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Original Scientific Paper

Precipitation and Hydrolysis of Thorium(IV) in Aqueous Solution: Thorium Nitrate — Potassium Hydroxide. I. Determination of Solubility Constants of $\text{Th}(\text{OH})_4$

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The precipitation and hydrolysis of thorium (IV) in aqueous solutions of thorium nitrate — potassium hydroxide was investigated at 20°C with a tyndallometer and a pH-meter. A three-dimensional precipitation diagram for a wide range of concentrations of both precipitating components was constructed. The concentration region of thorium hydroxide, the fast precipitation, the formation of sols and of stable clear solutions were observed.

The decreased precipitation of thorium hydroxide at pH between 9 — 10.4 is considered to be the effect of the carbonate ions present. By a very simple graphical tyndallometric method the solubility products of thorium hydroxide were directly determined as:

$$\log \bar{K}_{S_0} = -45.7; \log \bar{K}_{S_2} = -24.3$$

and the cumulative hydrolytic constant $\beta_2 = 1.029 \times 10^{-7}$ was calculated. The predominant hydrolytic species of thorium-ion in aqueous solution in equilibrium with the solid phase of $\text{Th}(\text{OH})_4$ were estimated. The predominant species is the free ion Th^{4+} for pH 3.4 and $[\text{Th}(\text{OH})_2^{2+}]_n$ for the pH between 3.5 and 4.1. At values lower pH 4.1 ionic species of thorium are formed with more than two OH^- ions per one thorium ion.

INTRODUCTION

There are different contradictory hypotheses¹⁻¹¹ about the hydrolytic species of thorium ions in aqueous solution. A fact surely established is the existence of the Th^{4+} ion in acid solutions at pH about 3.

By electrometric titration Hietanen² found the number of H^+ split off per thorium, at different pH values. The precipitation of thorium hydroxide occurs at higher concentrations of alkali hydroxide. Prasad and Dey¹²⁻¹⁶ investigated the precipitation of thorium hydroxide from aqueous solution of thorium chloride with different alkaline hydroxides. The authors found the precipitation complete after the addition of about four equivalents of alkali hydroxide.

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Several authors tried to determine the solubility product of thorium hydroxide¹⁷⁻²⁰ and obtained different values.

As shown earlier²¹ the precipitation phenomena are greatly influenced by concentrations of the reacting components. This influence can be distinctly shown in three-dimensional precipitation diagrams.^{22,23}

As a result of the tyndallometric studies of argentum bromide a simple graphical method for the determination of complex solubility constants was proposed.²⁴

The present paper shows the regions of precipitation of thorium hydroxide by means of the three-dimensional precipitation diagram.

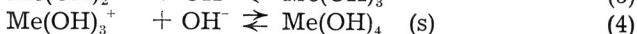
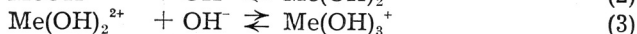
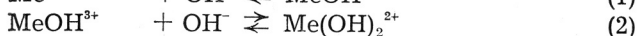
The hydrolytic species of thorium ions predominant in the aqueous phase which were in equilibrium with the solid phase were defined. The corresponding solubility constants of thorium hydroxide were determined graphically from tyndallometric measurements.

Mononuclear and polynuclear complexes could not be distinguished by this method. Only the average number of OH⁻ per Th necessary for the formation of solid thorium hydroxide Th(OH)₄ was evaluated.

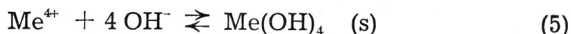
THEORETICAL CONSIDERATIONS

Evaluation of Solubility Products and Hydrolysis Constants from the Limiting Solubility Curves

The consecutive hydrolytic reactions of a Me⁴⁺ ion can be written in the simplest way:



and the over-all equation representing the formation of the precipitate:

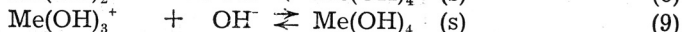
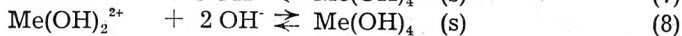
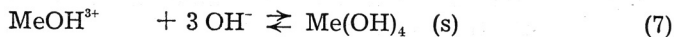


The consecutive stability constants for equilibria (1), (2) and (3) are K₁, K₂, and K₃, where:

$$K_n = \frac{[\text{Me(OH)}_n^{(4-n)+}]}{[\text{Me(OH)}_{n-1}^{(5-n)+}] [\text{OH}^-]} \quad (6)$$

$$n = 1, 2, 3$$

The reactions of the formation of Me(OH)₄ precipitate from different predominant hydrolytic species in the aqueous phase can be written as:



The logarithms of the concentration of metal ion were plotted against the pH-values, and the points at the boundary between clear solutions and turbid solutions were used to plot the solubility curve.

The solubility curve gives the corresponding values of concentrations of the metal ion and the pH required for the beginning of the precipitation as

a result of hydrolysis: (see eq. 5, 7, 8 and 9). This boundary concentration of metal ion was equal to the added solution concentration because no solid phase particles were formed *i.e.* all the added metal ions were present in the solution.

The hydrolytic equilibria are presented in the simplest way. Only an average number n of OH⁻ ions per one metal-ion necessary for the formation of Me(OH)₄ precipitate could be evaluated by the method.

The solubility constants derived from (5), (7), (8) and (9) are:

$$K_{S_0} = [\text{Me}^{4+}] \cdot [\text{OH}^-]^4 \quad (10)$$

$$K_{S_1} = [\text{MeOH}^{3+}] \cdot [\text{OH}^-]^3 = K_{S_0} \cdot K_1 \quad (11)$$

$$K_{S_2} = [\text{Me}(\text{OH})_2^{2+}] \cdot [\text{OH}^-]^2 = K_{S_0} \cdot K_1 \cdot K_2 \quad (12)$$

$$K_{S_3} = [\text{Me}(\text{OH})_3^+] \cdot [\text{OH}^-] = K_{S_0} \cdot K_1 \cdot K_2 \cdot K_3 \quad (13)$$

A general relation for the solubility product of metal hydroxide Me(OH)₄ is given by the equation:

$$K_{S(4-n)} = [\text{Me}(\text{OH})_{4-n}^{n+}] \cdot [\text{OH}^-]^n \quad (14)$$

where $n = 4, 3, 2, 1$

By substituting

$$[\text{OH}^-] = K_w \cdot 10^{\text{pH}} \quad (15)$$

in the equation (14) the following expression for $K_{S(4-n)}$ is obtained:

$$K_{S(4-n)} = [\text{Me}(\text{OH})_{4-n}^{n+}] \cdot K_w^n \cdot 10^{n \text{ pH}} \quad (16)$$

In order to get the values for $K_{S(4-n)}$ by the mentioned method the logarithm of eq. (16) has to be found. The relation obtained is a straight line equation and can be written in explicit form as

$$\text{pH} = -\frac{1}{n} \log [\text{Me}(\text{OH})_{4-n}^{n+}] + \frac{1}{n} \log K_{S(4-n)} - \log K_w \quad (17)$$

For the sake of simplicity a constant C is introduced for the segment on the pH-axis:

$$C_{4-n} = \frac{1}{n} \log K_{S(4-n)} - \log K_w \quad (18)$$

The slope of the straight line in eq. (17) is $-\frac{1}{n}$, where n is the average number of OH⁻ ions per one metal ion necessary for the formation of the solid phase Me(OH)₄ (s).

The cumulative hydrolytic constants $^*\beta$ can be determined by the use of the same graphical tyndallometric method.

According to the definition:

$$^*\beta_1 = \frac{[\text{MeOH}^{3+}][\text{H}^+]}{[\text{Me}^{4+}]} \quad (19)$$

$${}^*\beta_2 = \frac{[\text{Me}(\text{OH})_2^{2+}] [\text{H}^+]^2}{[\text{Me}^{4+}]} \quad (20)$$

$${}^*\beta_3 = \frac{[\text{Me}(\text{OH})_3^+] [\text{H}^+]^3}{[\text{Me}^{4+}]} \quad (21)$$

${}^*\beta$ can be also expressed in another way, by taking into account the solubility products or the consecutive stability constants. It is evident from relations (10)–(13) that:

$${}^*\beta_1 = K_w \cdot \frac{K_{S_1}}{K_{S_0}} = K_w \cdot K_1 = {}^*K_1 \quad (22)$$

$${}^*\beta_2 = K_w^2 \cdot \frac{K_{S_2}}{K_{S_0}} = K_w^2 \cdot K_1 \cdot K_2 = {}^*K_1 \cdot {}^*K_2 \quad (23)$$

$${}^*\beta_3 = K_w^3 \cdot \frac{K_{S_3}}{K_{S_0}} = K_w^3 \cdot K_1 \cdot K_2 \cdot K_3 = {}^*K_1 \cdot {}^*K_2 \cdot {}^*K_3 \quad (24)$$

If the logarithms of eqs. (22)–(24) are taken and the expressions for K_{S_0} , K_{S_1} , K_{S_2} and K_{S_3} from relation (18) are put into the relations obtained, the constants ${}^*\beta$ can be easily evaluated:

$$\log {}^*\beta_1 = n_1 C_1 - n_0 C_0 \quad (25)$$

$$\log {}^*\beta_2 = n_2 C_2 - n_0 C_0 \quad (26)$$

$$\log {}^*\beta_3 = n_3 C_3 - n_0 C_0 \quad (27)$$

The average numbers (the numbers of ligand per one metal ion necessary for the formation of precipitate according to eqs. (5), (7), (8) and (9))

n_0 , n_1 , n_2 , and n_3 were determined from the slope $\left(-\frac{1}{n}\right)$ of the tangents on the solubility curve (eq. 17); and the constants C_0 , C_1 , C_2 , and C_3 are the segments on the pH-axis.

RESULTS

Tyndallometric measurements

Precipitation phenomena of thorium hydroxide were examined in aqueous solutions of thorium nitrate and potassium hydroxide in a wide concentration range of both precipitating components.

Fig. 1 shows some typical 10 min. tyndallometric curves with the corresponding pH curves. Turbidity and pH values are plotted against the concentration of potassium hydroxide for several constant concentrations of thorium nitrate.

Owing to the hydrolysis of thorium ion pH was at first constant during the addition of potassium hydroxide. When all the hydrolytic steps of thorium were surpassed, a discontinuous change of pH was observed. At the beginning of thorium hydroxide precipitation a molar ratio of thorium nitrate to potassium hydroxide 1:1 was found, for concentrations of thorium between $1 \times$

$\times 10^{-1}M$ and $3 \times 10^{-4}M$. For lower concentrations of thorium, between $3 \times 10^{-4}M$ and $3 \times 10^{-5}M$, a higher potassium hydroxide to thorium nitrate ratio was required for the beginning of the precipitation. At concentrations of thorium nitrate lower than $3 \times 10^{-5}M$ the precipitate did not appear.

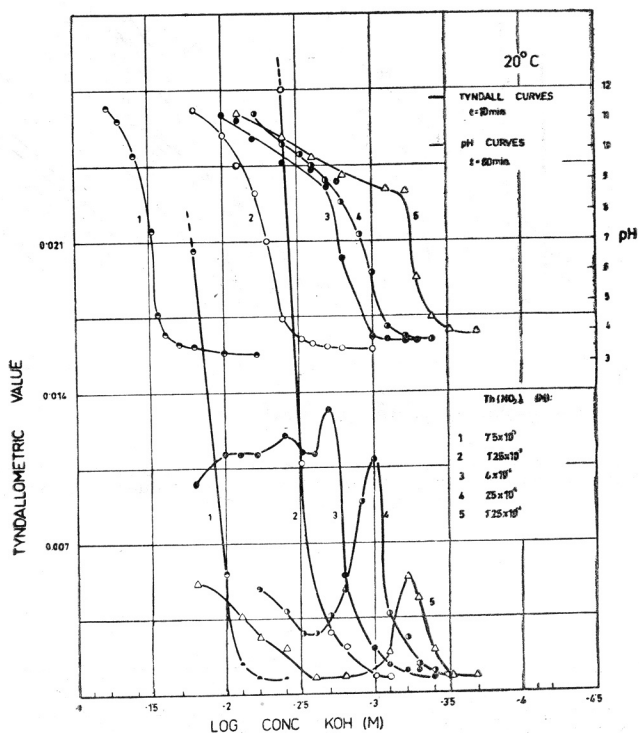


Fig. 1. 10 min. concentration tyndallograms and pH curves of the following systems:

1. $7.5 \times 10^{-3}M$ Th(NO₃)₄ - KOH var.
2. $1.25 \times 10^{-2}M$ Th(NO₃)₄ - KOH var.
3. $4 \times 10^{-4}M$ Th(NO₃)₄ - KOH var.
4. $2.5 \times 10^{-4}M$ Th(NO₃)₄ - KOH var.
5. $1.25 \times 10^{-4}M$ Th(NO₃)₄ - KOH var.

pH values were measured 24 hours after mixing.

At higher concentrations of thorium nitrate (curves 1 and 2 in Fig. 1.) the turbidity was high, the curves being very steep, and at $pH > 4$ already a fluffy thorium hydroxide precipitated fast.

At lower concentrations of thorium nitrate (curves 3—5 in Fig. 1) sols of low turbidity formed in the whole pH range. At concentrations of thorium less than $1 \times 10^{-4}M$ turbidities were low. In that way the boundary between clear and turbid systems could be found. Curves 3—5 in Fig. 1. show a decrease in the turbidity for the pH values between 9 and 10.

A three-dimensional tyndallogram was constructed showing turbidities (on z-axis) ten minutes after mixing the precipitation components (x axis = pH, y axis = log. concentration of thorium nitrate). Fig. 2 is a parallel projection of such a three-dimensional model. It consists of many parallel sections. At each section the concentration of thorium nitrate was kept cons-

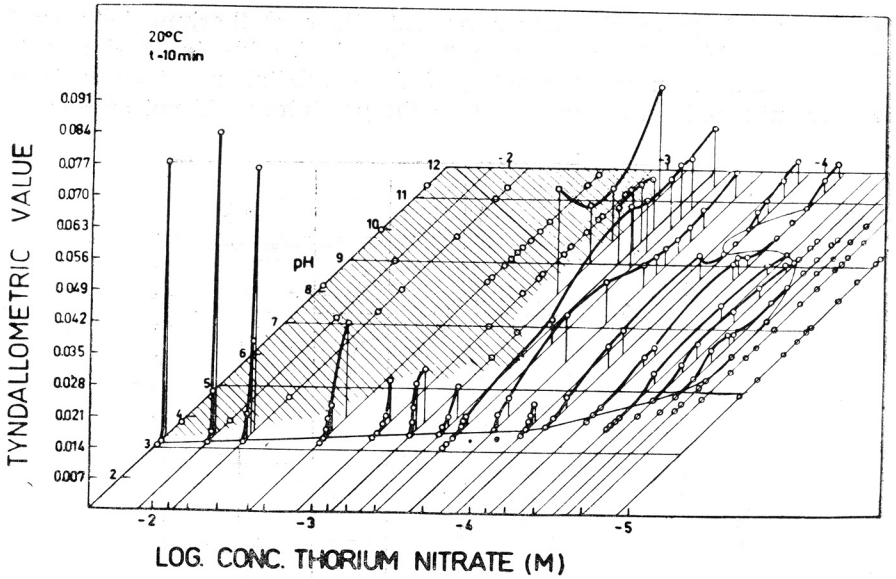


Fig. 2. The parallel projection of three-dimensional precipitation diagram of thorium hydroxide. Turbidities were measured 10 minutes and pH values 24 hours after mixing the precipitation components.

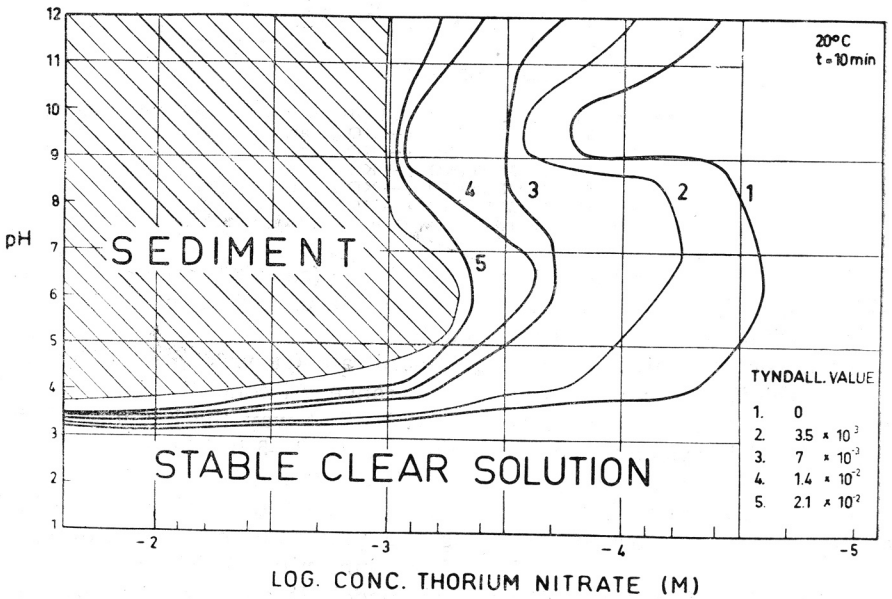


Fig. 3. The ground plan of the precipitation diagram shown in Fig. 2.

tant and pH was varied by the addition of potassium hydroxide as shown in Fig. 1.

Fig. 3 is the ground plan of the diagram in Fig. 2 giving the isohypsas of turbidity (curves 1—5). It shows the limits of the concentration regions of sedimentation and of stable clear solutions.

At higher concentrations of thorium nitrate the turbidity curves are steep and the area of sols is narrow. Fast precipitation occurs even at low pH values. At concentrations of thorium nitrate lower than $5 \times 10^{-4}M$ sols of low turbidity exist in a wide pH range. The region of stable clear solutions is the pH range 9—10.4 is shown for low concentrations of thorium. The lowest concentration of thorium nitrate for the precipitation to occur after the addition of potassium hydroxide is $3 \times 10^{-5}M$. At concentrations of thorium nitrate lower than $3 \times 10^{-5}M$ the systems are optically clear in the whole pH range.

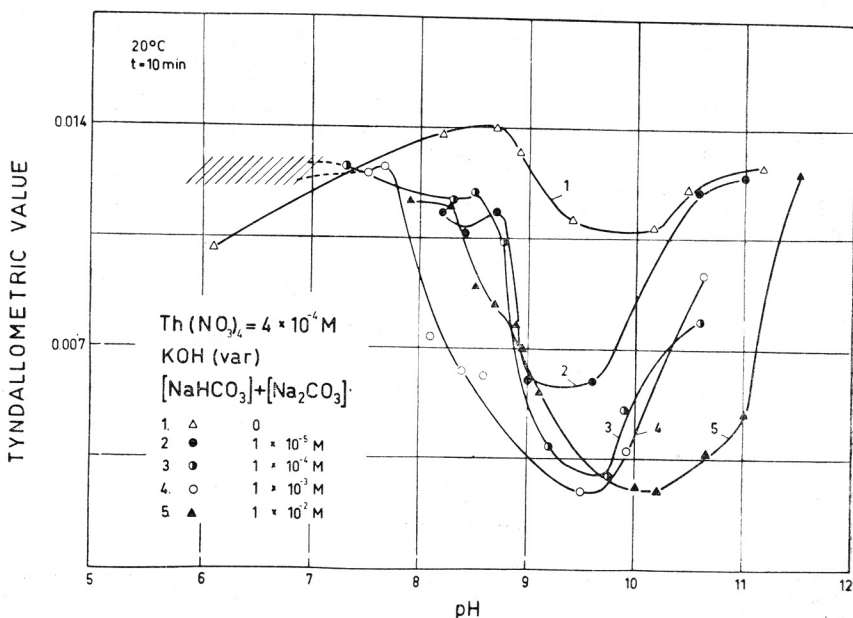


Fig. 4. The influence of present CO₂ on the precipitation of thorium hydroxide. Various concentration of NaHCO₃—Na₂CO₃ buffer systems (curves 2—5) were added to the systems Th(NO₃)₄ $4 \times 10^{-4}M$ —KOH var. (curve 1). Turbidity was measured 10 min. and pH 60 min. after mixing the reaction components.

Remarkable is the appearance of low turbidities and even of clear systems in Fig. 1, 2, and 3, between pH 9 and 10.4 for small concentrations of thorium nitrate. This is supposed to be an effect of CO₂ in air, in water and in potassium hydroxide solution.

In order to verify this hypothesis a constant concentration of thorium nitrate ($4 \times 10^{-4}M$) was taken and the pH was varied by adding potassium hydroxide as shown in Fig. 1.

Curve 1 in Fig. 4 shows the turbidities plotted against pH for these systems. Different buffer concentrations of NaHCO_3 — Na_2CO_3 (curves 2—5) at corresponding pH values were added to the systems represented by curve 1. Even a very small addition of the carbonate buffer (NaHCO_3 — Na_2CO_3) of total concentration $1 \times 10^{-5}M$ (about 40 times lower than the thorium nitrate concentration) causes a remarkable decrease of turbidity of sols between pH 9 and 10.4 where definite ratios of the concentrations of HCO_3^- and CO_3^{2-} ions exist in the solution. At pH = 9 there is about 95% HCO_3^- and 5% CO_3^{2-} and at pH = 10.4 there is about 50% HCO_3^- and 50% CO_3^{2-} of the total carbonate present in the system.

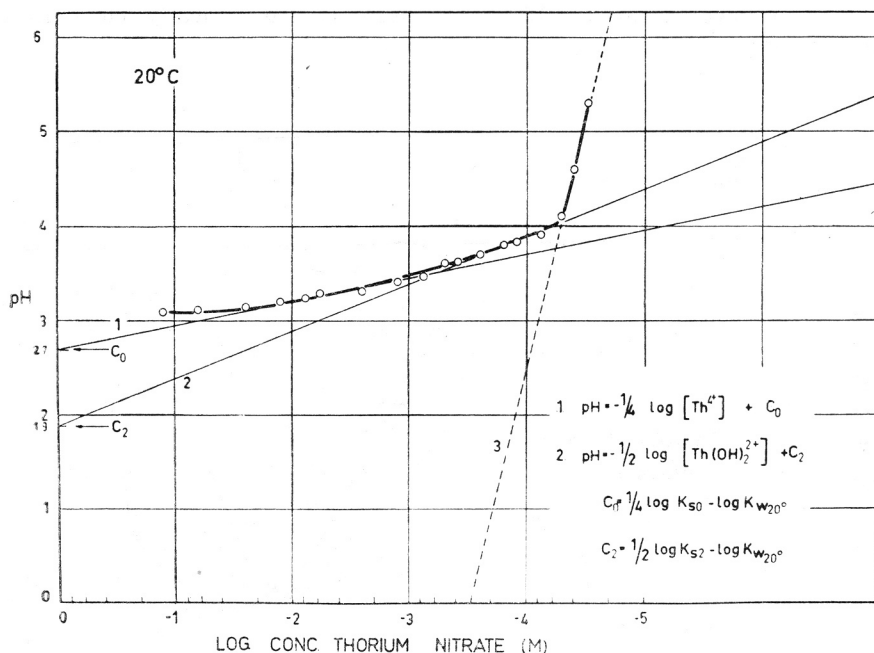


Fig. 5. The boundary between the stable clear solution and the range of formation of the solid phase of $\text{Th}(\text{OH})_4$ for various concentrations of $\text{Th}(\text{NO}_3)_4$ and the corresponding pH values (measured 24 hours after the mixing). Lines 1., 2., and 3. represent different equilibria between hydrolyzed thorium ions and formed precipitates.

The Solubility Product and the Hydrolytic Constant of Thorium Hydroxide

Our experiments for the determination of solubility constants from the solubility curve (Fig. 5) were based on the fact that the constitution of precipitated thorium hydroxide is $\text{Th}(\text{OH})_4$ ¹². In Fig. 5. pH is plotted against log. concentration of thorium nitrate for clear systems soon after the beginning of precipitation. This curve is a part of the isohypsa 1 in Fig. 3.

A part of the solubility curve is on the straight line 1 the slope of which is about $-\frac{1}{4}$ (for pH below 3.4) and the corresponding segment on the pH-axis is C_0 . The second part of the solubility curve (for pH between 3.4

and 4.1) is on the straight line 2. The slope of line 2 is $-1/2$ and the segment is C_2 .

$$C_0 = 2.7 \quad \text{and} \quad C_2 = 1.9$$

Using the equation (18) the following value for the solubility product at 20° C were obtained:

$$\log K_{S_0} = -45.9 \quad \text{and} \quad \log K_{S_2} = -24.5$$

If the solubility curve in Fig. 5 is constructed with the first turbid systems, the values for the segments on the pH axis are different ($C_0' = 2.8$ and $C_2' = 2.1$) and the slopes are the same. The solubility products are then higher:

$$\log K_{S_0}' = -45.5 \quad \text{and} \quad \log K_{S_2}' = -24.1$$

The average values are:

$$\log \bar{K}_{S_0} = -45.7 \quad \text{and} \quad \log \bar{K}_{S_2} = -24.3$$

DISCUSSION

Different values for the solubility product of thorium hydroxide were published in previous papers, but only a narrow range of thorium concentrations was investigated. The present paper deals with a broad range of concentrations of both precipitating components. Fig. 5 shows that for thorium concentrations between $2.5 \times 10^{-2}M$ and $6 \times 10^{-4}M$ the slow precipitation begins at pH 3.0 to 3.4. From the slope of the straight line 1 in Fig. 5 it is evident that in an aqueous solution the predominant ionic species in equilibrium with the solid phase of thorium hydroxide is the free thorium ion. The value of $\log \bar{K}_{S_0} = -45.7$ as calculated by us is in agreement with the results of other authors: Kovalenko — 44.7¹⁹, Korenman — 44.4²⁰, and Y. Oka — 44.9²⁵. Our pH values of the precipitation limit are somewhat lower than the cited values because of the small turbidities noticed by tyndallometric measurements. Lower values in the pH resulted in a lower solubility product.

In thorium concentrations between $6 \times 10^{-4}M$ and $6 \times 10^{-5}M$ the precipitation begins at pH 3.4 to 4.1. The slope of the precipitation limit (straight line 2 in Fig. 5) is $-1/2$ indicating that $[\text{Th}(\text{OH})_2^{2+}]_n$ is the predominant ionic species, in equilibrium with the solid phase of thorium hydroxide. Since the solubility curve is moderately curved without a significant break, the existence of ThOH^{2+} as well as that of Th^{4+} and $\text{Th}(\text{OH})_2^{2+}$ is not excluded.

The value obtained for $\log \bar{K}_{S_2} = -24.3$ is in agreement with Gayer and Leider's¹⁷ — 23.26. They assumed that the thorium hydrolytic ion species ThO^{2+} in aqueous solution is in equilibrium with the solid phase of thorium hydroxide. Our conclusion, that the predominant species is the free thorium ion in solutions below pH 3.4, and $[\text{Th}(\text{OH})_2^{2+}]_n$ between pH 3.4 and 4.1 is in accordance with the potentiometric work of Hietanen².

Kovalenko¹⁹ evaluated the solubility product in the thorium concentration range between $1 \times 10^{-4}M$ and $2 \times 10^{-3}M$. The author wrongly assumed that the change of the ionic strength of the solution was the reason of the change of the solubility product. In fact that occurs because the predominant ionic

species in aqueous solution in equilibrium with solid phase has changed from free thorium ion into aqueous thorium hydroxy-complex ion (most probably in $[\text{Th}(\text{OH})_2^{2+}]_n$ form).

Latimer's value of $\log K_{S_0} = -39$ calculated from the heat of formation of thorium hydroxide does not seem probable. The value of the cumulative constant of hydrolysis $\log {}^*\beta_2 = -7.0$ is somewhat greater than evaluated by other authors.

From the values ${}^*K_1 = -4.3$ and ${}^*K_2 = -3.4$ by Kraus and Holmberg[†] the cumulative constant of hydrolysis can be calculated as $\log {}^*\beta_2 = -7.7$.

K. Pan and T. M. Hseu⁸ investigated the hydrolysis of thorium in concentration range between $1 \times 10^{-2}M$ and $1 \times 10^{-4}M$. The authors concluded that, between pH 3 and 4, there is a mixture of Th^{4+} , ThOH^{3+} and $\text{Th}(\text{OH})_2^{2+}$. They have shown that stability constants depend on sodium perchlorate concentration. In $0.5M$ NaClO_4 $\log {}^*\beta_2$ is equal to -8.28 and at ionic strength extrapolated to zero $\log {}^*\beta_2 = -8.09$.

Our results concerning the existence of the predominant hydrolytic species in the form of $[\text{Th}(\text{OH})_2^{2+}]_n$ at pH between 3.5 to 4.1 are in accordance with the results of Chauvenet^{5,6}, of Schaal and Faucherre⁹, and of Souchay¹⁰. They concluded that the ratio $\text{Th} : \text{OH}^-$ is 1:2 at the hydrolytic species predominant in the solution.

From Hietanen's results² it is evident that the species ThOH^{3+} is not stable in the solution. We do not agree with the work of Kasper⁷ and Matijević⁴. Their opinion is that ThOH^{3+} is a stable ionic form. Matijević and coworkers suggested the existence of ThOH^{3+} in diluted solutions at pH about 7. In the present paper (Fig. 5) the experimental slope of the straight line 3 is -5 . It means that only one OH^- is necessary per 5 thorium ions for the formation of solid $\text{Th}(\text{OH})_4$. This relation indicates the existence of highly hydrolyzed polynuclear thorium ion species which is predominant in the solution above pH 4.1.

EXPERIMENTAL

Turbidity measurements were performed as described earlier²⁶ by the use of a Zeiss tyndallometer in connection with a Pulfrich photometer. A green filter (wave length $530 m\mu$) was used. The systems were prepared in glass tubes by mixing 5 ml. of thorium nitrate and 5 ml. of potassium hydroxide solutions. The concentration was always given for the whole volume i.e. for 10 ml. at 20°C . The glass tubes were thermostated in a constant temperature bath at $20^\circ \pm 0.1^\circ\text{C}$.

The systems for the determination of the solubility constants were thermostated for a week.

The acidity of the systems was measured with a glass electrode 60 min. after mixing the precipitation components

Materials

All the chemicals used were analytically pure, and all the solutions were prepared with bidistilled water.

Standard solution of thorium nitrate was prepared by dissolving Hopkin & Williams, Analar thorium nitrate. The concentration of thorium was determined gravimetrically by precipitation with oxalic acid²⁷, or by the ion exchange techniques²⁸ (Dowex — 50). Solutions of potassium hydroxide were standardized by acidimetric titration. Thorium nitrate solutions were freshly diluted from standard solutions (0.05 or $0.25 M$) $\text{Th}(\text{NO}_3)_4$ prior to each experiment.

REFERENCES

1. R. Holmberg and K. A. Kraus, *J. Phys. Chem.* **58** (1954) 325.
2. S. Hietanen, *Rec. trav. chim.* **75** No. 6 (1956) 711.
3. J. Lefebvre, *J. chim. phys.* **55** (1958) 227.
4. E. Matijević, M. B. Abramson, K. F. Schulz, and M. Kerker, *J. Phys. Chem.* **64** (1960) 1157.
5. E. Chauvenet and J. Tonnet, *Bull. Soc. Chim. France* **4**, **47** (1930) 701.
6. E. Chauvenet and Mm. Sonteyrand-Franck, *Bull. Soc. Chim. France* **47** (1930) 1218.
7. J. Kasper, *Dissertation*, The John Hopkins University Baltimore, Maryland (1941).
8. Kuan Pan and Tong Ming Haseu, *Bull. Chem. Soc. Japan* **28** (1955) 162.
9. R. Schaal and J. Faucherre, *Bull. Soc. Chim. France* **14** (1947) 927.
10. P. Souchay, *Bull. Soc. Chim. France* **15** (1948) 143.
11. G. Ludgren and L. G. Sillen, *Arkiv Kemi* **1** (1948) 277.
12. R. Prasad, *Kolloid-Z.* **174**, No. 2 (1961) 155.
13. R. Prasad, *Kolloid-Z.* **175**, No. 2 (1961) 136.
14. R. Prasad and A. Dey, *Kolloid-Z.* **175** (1961) 53.
15. R. Prasad and A. Dey, *J. Ind. Chem. Soc.* **37** (1960) 745.
16. R. Prasad and A. K. Dey, *Proc. Natl. Acad. Sci., India Sect. A* **28** (1959) 350.
17. K. H. Gayer and H. Leider, *J. Am. Chem. Soc.* **76** (1954) 5938.
18. W. M. Latimer, *Oxidation Potentials*, Prentice Hall, Inc., New York, N. Y., (1952) 299 p.
19. P. N. Kovalenko, *Zhur. Priklad. Khim.* **34**, No. 4 (1961) 789.
20. I. M. Korenman, *Zhur. Obsch. Khim.* **25** (1955) 1859.
21. B. Težak, E. Matijević, K. F. Schulz, J. Kratochvil, M. Mirnik, and V. B. Vouk, *Faraday Soc. Discussion*, No **18** (1954) 63.
22. B. Težak, H. Füredi, and M. Branica, *Proc. 2nd Int. Conf. Peaceful Uses Atomic Energy*, Geneva, 1958, Vol. **28** p. 250—252 (P. 2413).
23. H. Bilinski, H. Füredi, and B. Težak, Paper presented at the Symposium on Nuclear Fuels, Radovljica, Yugoslavia, April 20—25, 1961.
24. J. Kratochvil, *Dissertation*, Zagreb 1953.
25. J. Oka, *J. Chem. Soc. Japan* **59** (1938) 971.
26. B. Težak, E. Matijević, and K. Schulz, *J. Phys. Colloid Chem.* **55** (1951) 1557.
27. A. J. Vogel, *A Text-book of Quantitative Inorganic Analysis. Theory and Practice*, Second Ed. London—New York—Toronto. Longmans, Green & Co. (1957. New Impr.) **4**^o, 471 p.
28. O. Samuelson, *Ion Exchange in Analytical Chemistry*, John Wiley & Sons, Inc., New York, (1952).
29. I. I. Černjajev, V. A. Golovnja, and A. K. Molodkin, *Proc. 2nd Int. Conf. Peaceful Uses Atomic Energy*, Geneva, 1958, (P. 2136).

IZVOD

Taloženje i hidroliza torija(IV) u vodenoj otopini: torijev nitrat — kalijev hidroksid. I. Određivanje konstanata topivosti $\text{Th}(\text{OH})_4$

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Upotrebom tindalometra i pH-metra kod 20°C ispitivano je taloženje i hidroliza torija (IV) u vodenoj otopini torijev nitrat — kalijev hidroksid. Konstruiran je prostorni taložni dijagram za široko područje koncentracije obiju taložnih komponenta. Prikazana su koncentracijska područja, u kojima dolazi do momentanoga

taloženja torijeva hidroksida, gdje nastaju solovi i područje stabilnih bistrh otopina. Smanjenje taloženja torijeva hidroksida kod pH 9—10,4 nastaje zbog prisutnosti karbonat-iona. Upotrebom jednostavne grafičke tindalometrijske metode određeni su produkti topivosti torijeva hidroksida, koji iznose:

$$K_{S_0} = 1,3 \times 10^{-46} \text{ i } K_{S_2} = 2,9 \times 10^{-25}$$

i kumulativna hidrolitička konstanta $^*\beta_2 = 1,029 \times 10^{-7}$. Određene su hidrolitičke vrste torijeva iona, koje prevladavaju u vodenoj otopini u ravnoteži s krutom fazom. Dominantna je vrsta slobodnog iona Th^{4+} kod pH < 3,4 i $[\text{Th}(\text{OH})_2^{2+}]_n$ vrsta iona kod pH 3,5—4,1. Kod viših vrijednosti od pH 4,1 stvaraju se ionske vrste torija, koje imaju više od dva hidroksilna iona povezana na jedan torijev atom.

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