra[1] assumed that hydrox-

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

ides only are capable to reverse the charge on the surface of colloidal particles. We assume also that the adsorption of some kind of the hydroxy complexes in concentrated thorium nitrate solution must be responsible for resulting positive charge of our primarily negative sol particles. Thomas and Kremer,[2] Schaal and Faucherre,[3] Souchay[4] and others gave evidence for various hydroxy and oxy complexes of thorium, while Hindman,[5] and others have shown also for the similar plutonium ion, that in such systems there are many kinds of complex ions in equilibrium. *E.g.*, in our systems we may have the thorium hydroxy aquo complexes of various positive charge, say, from two to four, and in some regions with increasing concentration of thorium nitrate solution the hydrolysis becomes more pronounced giving, probably, also the polynuclear complexes discussed by Lundgren and Sillén[6] and others.[3,4] In acidified media the thorium hydroxy complexes are probably changing into bromo and nitrato complexes, respectively, and as such it seems that they loose their possibility for permanent fixation on the negative walls. Consequently, the probability for the reversal of charge is diminished, and the coagulation in region 3 proceeds as a result of the ionic association–dissociation equilibria between negative stabilizing ions and bi- and trivalent coagulating ions. Obviously, the adsorbability of specially composed complex ions is here competing with the coagulating mechanism of the negatively charged particles. With such a state of affairs the influence of the acidity, as manifested in Fig. 6, may be explained.

When the very diluted and thoroughly "aged" solutions were used, aquo complexes are probably formed which are of such stability that the acid ions cannot act as quick "penetrators" or "displacers" into the complex ion. Naturally, if we allowed the various equilibrium states in the formation of the hydroxy aquo complexes to be reached, it would be possible to observe the various coagulation effects according to the valency of the thorium complexes formed.

Assuming that the simplest reactions enhanced by diluting partially hydrolyzed thorium nitrate solution are

$$Th(H_2O)_2(OH)_2^{2+} + H_3O^+ \rightleftharpoons Th(H_2O)_3OH^{3+} + H_2O \quad (1)$$

$$Th(H_2O)_3OH^{3+} + H_3O^+ \rightleftharpoons Th(H_2O)_4^{4+} + H_2O \quad (2)$$

the concentrated solution would give preferentially the thorium hydroxy (or polynuclear oxy), and the diluted ones the thorium aquo complexes. All such complexes in higher concentrations should stabilize the sol particles causing the reversal of charge as a result of their high adsorbability on primarily negative particles.

It seems from our experiments that solutions of thorium nitrate in a region of small concentrations cannot produce by addition of the acid the quick response of the system from complex ions of lower valencies to those of higher valencies. Thus the maximum in the concentration region of 8 × 10^{-4} N thorium nitrate (Figs. 7 and 8) in partially "aged" solutions would indicate the presence of the bivalent $Th(H_2O)_2(OH)_2^{2+}$ (or $Th(H_2O)_2Br_2^{2+}$) ions, while the critical concentration of coagulation for this bivalent cation would be 4 × 10^{-4} N. In accordance with such a concept the critical concentration for trivalent $Th(H_2O)_3OH^{3+}$ (or $Th(H_2O)_3Br^{3+}$) is represented by ~3 × 10^{-5} N, while that for tetravalent $Th(H_2O)_4^{4+}$ is given by ~3 × 10^{-6} N thorium nitrate.

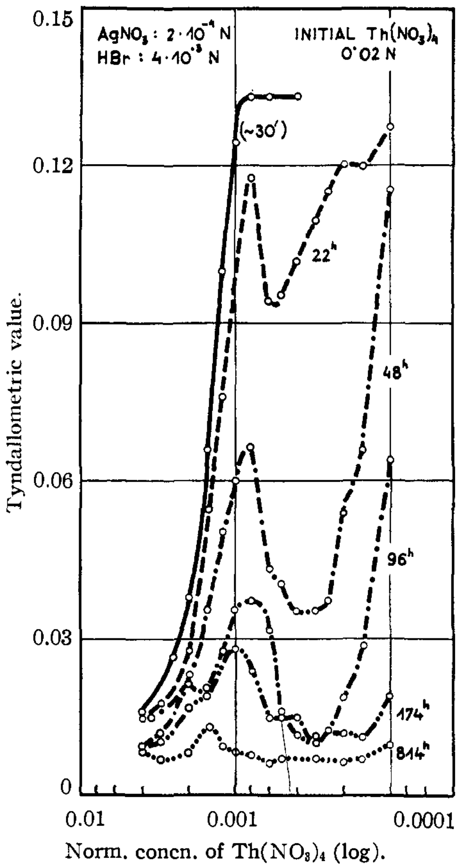

Fig. 8.—Effects of "aging" of the aqueous thorium nitrate solutions on the precipitation of the silver bromide sols ($AgNO_3$–HBr), 10 minutes after mixing the reacting components.

By complete "aging" of the thorium nitrate solution the formation of trivalent hydroxy aquo complex probably prevails, and in more diluted and acidified media the equilibria are finally shifted further to the side of the tetravalent thorium aquo complex. In this region the acidity of the media may influence the process leading toward the tetravalent complex (hydrogen-ion effect), but also to the trivalent complex by penetration of the anion into the primary complex (anionic effect). Therefore such systems are very sensitive on the concentrational relations between all the component parts, as well as on the mode of preparation, explaining also the irregularities of this region mentioned in the Part I.

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(2) A. W. Thomas and C. B. Kremer, THIS JOURNAL, 57, 1821, 2538 (1935).

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(4) P. Souchay, *ibid.*, 143 (1948).

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(6) G. Lundgren and L. G. Sillén, *Arkiv kem.*, 1, 277 (1949).