

CCA-410

541.18.041:542.938:546.841

Original Scientific Paper

Precipitation and Hydrolysis of Thorium(IV) in Aqueous Solution. III. The Composition of the Precipitates in the System Thorium Nitrate — Potassium Phthalate

H. Bilinski *

Department of Physical Chemistry, Institute »Ruđer Bošković«, Zagreb, Croatia,
Yugoslavia

Received December 10, 1965

Precipitation from water solutions of thorium nitrate and potassium phthalate was investigated for a broad range of concentrations of both precipitation components. The influence of pH and of time on the formation of various precipitates was studied, the composition and characteristics of the precipitates being determined by chemical analysis, and IR and NMR spectra. The following precipitates were characterized:

- Th(OH)₄ without water of crystallization;
- Th(Phthalate)₂ without water of crystallization;
- Thorium hydroxide-phthalate polymer with unknown formula.

An empirical formula was derived, which shows the conditions for precipitation of thorium hydroxide in the presence of potassium phthalate. In the soluble mixed hydroxo-phthalato thorium complex, two OH⁻ ions are bound per one thorium.

INTRODUCTION

In literature one can find only few data on the composition of the compounds formed between thorium and organic dicarboxylic acids. For instance very little has been published about thorium phthalate. M. Bobtelsky and B. Gadda¹ reported some results of heterometric titration of thorium nitrate with potassium phthalate. From several titration curves and rather qualitative data they concluded the existence of several complexes. Težak *et al.*^{2,3} in an investigation of precipitation in the system thorium nitrate — potassium phthalate observed the existence of optically clear systems even at high pH values. We have recently investigated⁴ the influence of pH and neutral electrolytes on the precipitation and dissolution in the system: thorium nitrate — potassium phthalate. Three — dimensional concentration diagrams were given.

The subject of this paper is the composition and properties of various precipitates and soluble complexes formed in this system after complete equilibrium has been attained.

EXPERIMENTAL

Turbidity measurements were performed with a Zeiss tyndallometer joined to a Pulfrich photometer. The method was described earlier.^{4,5} The systems

* Presented in part in Ph. D. Thesis Faculty of Science, the University of Zagreb, Zagreb, 1964.

were prepared in glass tubes by mixing 5 ml. of a solution of thorium nitrate + HNO_3 and 5 ml. of a solution of potassium phthalate + KOH . The pH value was varied by varying the amounts of HNO_3 and KOH . The concentrations given are always the total concentrations in the whole mixture. The glass tubes with samples were kept for a week in a constant temperature bath at $20^\circ \pm 0.1$ C, except those in Figs. 1, 2 and 5, which were kept for 24 hours. Numerous experiments have shown that in this system complete equilibrium is attained after 7 days. The acidity was measured with a glass electrode and a pH meter (Radiometer pHM3), 24 hours or 7 days after mixing. The precipitates were observed under a microscope. IR spectra of the precipitates were measured with a *Perkin Elmer 221* spectrophotometer, using the KBr method.

The precipitates were separated from the mother liquor and dried to constant weight at 85° C. Thorium was determined as ThO_2 by igniting at 600° C. The presence of OH or H_2O in the precipitates was tested using proton magnetic resonance.

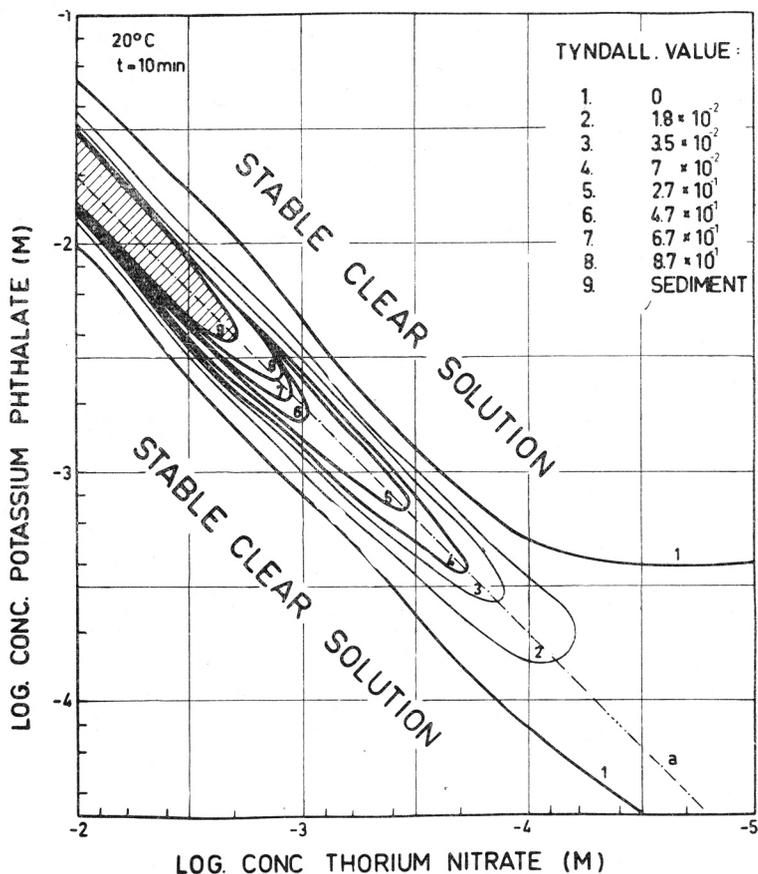


Fig. 1. The ground plan of a three-dimensional concentration tyndallogram. The turbidity is plotted versus the log. concn. of thorium nitrate and potassium phthalate. The turbidities were measured 10 min. after mixing.

Solubility Studies

Fig. 1 gives results for measurements, where thorium nitrate and potassium phthalate were mixed without addition of HNO_3 or KOH . The turbidity 10 minutes after mixing is plotted (perpendicular to the paper) as a function of the total thorium and phthalate. The diagram shows the height curves of equal turbidity (curves 1—9). It was constructed from many parallel sections in which the concentration of thorium was constant and the concentration of phthalate varied. The diagram shows clearly the narrow range of formation of the solid phase, whose composition was to be determined.

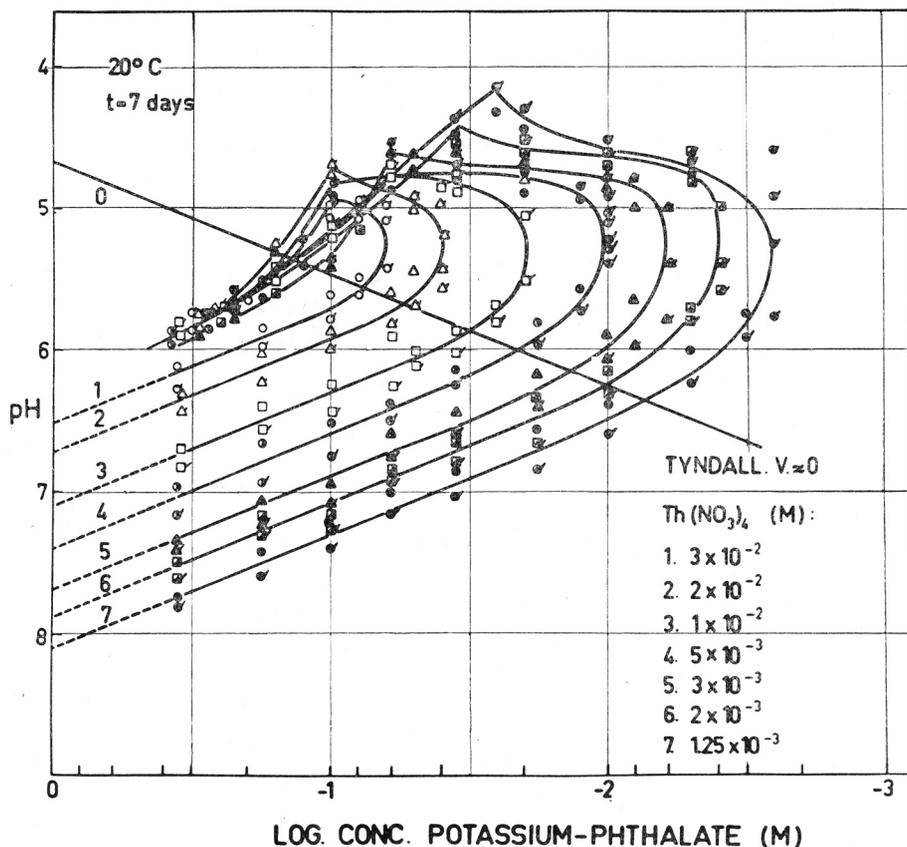


Fig. 2. pH curves of the cross-sections from Fig. 1 and for 1×10^{-1} M $\text{Th}(\text{NO}_3)_4$. Curve b connects the pH values in the precipitation maxima for different thorium concentrations. The straight line a shows the ratio of the components in the maxima of precipitation.

Fig. 2 shows how pH varies in nine cross-sections (eight of them are in Fig. 1) around the precipitation region. The pH values in the precipitation maxima, for various concentrations of thorium, are joined by a broken curve. The ratio of the molar concentrations of the precipitation components in these maxima is constant, namely $[\text{Th}]_{\text{tot}} : [\text{Phthalate}]_{\text{tot}} = 1 : 2$ which is evident from

the straight line *a* in Figs. 1 and 2. No precipitate was observed if less than 1 or more than 4 phthalate were added per Th.

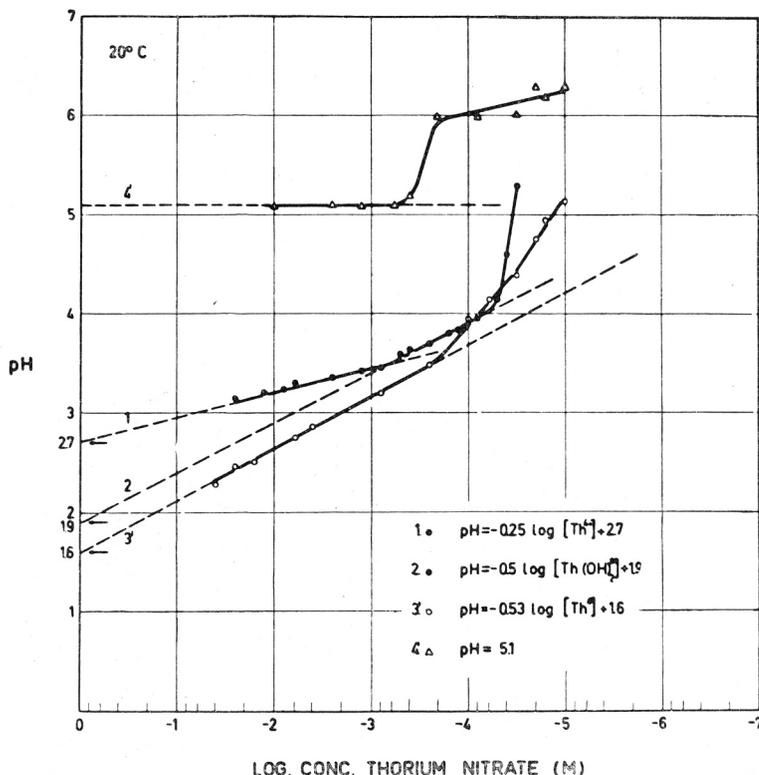


Fig. 3. pH plotted against log. concn. of thorium nitrate, of the boundary surface between the stable clear solution and the formation of the colloid precipitate. Line 4' (triangles) and line 3' (circles) correspond to the two limits "1" in Fig. 1. Lines 1 and 2 (dots) are the tangents on the solubility curve of thorium hydroxyde.

In Fig. 3 the circles give the pH for 1 phthalate added per thorium (curve 3') and the triangles (curve 4') give the pH for 4 phthalate added per thorium. Curve 3' for $[\text{Th}]_{\text{tot}} > 2.5 \times 10^{-4} M$ is a straight line of slope $-0.53 (\approx 1/2)$. For comparison the solubility curve of thorium hydroxide⁶ is also given, curve 1 with black dots. Curve 4' is horizontal at $\text{pH} \approx 5.1$ for $[\text{Th}]_{\text{tot}} 5 \times 10^{-4} M$ and represents the dissolution of this solid phase in excess of phthalate.

Fig. 4 shows another series of experiments in which $[\text{Th}]_{\text{tot}}$ was always $3 \times 10^{-3} M$, $[\text{Phthalate}]_{\text{tot}}$ was varied and pH was also varied, by addition of HNO_3 or KOH . The diagram consists of many parallel cross-sections, in each of which the total concentration of phthalate is constant. pH was measured 7 days after mixing. The various symbols (appearing in regions 1,2,3,5) stand for different types of precipitate, as observed under a microscope. In region 4 the solution was clear, so that soluble complexes must prevail.

In the region 1 of Fig. 4 relatively big prisms are formed after several hours. They melt in the electron microscope. Their IR spectra showed their identity with phthalic acid, which is only slightly soluble in water.

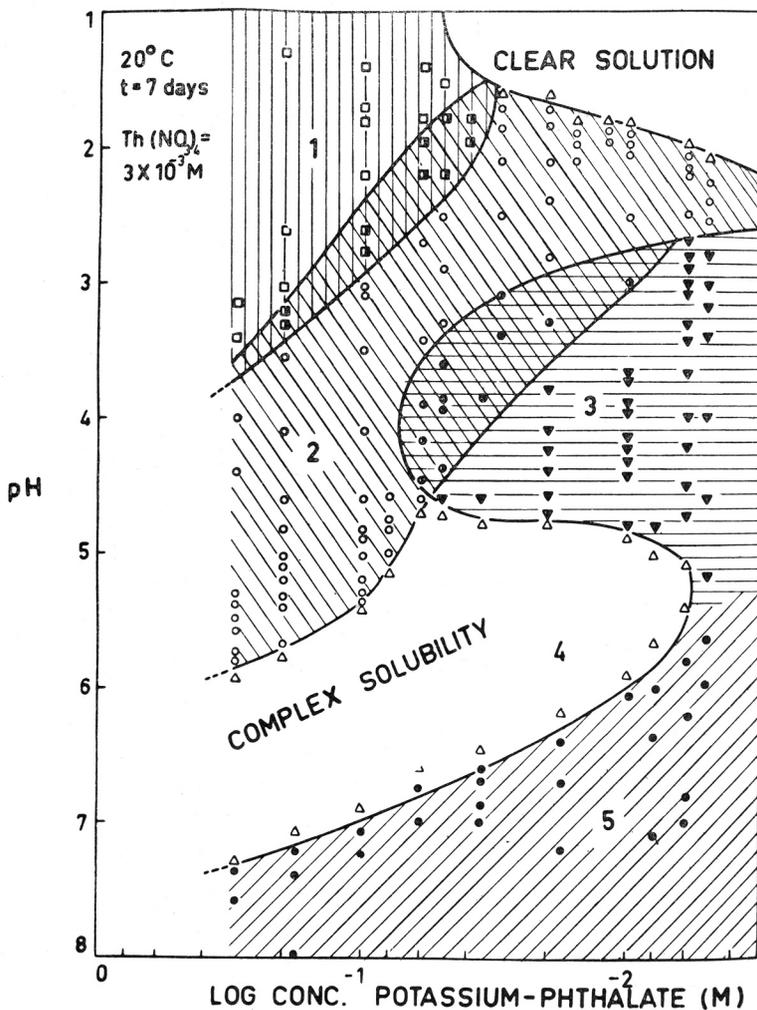


Fig. 4. The ground plan of the precipitation diagram formed in mixtures with $3 \times 10^{-3} M$ Th(NO₃)₄, K₂-phthalate var., pH var., after the final equilibrium was attained. The different precipitation regions (1, 2, 3 and 5) were determined with the microscope 7 days after mixing the precipitation components.

In region 2, crystallization occurs slowly and final equilibrium is attained only after standing for 7 days. Long thin needles are found in this region and they often gather to star-like groups. It was very easy to distinguish between samples from region 1, region 2, and the overlapping region, where both precipitates are formed. Gravimetric analyses showed that the compound in region 2 contains 41.4% \pm 1.09 of thorium, the same for different samples.

Region 3 of Fig. 4 contains the same colloid precipitate as obtained in the experiments in Fig. 1. Chemical analyses are presented in Table 1.

TABLE I
The results of chemical analysis of the colloid precipitates formed at the ratio
[Th] : [Phthalate] = 1 : 2

[Th] _{tot}	[Phth] _{tot}	Precipitate dried	% Th in precipitate	% lost by igniting at 600° C
2×10^{-3}	4×10^{-3}	at 85° C	49.6	43.5
2×10^{-3}	4×10^{-3}	over CaCl ₂	48.4	45.0
2×10^{-3}	4×10^{-3}	over CaCl ₂	48.0	45.5
3×10^{-3}	6×10^{-3}	over CaCl ₂	47.6	45.5 (24.95% C + 2.42% H)
3×10^{-3}	6×10^{-3}	over CaCl ₂	47.5	45.7 (24.27% C + 2.65% H)
5×10^{-3}	1×10^{-2}	over CaCl ₂	46.2	47.3
5×10^{-3}	1×10^{-2}	at 85° C	47.2	46.2
5×10^{-3}	1×10^{-2}	at 85° C	47.3	46.2

Regions 2 and 3 in Fig. 4 have a region of overlap where the colloid precipitate appears immediately and the crystals several hours after mixing.

In region 5 of Fig. 4 fluffy thorium hydroxide was precipitated. Its IR spectrum was identical with that of pure thorium hydroxide, obtained by precipitation with potassium hydroxide.

In region 4 a stable, soluble complex is formed, which we could not isolate in a solid salt. No other analogous complex with a dicarboxylic acid has been isolated in a solid salt, as far as the author knows.

The addition of thorium nitrate solution to a solution of potassium phthalate lowered the pH of the latter and an attempt was made to determine the number of OH ions bound per thorium in the complex. A series of mixtures was prepared with constant total concentration of phthalate and varying amounts of nitric acid. After 24 hours at 20° C, pH was measured. Curve 0 in Fig. 5 gives pH as a function of the total added amount of nitric acid. It may be called a »titration curve«, and it shows how much HNO₃ is necessary to lower the original pH (7.34) of $3.6 \times 10^{-2} M$ potassium phthalate solution to some given value.

Curves 1—4 in Fig. 5 are calculated for a mixture (36 mM phthalate, 3mM Th⁴⁺), under the assumption that one, two, three or four OH are bound per thorium in the complex and that the H⁺ consumption of the phthalate is that given by curve 0.

The experimental values for such a mixture on adding H⁺ or OH⁻ always coincide with curve 2. Similar results were found in experiments with other concentrations of thorium and potassium phthalate. We may then conclude, that most probably two OH⁻ ions are bound per thorium ion.

Fig. 6 shows another series of experiments. For each total phthalate concentration, the highest and lowest pH are given that give a clear solution

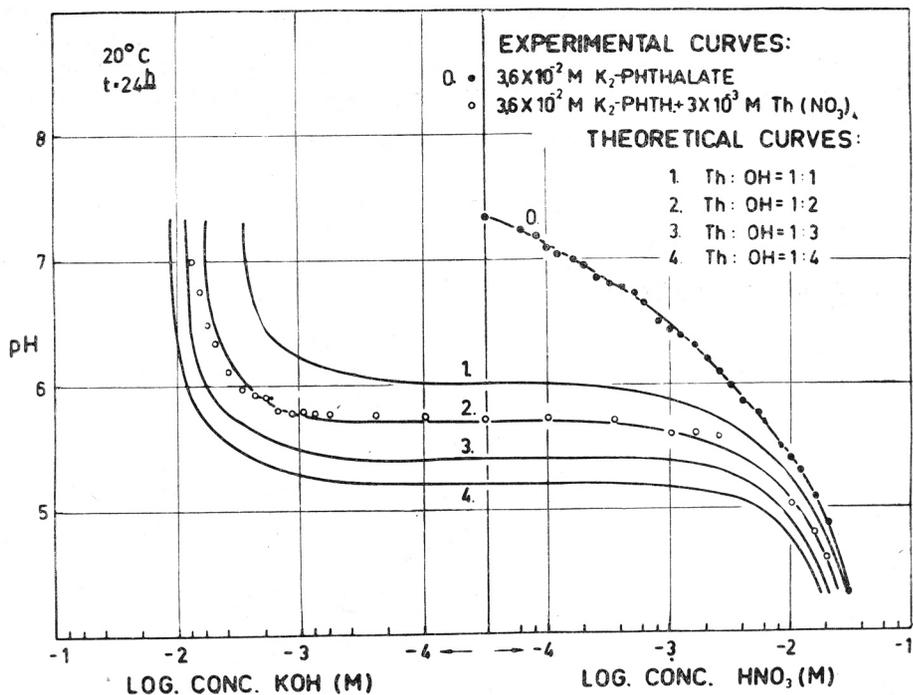


Fig. 5. The change of pH of 3.6×10^{-2} M potassium phthalate solution after adding HNO_3 (curve 0). Curves 1-4 are theoretical and calculated for different ratio Th:OH = 1:1, 1:2, 1:3 and 1:4. They show the change of pH of 3.6×10^{-2} M potassium phthalate after adding HNO_3 or KOH in the presence of 3×10^{-3} M thorium nitrate.

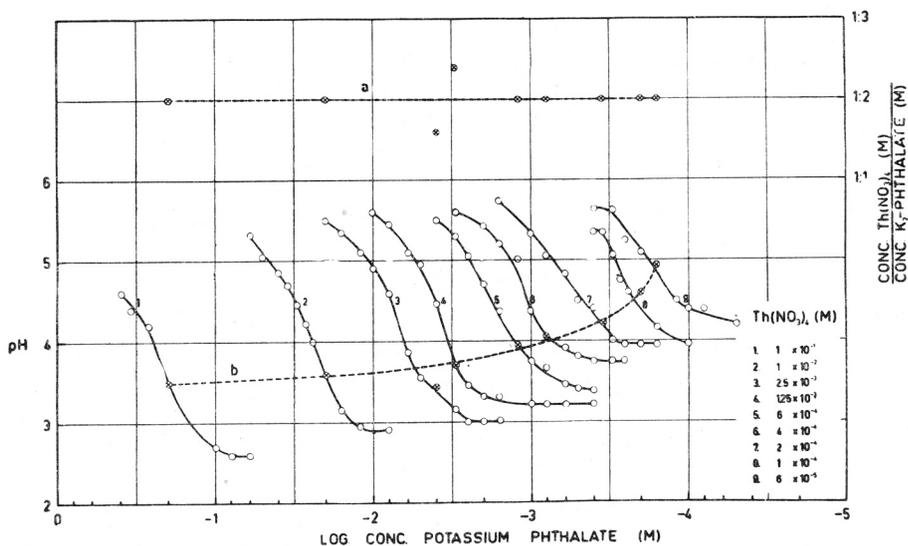


Fig. 6. The regions of stable soluble complexes for different concentrations of thorium, shown by height curves of turbidity approximately O.

(turbidity approximately 0), for various total concentrations of thorium. The region of soluble complexes becomes more and more narrow as the concentration of thorium increases. For each $[\text{Th}]_{\text{tot}}$, the limit where Th hydroxide precipitates is practically a straight line of slope 0.8, with the equation:

$$\text{pH} = 0.8 \log [\text{phthalate}]_{\text{tot}} + b_0 \quad (1)$$

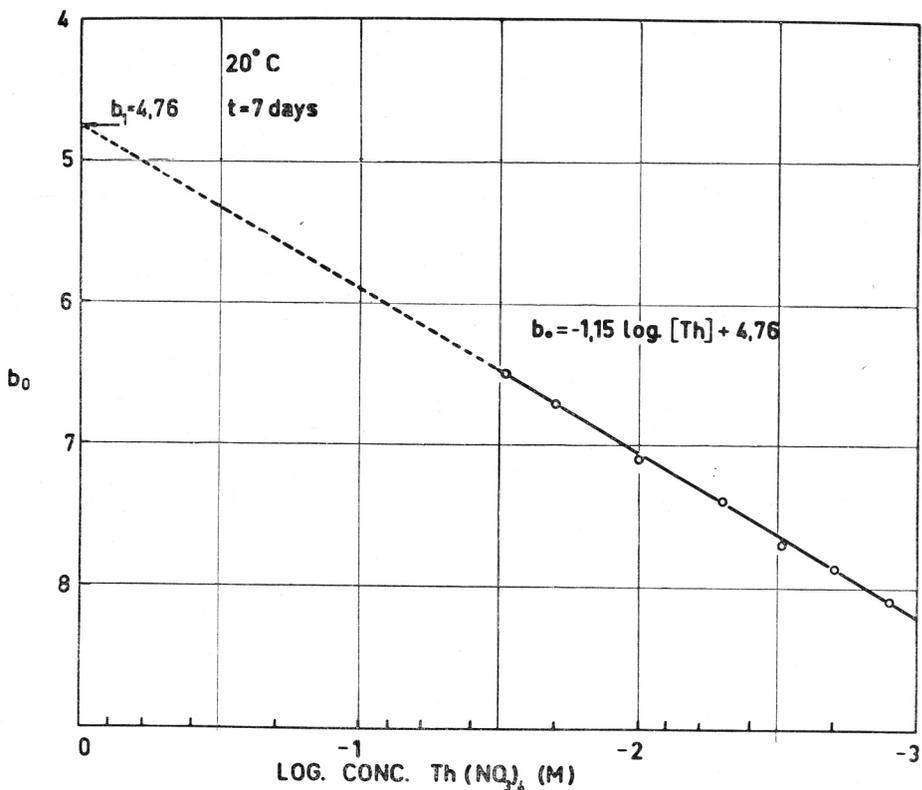


Fig. 7. b_0 (from equation 2), plotted against the thorium concentration.

Fig. 7 shows that b_0 changes linearly with $\log [\text{Th}]_{\text{tot}}$. The equation of the line is:

$$b_0 = -1.15 \log [\text{Th}]_{\text{tot}} + 4.76 \quad (2)$$

These two equations may be combined to an empirical law, saying that in the presence of excess of phthalate ions, thorium hydroxide precipitates if

$$\text{pH} \geq 0.8 \log [\text{phthalate}]_{\text{tot}} - 1.15 \log [\text{Th}]_{\text{tot}} + 4.76 \quad (3)$$

However as seen from Fig. 6 the straight line (1) and hence (3) are valid only up to the line O, which has the equation

$$\text{pH} = -0.8 \log [\text{phthalate}]_{\text{tot}} + 4.68 \quad (4)$$

and corresponds to approximately 3 phthalate per thorium. At lower pH the solubility curve for constant $[\text{Th}]_{\text{tot}}$ is bent. The two solid phases, thorium

hydroxide and thorium hydroxide phthalate, are not separated by the soluble complex, but appear at the same time at the right hand extreme of the curve. From Fig. 6 one can calculate that this corresponds to a ratio 2 phthalate per thorium, and pH 5.4, which is very near to pK_2 of phthalic acid ($pK_2 = 5.51$).

NMR studies of the solid phases and discussion of their composition

In Fig. 4 we see that three solid phases (2, 3 and 5) are formed in addition to phthalic acid (1). The presence of OH or H₂O in these three solids was studied by proton magnetic resonance.

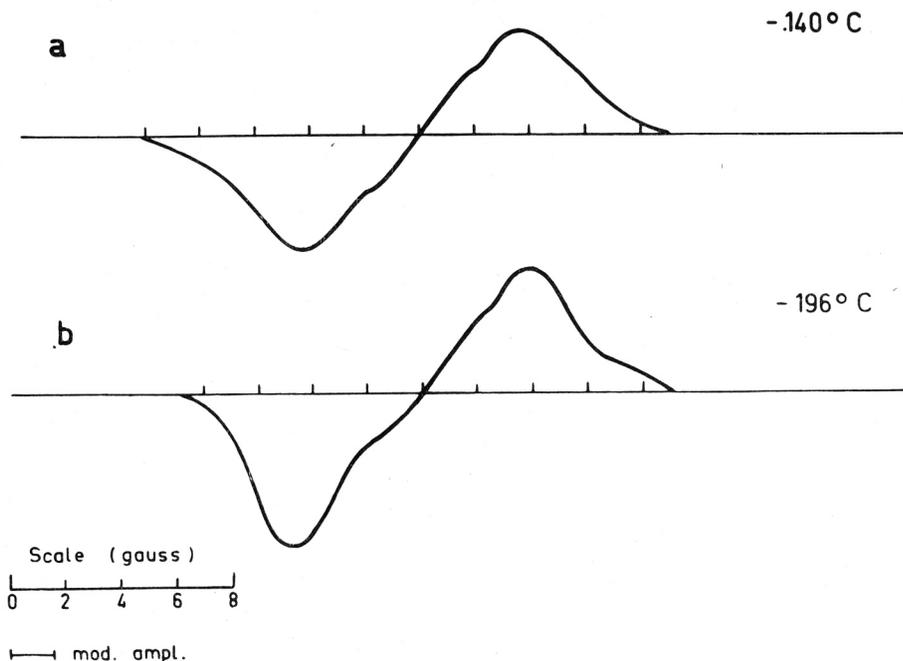


Fig. 8. Proton magnetic resonance of crystals formed in a mixture $3 \times 10^{-3} M \text{ Th}(\text{NO}_3)_4$, $2 \times 10^{-2} M \text{ K}_2\text{-phthalate}$, $2 \times 10^{-2} M \text{ HNO}_3$ (a); and of phthalic acid (b).

In Fig. 8, curve *a* corresponds to the crystals in region 2 and curve *b* to pure phthalic acid, dried to constant weight. It is evident that the precipitate in region 2 does not contain water of crystallization and that its spectrum is very similar to the NMR spectrum of pure phthalic acid, but differing to a great extent from the spectrum of thorium hydroxide-phthalate. The formula $\text{Th}(\text{phthalate})_2$ gives the best agreement with the experimental results. It is not yet known if phthalate ions are bidentate or tetradentate in this compound.

Fig. 9 presents the NMR spectra of the colloid precipitate in region 3 of Fig. 4 at 20°C and -196°C . Two parallel independent precipitations gave the same results. Both spectra show two maxima with the line width 7.0 G and 2.8 G. It is evident that the precipitate does not contain water of crystallization. Both maxima belong to rather isolated protons, suggesting two species of isolated protons.

From the slope $-1/2$ of the straight line 3' in Fig. 3, according to the results for thorium hydroxide⁶ it can be concluded that, most probably two

OH groups per thorium are bound in the solid phase. The analysis (see Table 1) showed that 1 to 2 phthalate ions are bound per thorium.

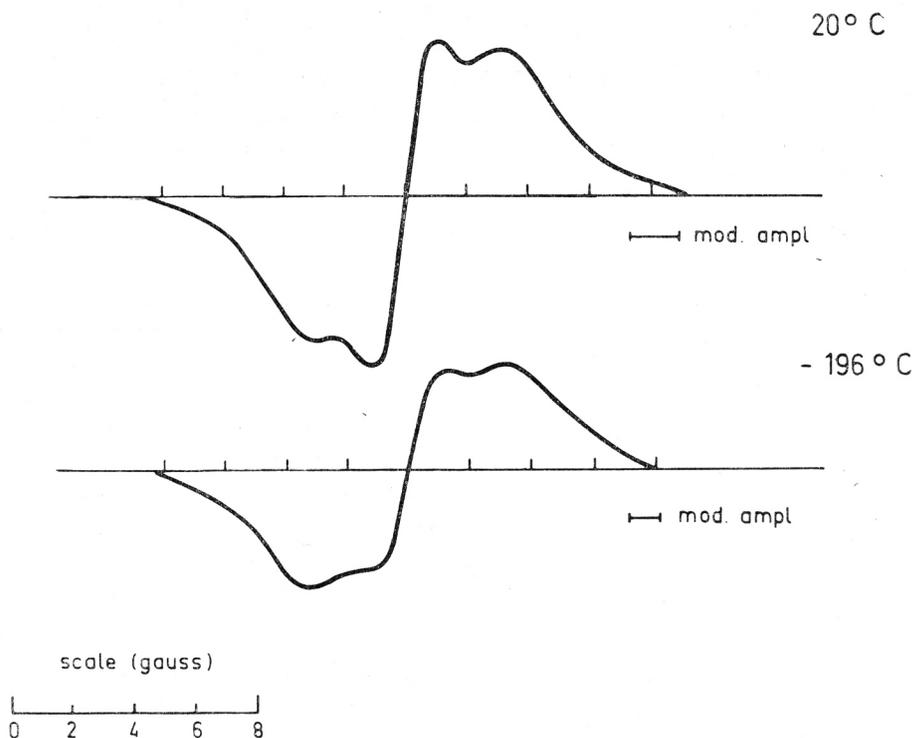


Fig. 9. Proton magnetic resonance of the colloid precipitate, formed in a mixture $\text{Th}(\text{NO}_3)_4$ 3×10^{-5} M, K_2 -phthalate 6×10^{-3} M, at 20°C and at -196°C .

The relation of the first moments of the central and outer maxima is 1 : 13, which does not change from the room temperature down to the lower one. The line shape of the spectrum and the line width remain the same only the central maximum is less developed at -196°C . These results suggest that the central maximum might be due to hydrogen in OH groups (and in COOH groups if they are free), while the outer maximum would correspond to hydrogens in the benzene ring. The final conclusion is that according to 1 : 13 area ratio the sample ought to be in a polymeric form.

The second moment which corresponds to the protons in the benzene ring is 2.4 G^2 . If the central thorium atom is considered with phthalate and hydroxide groups bound to it, and if the distance Th—O (2.4 – 2.8 \AA) is taken into account the contribution of the protons from OH can be neglected. The experimental second moment is 7.5 G^2 at -196°C indicating a high intermolecular contribution in accordance with the above conclusion on some kind of polymerization, or a very close packing of phthalate units.

One requirement for such polymerization of the molecular units would be hydrogen bonding. The IR spectrum of this colloidal precipitate shows a very broad adsorption band between 3600 and 2800 \AA , characteristic for strong hydrogen bonds. This part of the spectrum is very much alike the IR spectrum

of thorium hydroxide⁷ in the same range. As Dobry *et al.*⁸ have shown, thorium hydroxide has condensed molecules similar to organic polymers.

From the line-shape and the line width of the NMR spectrum of pure thorium hydroxide corresponding to the one-spin system, it is evident that the precipitate does not contain water of crystallization. Polymerization of thorium hydroxide probably occurs through OH groups. It can be presumed that the polymerization of thorium hydroxide-phthalate occurs through OH or through free COOH groups if they exist.

According to the results of chemical analyses shown in Table 1, neither the formula $\text{Th}(\text{OH})_2$ phthalate [with theoretical values Th 54%, C 22.4%, H 1.4% and O 22.3%], nor the formula $\text{Th}(\text{OH})_2$ (H-phthalate)₂ (with theoretical values Th 39%, C 32.2%, H 2% and O 26.8%) is satisfactory. Meanwhile, such results of analyses demand much smaller ratio of the first moments. Thus the exact formula remains undetermined.

An attempt to find the composition, polynuclear size and stability constants of the soluble complex in region 4 of Fig. 4 will be made by precise EMF measurements and by Letagrop computer program⁹ in one of our next papers.

Acknowledgments: The author wants to thank Mgr Z. Vekšli for the NMR measurements and for the interpretation and discussions on the composition of the solid phases investigated; to Prof. B. Težak for his interest in this work, to Dr. M. Branica and Dr. S. Maričić for discussing the results; and in particular thank to Prof. L. G. Sillén who was kind to read the manuscript and suggest many improvements.

REFERENCES

1. M. Bobtelsky and B. Gadda, *Bull. Soc. Chim. France* **1953**, 382.
2. B. Težak, E. Matijević, J. Kratochvil, and H. Füredi, *Symposium on Co-ordination Chemistry*, Copenhagen, August 9—13 (1953).
3. B. Težak, H. Füredi, and M. Branica, *Proc. 2nd Int. Cong. Peaceful Uses of Atomic Energy*, Geneva (1958), Vol. **28**, pp. 250—252 (P. 2413).
4. H. Bilinski, H. Füredi, and B. Težak, *Croat. Chem. Acta* **35** (1963) 31.
5. B. Težak, E. Matijević, and K. Schulz, *J. Phys. Colloid Chem.* **55** (1951) 1557.
6. H. Bilinski, H. Füredi, M. Branica, and B. Težak, *Croat. Chem. Acta* **35** (1963) 19.
7. C. W. F. T. Pistorius, *J. Inorg. Nucl. Chem.* **15** (1960) 187.
8. A. Dobry, S. Guinand, and Mathieu, *J. Chim. Phys.* **50** (1953) 501.
9. N. Ingri and L. G. Sillén, *Arkiv Kemi* **23**, (1964) 97.

IZVOD

**Taloženje i hidroliza torija (IV) u vodenoj otopini.
III. Sastav taloga u sistemu torijev nitrat-kalijev ftalat**

H. Bilinski

Ispitivano je taloženje torija (IV) u vodenim otopinama torijevog nitrata i kalijevog ftalata, u širokom području obiju taložnih komponenata. Ispitan je utjecaj pH i vremena na stvaranje različitih vrsti taloga, koji su identificirani mikroskopom. Sastav i karakteristike nastalih taloga određene su metodama kemijske analize, te spektrima IR i NMR. Utvrđeno je nastajanje taloga $\text{Th}(\text{OH})_4$ bez kristalne vode: $\text{Th}(\text{ftalat})_2$, bez kristalne vode, i polimera torijevog hidroksi-ftalata, čija formula upotrebljenim metodama nije mogla biti određena. Postavljena je empirijska formula za taloženje torijevog hidroksida u prisustvu kalijevog ftalata. Određen je broj OH-iona po jednom toriju u topljivom miješanom torij hidroksi-ftalat kompleksu.