# Precipitation and Hydrolysis of Thorium in Aqueous Solution. V. Studies of the System: Thorium Nitrate-Ammonium Oxalate*

## H. Bilinski and N. Ingri**

*Department of Physical Chemistry, Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia and The Royal Institute of Technology, Stockholm, Sweden*

The precipitation of thorium from aqueous solution of thorium nitrate (1.25 m$M$) and ammonium oxalate (2.5—80 m$M$) was investigated at $p$H from 1 to 10. The following precipitates were identified with the brutto formula: $Th(OH)_4$ and $Th(C_2O_4)_2 \times 6 H_2O$ (by means of chemical analyses). The soluble thorium oxalato complex is formed between these two precipitates and contains 4 oxalate bound to thorium, with the simplest formula $[Th(C_2O_4)_4^{4-}]$ (as determined by coulometric titration). Using $\log K_0 = 34.8$ for the dissolution constant of thorium hydroxide in ammonium oxalate $\beta_4$ for thorium oxalate was obtained: $1.58 \times 10^{24}$.

## INTRODUCTION

In the process of extraction and purification of thorium from natural sources, the precipitation with oxalic acid is sometimes used. This is based on the observation that up to 92% of thorium, originally present in monazite, is recovered. Interest in selective precipitation is augmented by the fact that it can be applied to the separation of thorium from the rare earth elements, iron, titanium, uranium and others. There is considerable diversity in literature data on the composition of soluble thorium oxalato complexes.

Hauser and Wirth[1] concluded that in excess of oxalate $[Th_2(C_2O_4)_5^{2-}]$ complex is formed. Britzinger and Ekhardt[2] assumed the existence of $[Th_2(C_2O_4)_8^{8-}]$, while Bose and Chowdhury[3] reported $[Th(C_2O_4)_4^{4-}]$. In the recent work Lu and Hsu[4] indicated the existence of $[Th(C_2O_4)_3^{2-}]$. Kurup, Nair, and Moosath[5] suggested that two complexes are formed with the ratio $[Th(C_2O_4)_2]$ : : $[(NH_4)_2C_2O_4] = 1 : 8$ and $1 : 4$. Grinberg and Petrzhak[6], Bobtelsky and Bassat[7], Yatsimirskii and Zhukov[8], Korenmann and Korolikhin[9] and Lu and Hsu[4] agree that in excess of thorium in solution the $[ThC_2O_4^{2+}]$ complex is formed. In addition Bobtelsky and Bassat[7] suggested $[Th_2(C_2O_4)_3^{2+}]$ and $[Th_3(C_2O_4)_5^{2+}]$ complexes are formed, whereas Yatsimirskii and Zhukov[8] suggested a $[Th_2C_2O_4OH^{+5}]$ complex. Težak et al.[10] found that an isoelectric precipitation maximum is observed if sodium oxalate is added in slight excess to thorium nitrate solution. If the concentration of oxalate is approximately 4 times higher

---

than that of thorium, only soluble complexes are formed. The composition of the solid phase and the solubility region was not given.

In previous papers of this series[11-14] it was shown that the pH and the concentration of the precipitation components influence the formation of various complexes. In this work the effect of pH upon the formation of precipitates in the system thorium nitrate—ammonium oxalate has been investigated keeping the concentration of thorium nitrate constant (1.25 mM) while systematically varying the concentration of ammonium oxalate. In addition titration studies have been undertaken in order to obtain information on the number of oxalate ions bound to one thorium if the complexes are formed in excess of oxalate.

<div align="center">EXPERIMENTAL</div>

### Reagents and Analyses

The standard solution of thorium nitrate was prepared by dissolving Hopkin and Williams Analar thorium nitrate in distilled water. For titration experiments the thorium perchlorate solution was prepared by dissolution of thorium nitrate in perchloric acid and subsequent evaporation. The concentration of thorium was determined gravimetrically by precipitation with oxalic acid, heating, and weighing as $ThO_2$. Thorium nitrate and thorium perchlorate solutions were freshly diluted bofere each experiment from a standard stock solutions. The concentration of ammonium oxalate and oxalic acid solutions (Merck, p. a.) were determined by titration with permanganate. Oxalic acid, used in titrations was recrystallized twice before use.

The solution of $NaClO_4$ was prepared from $Na_2CO_3$ and reagent grade perchloric acid, following the procedure described by Biedermann.[15,16]

The precipitates of thorium oxalate were separated by centrifugation from the mother liquor, and dried in air at room temperature, at $76^0$ C and over $CaCl_2$. Analysis was made for the content of $NH_4$, $ThO_2$, C and H.
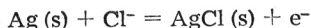
### Procedure

Turbidity measurents were performed using the method described earlier[17]. Systems were prepared in test tubes by mixing 5 ml of solution of thorium nitrate with $HNO_3$ and 5 ml of ammonium oxalate with KOH. The concentrations given are for the total volume of 10 ml. The test tubes with samples were kept in a constant temperature bath at $20.0 \pm 0.1^0$ C for 24 hr. The acidity was measured using a glass and a calomel electrode. For titration experiments the Ag, AgCl-electrode was used as the reference electrode. It was prepared according to Brown[18], by electrodepositing silver on a platinum foil and afterwards chloridizing the silver as anode in dilute HCl.
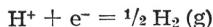
In potentiometric titrations the total concentration of thorium and oxalate ions was kept constant; the hydrogen ion concentration, h, was decreased by means of coulometer. In this way the same effect was obtained as if the $OH^-$ ions were added to the solution. The coulometer arrangement was the following one:

<div align="center">(—) Pt | equilibrium solution | 0.5 M NaCl | Ag (+)</div>
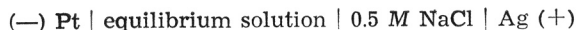
with the anodic reaction:

<div align="center">$Ag (s) + Cl^- = AgCl (s) + e^-$</div>

and the cathodic reaction:

<div align="center">$H^+ + e^- = 1/2 H_2 (g)$</div>

The number of microequivalents of reduced hydrogen ions was measured with a Leeds and Northrup Coulometric Analyzer.

In order to keep the activity factors constant all solutions were made 1 M in $NaClO_4$.

For the determination of the hydrogen ion concentration the following cell was used:

<div align="center">Glass electrode | equilibrium solution | RC</div>

where RC is the reference half cell:

<div align="center">$RC = 1\ M\ NaClO_4\ |\ 1.00\ M\ Na^+,\ 0.98\ M\ ClO_4^-,\ 0.02\ M\ Cl^-\ |\ AgCl,\ Ag$</div>
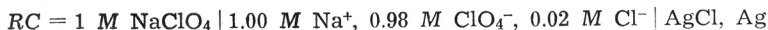
The salt bridge was of the »Wilhelm« type[19], for which the liquid junction potential can be neglected.

Fig. 1 represents the precipitation diagram of thorium oxalate. The region of soluble complexes was distinguished from the precipitation regions by observing the differences in scattering intensities. At $pH$ 6 to 8, the precipitate
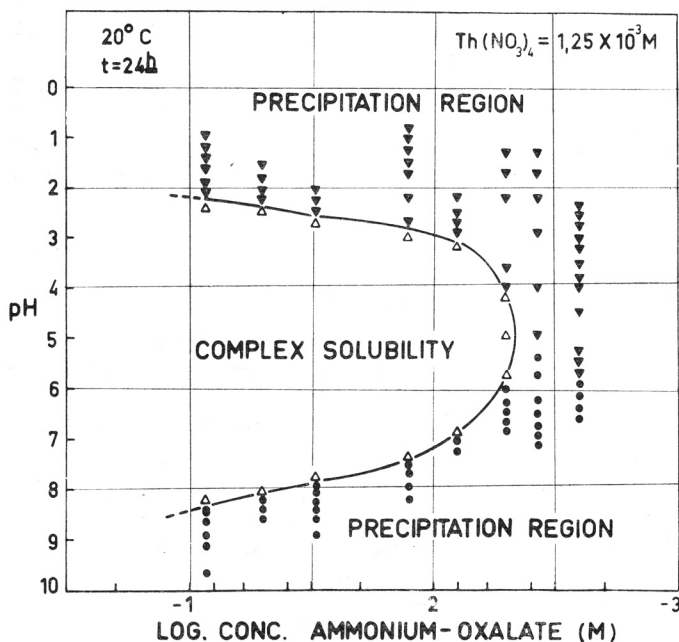


Fig. 1. The ground plan of the precipitation diagram formed in mixtures with 0.00125 $M$ Th(NO₃)₄, (NH₄)₂C₂O₄ var., $pH$ var., after the equilibrium is attained. Precipitation regions were determined by a tyndallometer 24 hr after mixing the precipitation components.

is fluffy thorium hydroxide, while at $pH < 2$—3 the precipitate is crystalline thorium oxalate. The results of several analyses of thorium oxalate precipitated with ammonium oxalate and that formed in excess of oxalic acid is given in Table I.

The soluble complex existing in the complex solubility region has not been isolated in the solid form. According to Yatsimirskii and Zhukov[8], the formation of mixed thorium hydroxo oxalate complexes is a possibility. In order to determine the probable number of the OH ions bound to thorium in the soluble complex, the same method was used as in the previous papers[13—14]. A series of solutions were prepared with a constant total concentration of oxalate and varying amounts of nitric acid and potassium hydroxide. The systems were kept at 20⁰ C 24 hr. to equilibrate and then the $pH$ was measured.

Curve 0 (Fig. 2) represents the titration curve of ammonium oxalate with nitric acid and potassium hydroxide. Curves 1—4 are calculated for a mixture (12.5 m$M$ ammonium oxalate, 1.25 m$M$ thorium nitrate), assuming that one,

TABLE I

*The Results of Chemical Analyses of Thorium Oxalate Formed in Solution Containing 1.25 mM [Th]$_{tot}$*

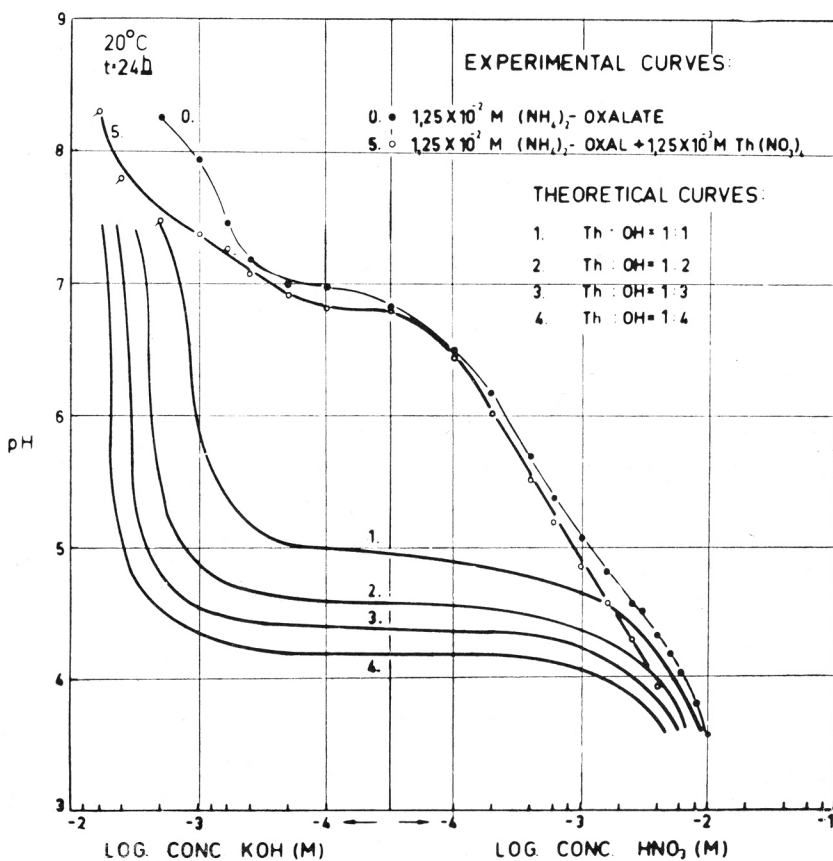| [(NH$_4$)$_2$C$_2$O$_4$]$_{tot}$ in mM | [H$_2$C$_2$O$_4$]$_{tot}$ in mM | [HNO$_3$]$_{tot}$ in mM | Precipitate dried | % Th | % C | % H |
|---|---|---|---|---|---|---|
| 2.5 | | 3 | CaCl$_2$ | 45.40 | 9.87 | 2.42 |
| 2.5 | | 3 | CaCl$_2$ | 45.62 | 9.83 | 2.47 |
| 2.5 | | 1 | CaCl$_2$ | 45.50 | 9.64 | 2.73 |
| 2.5 | | 1 | CaCl$_2$ | 44.60 | 9.17 | 2.55 |
| 2.5 | | 1 | 76° | 51.40 | 10.72 | 1.17 |
| 2.5 | | 1 | in air | 44.55 | 9.22 | 2.40 |
| | 10 | | 76° | 52.10 | 10.54 | 1.04 |
| | 10 | | CaCl$_2$ | 51.40 | 10.81 | 2.48 |
| | 10 | | in air | 45.18 | 9.77 | 2.79 |



Fig. 2. The change of $p$H of the 0.0125 $M$ (NH$_4$)$_2$C$_2$O$_4$ solution after adding HNO$_3$ and KOH (curve 0). Curves 1—4 are theoretical and calculated for different ratio Th : OH = 1 : 1, 1 : 2, 1 : 3 and 1 : 4. They show the change of $p$H of 0.0125 $M$ (NH$_4$)$_2$C$_2$O$_4$ after adding HNO$_3$ or KOH in the presence of 0.00125 $M$ Th(NO$_3$)$_4$, if OH is bound to thorium.

two, three, and four hydroxyl ions, respectively, are bound to thorium in the complex and that the $H^+$ consumption is that given by curve 0. The experimental titration curve, 5, for such a mixture consisting of 12.5 m$M$ ammonium oxalate and 1.25 m$M$ of thorium nitrate almost coincide with curve 0, which is a titration curve of only 12 m$M$ ammonium oxalate.

The dissociation constants of oxalic acid in 1 $M$ NaClO$_4$ determined separately, using the coulometric titration technique and computer calculations (program Letagrop[20]) are: $pK_1 = 1.02$; $pK_2 = 3.53$. These values are almost identical to those obtained by Sekine[21] ($pK_1 \approx 1.0$; $pK_2 = 3.54$). Using $K_1$ and $K_2$, the constants $\beta_1^H$ and $\beta_2^H$ can be calculated as

$$\beta_1^H = K_2 = \frac{[C_2O_4H^-]}{[C_2O_4^{2-}][H^+]} = 3.35 \times 10^3$$

$$\beta_2^H = K_1K_2 = \frac{[C_2O_4H_2]}{[C_2O_4^{2-}][H^+]^2} = 3.48 \times 10^4$$

According to the definition, $n_H$ is the average number of hydrogen ions, bound to that amount of ligand, which is not bound to metal:

$$n_H = \frac{H - h + OH}{A - \bar{n}B} = \frac{\sum\limits_0^J j\,\beta_j^H\,h_j}{\sum\limits_0^J \beta_j^H\,h_j}$$

In the case of oxalic acid $j = 2$ and the expression for $n_H$ reads:

$$n_H = \frac{3.35 \times 10^3\,h + 2 \times 3.48 \times 10^4\,h^2}{1 + 3.35 \times 10^3\,h + 3.48 \times 10^4\,h^2}$$

The value for $n_H$ was calculated for all titrations made and was plotted against $-\log h$ in Fig. 3.

The method of competitive reactions, introduced by Bjerrum[22] can be used only when $n_H$ is less than 1 and not too close to zero. For oxalic acid, which has a rather low value for the constant $pK_2 = 3.53$ in 1 $M$ NaClO$_4$, $n_H$ has low values at $pH > 4.5$, because almost all oxalate present is in the form $C_2O_4^{2-}$. There was hardly any difference in the titration curve of pure oxalic acid and of the oxalic acid + thorium perchlorate, at higher $pH$ values. However, between $pH$ 2.5 and 3, where the difference should be the greatest, thorium oxalate starts to precipitate. In order to avoid the precipitation of thorium oxalate, only solutions with rather high excess of oxalate were titrated, but the effect of thorium concentration was difficult to observe. By the coulometric titration method it was possible to measure very small changes in the OH concentration and to prevent introduction of impurities which are present even in purified hydroxide solution.

From titration data and the calculated $n_H$ values, the average number of oxalate bound to thorium, $\bar{n}$ can be calculated as

$$\bar{n} = \frac{A - (H - h + K_w\,h^{-1})\,n_H^{-1}}{B}$$

The mean value from 57 points is $\overline{n} = 3.86$. A is the total concentration of ligand, B is the total concentration of metal and H is the analytical concentration of hydrogen ions.

The concentration of the free ligand, $a$, is

$$a = \frac{A - \overline{n}\,B}{\overset{J}{\underset{0}{\Sigma}}\,\beta_j^H\,h_j}$$

All experimental data (A, B, H, E) and calculated values ($E_0$, $-\log h$, $n_H$, $\overline{n}$, $\log a$) from titration measurements are represented in Table II.
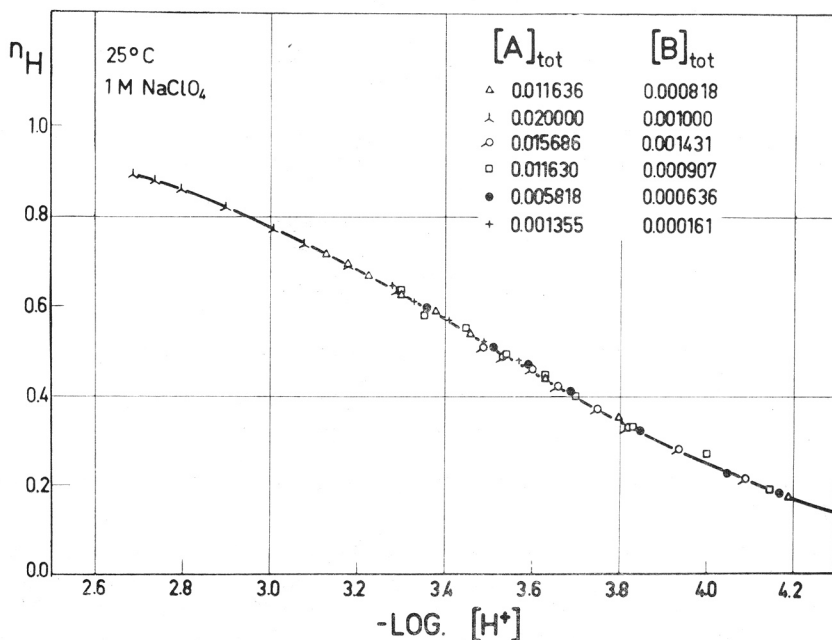


Fig. 3. From eq. (4) the value for $n_H$ was calculated and plotted against $-\log h$, for all points in six titrations listed in Table II.

TABLE II

*Experimental Data from EMF Measurements for 25⁰ C and 1 M NaClO₄*

|  | H | E | $-\log h$ | $n_H$ | $\tilde{n}$ | $\log a$ |
|---|---|---|---|---|---|---|
| B = 0.001431 | 0.005552 | +189.1 | 3.4942 | 0.5064 | 3.7399 | —2.2793 |
| A = 0.015686 | 0.005225 | +186.3 | 3.5415 | 0.4929 | 3.9597 | —2.2929 |
| $E_0$ = 395.78 | 0.004833 | +182.9 | 3.5990 | 0.4595 | 3.9181 | —2.2629 |
|  | 0.004506 | +179.4 | 3.6582 | 0.4257 | 3.9241 | —2.2372 |
|  | 0.003918 | +173.9 | 3.7511 | 0.3741 | 3.9730 | —2.2031 |
|  | 0.003526 | +169.8 | 3.8205 | 0.3373 | 3.9691 | —2.1781 |
|  | 0.002872 | +162.5 | 3.9439 | 0.2767 | 3.9954 | —2.1419 |
|  | 0.002218 | +154.0 | 4.0876 | 0.2154 | 4.0289 | —2.1088 |

|  | H | E | $-\log h$ | $n_{\mathrm{H}}$ | $\tilde{n}$ | $\log a$ |
|---|---|---|---|---|---|---|
| B = 0.001000<br>A = 0.020000<br>$E_0$ = 347.76 | 0.01661 | +188.7 | 2.6891 | 0.8933 | 3.6960 | —2.6910 |
|  | 0.01611 | +185.8 | 2.7381 | 0.8774 | 3.7224 | —2.6465 |
|  | 0.01561 | +182.3 | 2.7973 | 0.8584 | 3.6731 | —2.5957 |
|  | 0.01468 | +176.3 | 2.8987 | 0.8215 | 3.6677 | —2.5105 |
|  | 0.01361 | +169.6 | 3.0120 | 0.7748 | 3.6900 | —2.4205 |
|  | 0.01294 | +165.4 | 3.1828 | 0.7422 | 3.6756 | —2.3654 |
|  | 0.01192 | +159.5 | 3.1828 | 0.6937 | 3.7624 | —2.2968 |
|  | 0.01088 | +153.0 | 3.2926 | 0.6348 | 3.6642 | —2.2210 |
|  | 0.00861 | +139.9 | 3.5141 | 0.5089 | 3.6825 | —2.0947 |
| B = 0.000907<br>A = 0.011630<br>$E_0$ = 350.53 | 0.005445 | +155.6 | 3.2955 | 0.6337 | 4.2293 | —2.5405 |
|  | 0.005119 | +152.1 | 3.3547 | 0.5836 | 3.9305 | —2.4713 |
|  | 0.004725 | +146.6 | 3.4477 | 0.5478 | 4.0309 | —2.4411 |
|  | 0.004190 | +141.2 | 3.5390 | 0.4936 | 4.1092 | —2.3979 |
|  | 0.003724 | +136.0 | 3.6269 | 0.4434 | 4.1499 | —2.3579 |
|  | 0.003376 | +131.9 | 3.6962 | 0.4039 | 4.1555 | —2.3286 |
|  | 0.002794 | +124.0 | 3.8298 | 0.3325 | 4.0485 | —2.2745 |
|  | 0.002259 | +116.5 | 3.9566 | 0.2718 | 4.1092 | —2.2397 |
|  | 0.001585 | +105.0 | 4.1510 | 0.1925 | 4.1510 | —2.1972 |
|  | 0.001027 | + 91.8 | 4.3741 | 0.1235 | 4.0287 | —2.1555 |
|  | 0.000701 | + 81.0 | 4.5567 | 0.0859 | 4.1841 | —2.1450 |
| B = 0.000818<br>A = 0.011636<br>$E_0$ = 350.53 | 0.006815 | +165.3 | 3.1315 | 0.7193 | 3.8963 | —2.6168 |
|  | 0.006524 | +162.3 | 3.1822 | 0.6939 | 3.8888 | —2.5805 |
|  | 0.006233 | +159.3 | 3.2330 | 0.6677 | 3.8594 | —2.5794 |
|  | 0.005869 | +155.4 | 3.2989 | 0.6322 | 3.8484 | —2.5018 |
|  | 0.005413 | +150.6 | 3.3801 | 0.5866 | 3.8130 | —2.4508 |
|  | 0.005051 | +146.0 | 3.4578 | 0.5421 | 3.6210 | —2.3991 |
|  | 0.004724 | +142.7 | 3.5136 | 0.5092 | 3.6189 | —2.3696 |
|  | 0.004033 | +136.0 | 3.6269 | 0.4434 | 3.7567 | —2.3210 |
|  | 0.003178 | +126.0 | 3.7959 | 0.3501 | 3.6870 | —2.2513 |
|  | 0.002269 | +114.0 | 3.9988 | 0.2516 | 3.6858 | —2.1902 |
|  | 0.001578 | +102.4 | 4.1949 | 0.1769 | 3.7616 | —2.1521 |
|  | 0.001069 | + 91.0 | 4.3877 | 0.1210 | 3.8386 | —2.1268 |
| B = 0.000636<br>A = 0.005818<br>$E_0$ = 296.68 | 0.002705 | +102.8 | 3.2778 | 0.6436 | 3.8268 | —2.9144 |
|  | 0.002468 | + 97.9 | 3.3606 | 0.5975 | 3.7985 | —2.8611 |
|  | 0.002250 | + 93.2 | 3.4401 | 0.5519 | 3.7687 | —2.9285 |
|  | 0.002068 | + 89.1 | 3.5094 | 0.5116 | 3.7403 | —2.7705 |
|  | 0.001868 | + 84.6 | 3.5855 | 0.4674 | 3.7341 | —2.7357 |
|  | 0.001614 | + 78.6 | 3.6869 | 0.4094 | 3.7372 | —2.6914 |
|  | 0.001250 | + 69.0 | 3.8492 | 0.3225 | 3.7402 | —2.6325 |
|  | 0.001068 | + 63.3 | 3.9456 | 0.2760 | 3.7071 | —2.6012 |
|  | 0.000887 | + 57.0 | 4.0521 | 0.2296 | 3.6814 | —2.5762 |
|  | 0.000705 | + 50.0 | 4.1704 | 0.1847 | 3.7199 | —2.5507 |
|  | 0.000523 | + 50.0 | 4.1704 | 0.1847 | 3.7199 | —2.5507 |
|  | 0.000523 | + 40.8 | 4.3260 | 0.1367 | 3.6572 | —2.5209 |
|  | 0.000341 | + 29.0 | 4.5244 | 0.0910 | 3.7655 | —2.5072 |
| B = 0.000161<br>A = 0.001355<br>$E_0$ = 360.33 | 0.000994 | +166.3 | 3.2803 | 0.6474 | 3.9051 | —3.5560 |
|  | 0.000913 | +163.1 | 3.3344 | 0.6123 | 3.8431 | —3.5421 |
|  | 0.000800 | +158.6 | 3.4105 | 0.5690 | 3.9144 | —3.5039 |
|  | 0.000671 | +153.7 | 3.4933 | 0.5210 | 4.2343 | —3.4909 |
|  | 0.000591 | +149.4 | 3.5660 | 0.4787 | 4.2691 | —3.4582 |

### DISCUSSION

From the results of analyses of thorium oxalate (Table I) it can be concluded that the brutto formula of thorium oxalate precipitated with ammonium oxalate in the excess of oxalic acid is the same: $Th(C_2O_4)_2 \times 6 H_2O$, with theoretical values 44.9% Th, 9.3% C and 2.3% H. The agreement is satisfactory for the two samples dried in air.

From the coincidence of curves 5 and 0 in Fig. 2, it can be concluded that the thorium oxalato complex does not contain hydroxyl groups, and that it differs in this respect from thorium phthalate[13] and thorium maleate[14] complexes. This is in disagreement with the results of Yatsimirskii and Zhukov[8], who suggested the existence of mixed thorium oxalate complexes.

Because of the very limited pH range, in which the titration of oxalic acid is possible, and because of the fact that the oxalate ion was in great excess in the investigated solutions, only that part of the $\bar{n}$ curve was obtained over which $\bar{n}$ is independent of log $a$. It was impossible to calculate the equilibrium constant from titration data. It seems, however, that the most probable species existing in the range of complex solubility (Fig. 1) is the complex $[Th(C_2O_4)_4{}^{4-}]$, or its dimer.

If the simplest formula for thorium oxalate $[Th(C_2O_4)_4{}^{4-}]$ is accepted, then it is possible to calculate the constant $\beta_4$, using the solubility data of thorium hydroxide in ammonium oxalate. The only value for $\beta_4$ reported in literature is that of Bose and Chowdhury[3]: $\beta_4 = 3.05 \times 10^{24}$.

The equation describing the dissolution of thorium hydroxide in the presence of ammonium oxalate can be given as:

$$Th(OH)_{4(s)} + 4 C_2O_4{}^{2-} + 4 H^+ = [Th(C_2O_4)_4{}^{4-}] + 4 H_2O$$
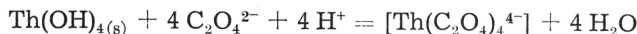
The equilibrium constant for this reaction calculated from the solubility curve of thorium hydroxide in the presence of ammonium oxalate is log $K_0 = 34.8$. For excess of oxalate, the assumption was made that $[Th(C_2O_4)_4{}^{4-}] = (Th)_{tot}$, and that the concentration change due to oxalate bound to the thorium complex can be neglected. If the following reaction is assumed:

$$Th^{4+} + 4 C_2O_4{}^{2-} = [Th(C_2O_4)_4{}^{4-}],$$
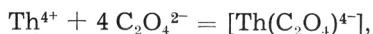
the constant $\beta_4$ is:

$$\beta_4 = K_0 K_w^4 K_{SO}{}^{-1} = 1.58 \times 10^{24}.$$

Titration data seem to confirm the earlier assumption of the existence of the complex $[Th(C_2O_4)_4{}^{4-}]$ as the predominant species in excess of oxalate.

### REFERENCES

1. O. H a u s e r  and  F. W i r t h, *Z. Angew. Chem.* **22** (1909) 484.
2. H. B r i t z i n g e r, and W. E k h a r d t, *Z. Anorg. Allgem. Chem.* **224** (1935) 93.
3. M. B o s e  and D. M. C h o w d h u r y, *J. Ind. Chem. Soc.* **31** (1954) 111.
4. C h a o  T a  L u  and  S h a o  C h'u a n  H s u, *Chung Kuo K'o Hsueh Yuan Ying Yung Hua Hsueh Yen Chiu So Chi K'an* **14** (1965) 19. cit. C. A. **64**, 8981a.
5. K. N. N. K u r u p, K. V. N a i r, and S. S. M o o s a t h, *Proc. Ind. Acad. Sci.* **47A** (1958) 373.

6. A. A. Grinberg and G. I. Petrzhak, *Trudy Rad. Inst. Khim. i Geokhim.* **7** (1956) 50.
7. M. Bobtelsky and A. B. Bassat, *Bull. soc. chim. France* **1958**, 233.
8. K. B. Yatsimirski and Yu. A. Zhukov, *Zh. Neorg. Khim.* **7** (1962) 1583.
9. I. M. Korenman and V. V. Korolikhin, *Trudy po Khim i Khim. Tekhnol.* **3** (1960) 106.
10. B. Težak, M. Branica, H. Füredi, and N. Šimunović, *Proc. Intern. Conf. Peaceful Uses of Atomic Energy,* Geneva **7** (1955) 401P/991.
11. H. Bilinski, H. Füredi, M. Branica, and B. Težak, *Croat. Chem. Acta* **35** (1963) 19.
12. H. Bilinski, H. Füredi, and B. Težak, *Croat. Chem. Acta* **35** (1963) 31.
13. H. Bilinski, *Croat. Chem. Acta* **38** (1966) 71.
14. H. Bilinski and Z. Despotović, *Croat. Chem. Acta* **39** (1967) 165
15. G. Biedermann, *Arkiv Kemi* **9** (1956) 277.
16. G. Biedermann, Dissertation, Svensk Kemisk Tidskrifft **76** (1964) 4.
17. B. Težak, E. Matijević, and K. Schulz, *J. Phys. Colloid Chem.* **55** (1951) 1557.
18. A. S. Brown, *J. Am. Chem. Soc.* **56** (1934) 646.
19. W. Forsling, S. Hietanen, and L. Sillén, *Acta Chem. Scand.* **6** (1952) 901.
20. N. Ingri and L. G. Sillén, *Arkiv Kemi* **23** (1964) 97.
21. T. Sekine, *Acta Chem. Scand.* **19** (1965) 1476.
22. J. Bjerrum, *Z. Anorg. Allgem. Chem.* **119** (1921) 179.

## IZVOD

### Taloženje i hidroliza toriuma (IV) u vodenim otopinama. V. Kompleksi toriuma s oksalat ionima

#### H. Bilinski i N. Ingri

Ispitano je taloženje toriuma iz vodene otopine torium nitrata (1.25 mM) i amonium oksalata (2.5—80 mM) u pH području od 1 do 10. Kemijskom analizom utvrđeni su talozi $Th(OH)_4$ i $Th(C_2O_4)_2 \times 6 H_2O$. Topivi torium oksalato kompleks, koji nastaje u suvišku amonijeva oksalata, sadrži četiri oksalat iona na jedan torium: $[Th(C_2O_4)_4^{-4}]$, što je utvrđeno kulometrijskom titracijom.

Pomoću konstante otapanja torium hidroksida u amonium oksalatu (log $K_0$ = = 34.8), izračunata je konstanta torium oksalata $\beta_4 = 1{,}58 \times 10^{24}$.

INSTITUT »RUĐER BOŠKOVIĆ«
ZAGREB, JUGOSLAVIJA
I
ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM, ŠVEDSKA