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Original Scientific Paper

Precipitation and Hydrolysis of Thorium in Aqueous Solution. IV. Studies of the Systems: Thorium Nitrate—Sodium Fumarate and Thorium Nitrate—Potassium Maleate

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Precipitation of thorium from aqueous solutions of thorium nitrate and sodium fumarate and potassium maleate respectively has been investigated for a broad range of concentrations of precipitation components and *p*H. From the results of chemical analyses and from the DTA and IR spectra the most probable formulas of the formed precipitates are: $Th(H\text{-fumarate})_2(OH)_2 \times 5\,H_2O$ and $[{}^{OH}_{OH}\,Th^{OH}_{OH}\,(Mal\,Th^{OH}_{OH})_4] \times 6\,H_2O$. In the soluble mixed hydroxo maleato thorium complex, which is in equilibrium with thorium hydroxide, probably three hydroxide ions are bound to one thorium. It has been found that with fumarate ion thorium does not form a soluble complex.

INTRODUCTION

Precipitation, hydrolysis and complex formation of thorium ion in the presence of fumarate and maleate ions have not been extensively investigated in the past. In 1902 Metzger[1] found that maleic acid does not precipitate thorium from aqueous solution; however, it is quantitatively precipitated from saturated fumaric acid in 40% ethanol, but the conditions must not be too acid. Füredi[2] showed that a pronounced isoelectric precipitation maximum is formed if potassium maleate is added in slight excess to thorium nitrate solution. If the concentration of maleate is about 10 times higher than that of thorium, only soluble complexes are formed. When sodium fumarate was added to thorium nitrate, the precipitation occurred in the whole investigated range. The influence of *p*H was not investigated and no information about the composition of the solid phase and of the soluble complex was given[2]. Cerkovnickaja and Charikov[3] showed that maleic acid forms a soluble complex with thorium even at rather high *p*H. The crystal precipitate of $Th(OH)_2$ fumarate $\times$ 4 H_2O has been found at a *p*H between 2 and 5 if fumarate ions are present in an aqueous solution of thorium nitrate.

The existence of soluble thorium complexes in the presence of excess of phthalate[5,6] and oxalate[7] at rather high *p*H values was investigated in detail earlier. Fumaric and maleic acid were chosen as an example of the complex formation of thorium with ligands having *cis* and *trans* isomeric forms. Being a *trans* isomer, fumaric acid cannot form chelate complexes and may therefore be attached to one thorium atom only with one carboxyl group.

The TGA curve of thorium fumarate precipitated by Metzger's procedure[1] exhibits a peculiarity, namely that after destruction of the anhydrous salt the curve does not straighten out until the ThO_2 horizontal is encountered at 405° [4]. To our knowledge the TGA curve of thorium maleate has not been described in the literature as yet.

EXPERIMENTAL

Turbidity measurements were performed with a Zeiss tyndallometer attached to a Pulfrich photometer. The method has been described earlier[8,9]. In the present work the systems were prepared in test tubes by mixing 5 ml. of a solution of thorium nitrate + HNO_3 and 5 ml. of a solution of sodium fumarate + NaOH; in another series of experiments potassium maleate was used instead of sodium fumarate. The required *p*H values were obtained by varying the amounts of nitric acid and potassium hydroxide. The concentrations given are always the total concentrations in the whole volume of 10 ml. The samples in test tubes were kept in a constant temperature bath at 20.0 ± 0.1° C for 24 hours. The crystalline precipitates of thorium fumarate were observed under a light microscope. The crystals were easily distinguished from the colloid precipitates formed either at a lower molar ratio of fumarate to thorium, or at the same molar ratio but higher *p*H value. Several precipitates were observed under an electron microscope: Trüb, Täuber & Co. (Model KM-4).

The *p*H was measured with a glass and calomel electrodes using a Pye — *p*H meter. The precipitates were separated from the mother liquor by centrifugation and dried to constant weight. The analyses were made on thorium (by igniting the precipitate at 600° C to ThO_2), carbon and hydrogen (by organic elementary analysis). The IR spectra of the precipitates were measured with a Perkin Elmer 221 spectrophotometer, using the nujol and KBr technique.

The DTA measurements were performed with a DTA apparatus which is a commercial unit manufactured by the Gebrüder Netzsch (Selb/Bayern — Germany). A measuring head with a platinum cup according to Schwite was used for dynamical differential calorimetry, at a heating rate of 5° C/minute.

The TGA measurements were performed with a Cahn RG recording electromicrobalance (sensitivity 10^{-6} grams). 4—5 milligrams of a sample were placed in a platinum micro-pan and heated in air at rate of 4° C/minute.

RESULTS

The influence of *p*H upon precipitation in the system thorium nitrate—sodium fumarate was examined at a constant concentration of added thorium nitrate (1.25 m*M*) and at varied concentrations of sodium fumarate. The turbidity was observed 24 hours after mixing as a function of the *p*H and the total concentration of sodium fumarate. By the tyndall effect the region of clear solution could be distinguished from the precipitation region (Fig. 1). The mentioned effect could not be employed either for the distinction between crystalline and colloidal precipitates or for the measurements of real turbidity of the crystalline precipitate. However, with a light microscope two different kinds of precipitates were observed. With an electron microscope several samples near the boundary between the two solid phases were observed.

Fig. 2 represents electron micrographs a) of thorium hydroxide formed in region 2 and b) of thorium fumarate formed in region 1 (Fig. 1).

The white crystalline thorium fumarate is formed in excess of sodium fumarate (region 1 in Fig. 1), showing a precipitation maximum at $pH \approx 3$. Reproducible chemical analyses were obtained only if thorium solution was added to fumarate solution. In Table I the results of chemical analyses are compared with the TGA results, both made in duplicate. The analysed precipitates were formed at the total concentrations of the precipitating components: 1.25 m*M* thorium nitrate, 60 m*M* sodium fumarate and 30 m*M* nitric acid.

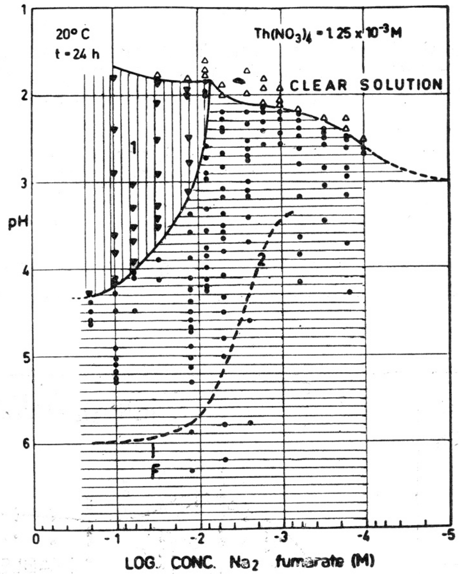

Fig. 1. The ground plan of the precipitation body formed in aqueous solution of 0.00125 *M* thorium nitrate in a broad *p*H range at varying concentrations of sodium fumarate. The crystalline precipitate (region 1) and gelatinous precipitate (region 2) were determined by microscope.

Fig. 2.

a) Electron micrograph of thorium hydroxide formed at *p*H = 4.48 is represented. The concentration of the reactants is 1.25 m*M* thorium nitrate, 100 m*M* sodium fumarate and 10 m*M* nitric acid.

b) Electron micrograph of thorium fumarate precipitated at *p*H = 4.18 is represented. The concentrations of the reactants is 1.25 m*M* thorium nitrate, 100 m*M* sodium fumarate and 20 m*M* nitric acid. The enlargement is 10 500 times.

TABLE I

The results of chemical analyses and TGA measurements of the crystalline precipitates formed in solution containing 1.25 m*M* $[Th]_{tot}$, 60 m*M* $[Fumarate]_{tot}$, 30 m*M* $[HNO_3]_{tot}$. Precipitate dried in air at room temperature.

Chemical analyses			TGA measurements			
% Th	% C	% H	% Th	% C	% H	Th : Fumature : H_2O
39.20	16.40	2.28	39.48	16.28	3.10	1 : 1.99 : 7.12
39.62	16.23	2.43	40.00	16.23	3.03	1 : 1.92 : 7.08

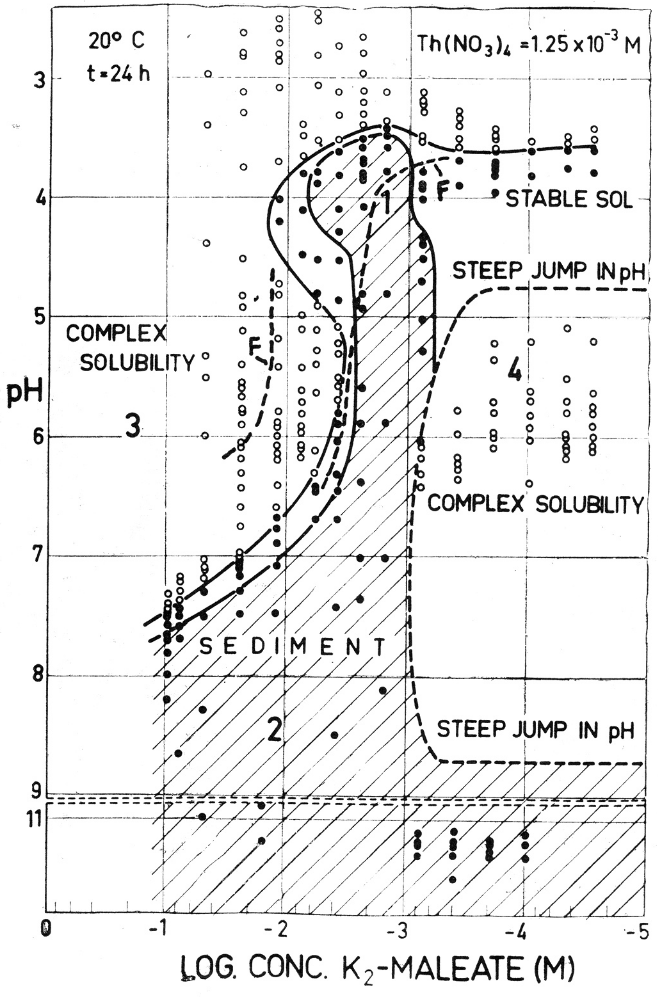

Fig. 3. The ground plan of the precipitation body formed in aqueous solution of 0.00125 *M* thorium nitrate in a broad *p*H range at varying concentrations of potassium maleate. The precipitation regions were determined by a tyndallometer.

In region 2 of Fig. 1 fluffy particles are formed. Probably a mixture of thorium fumarate and hydroxide is precipitated at lower *p*H values, while at a *p*H above 4 only thorium hydroxide is precipitated. The region of soluble complex at high *p*H values does not exist. For comparison the single cross-section through region 2 in the precipitation diagram of thorium fumarate, obtained by Füredi[2] is plotted in Fig. 1 (dotted curve with symbol F).

Fig. 3 shows a series of experiments in which $(\mathrm{Th})_{\mathrm{tot}}$ was always 1.25 m*M*, $(\mathrm{Maleate})_{\mathrm{tot}}$ was varied as well as the *p*H, by addition of HNO_3 or KOH. The precipitation regions 1 and 2, surrounded by the regions of complex solubility 3 and 4 were observed by tyndallometric measurements. In the precipitation region (1 and 2) there is a precipitation minimum existing between *p*H 5 and 6. Region 1 is very narrow, having a precipitation maximum at *p*H about 4 and the molar ratio of precipitation components $(\mathrm{Th})_{\mathrm{tot}} : (\mathrm{Maleate})_{\mathrm{tot}} = 1 : 2$. For comparison the two *p*H curves of the thorium maleate system, given by Füredi[2] are plotted in Fig. 3 (dotted lines, symbol F). One of the curves crosses the precipitation region 1 and the other is in region 3 of the soluble complex. The precipitates obtained (at the total concentrations of precipitating components 1.25 m*M* thorium nitrate, 2.5 m*M* potassium maleate and 1 m*M* potassium hydroxide; region 1, Fig. 3), were dried in various ways and analysed in the same way as was thorium fumarate. The results of the chemical analyses of thorium maleate and the TGA data are shown in Table II.

TABLE II

The results of chemical analyses and TGA measurements of the colloid precipitates formed in solution containing 1.25 m*M* $[\mathrm{Th}]_{\mathrm{tot}}$, 2.5 m*M* $[\mathrm{Maleate}]_{\mathrm{tot}}$, 1 m*M* $[\mathrm{KOH}]_{\mathrm{tot}}$.

Precipitate dried (room temp.)	Chemical analyses			TGA measurements			
	% Th	% C	% H	% Th	% C	% H	Th : Maleate : H_2O
in air	58.0 58.7	9.55 9.69	1.81 2.11	59.76	10.04	1.70	1.25 : 1 : 3.05
in $CaCl_2$	59.3 58.6 58.3	10.86 10.76 10.34	1.63 1.89 1.53				

The TGA curve of thorium fumarate is represented in Fig. 4 together with that of thorium maleate.

At 31° C thorium fumarate (Fig. 4.1) starts to lose water. At 127° C a short level is observed which corresponds to the anhydrous salt. Anhydrous thorium fumarate decomposes at 146° C and pure ThO_2 is obtained above 583° C. The DTA patterns are shown in Fig. 5. Thorium fumarate (Fig. 5.1) shows two minima at 60° C and 77° C respectively.

Thorium maleate (Fig. 4.2) loses water from 35° C to 213° C. The anhydrous salt is stable between 213° C and 287° C. Destruction of organic matter then takes place and at 505° C thorium oxide is present quantitatively.

The DTA diagram of thorium maleate (Fig. 5.2) shows only one broad minimum at 71° C.

The DTA maxima, corresponding to the destruction of the organic matter are not of interest for this work and therefore are not represented in Fig. 5.

The soluble complexes of thorium maleate are formed in regions 3 and 4, Fig. 3. Their exact formulas and stability constants are not known as yet.

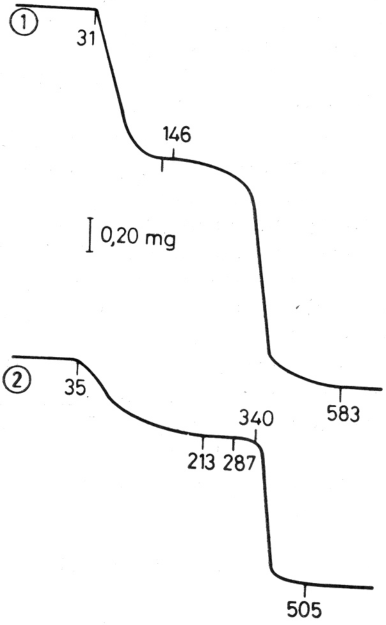

Fig. 4. TGA diagrams: 1. for 3.94 mg. of thorium fumarate; 2. for 4.00 mg. of thorium maleate. Heat ratio is 4^0 C/minute.

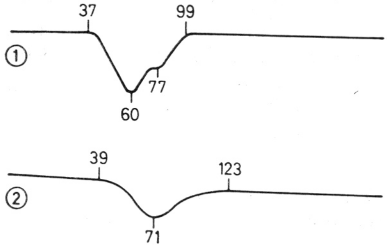

Fig. 5. DTA curves: 1. for thorium fumarate; 2. for thorium maleate. Heat ratio is 5^0 C/minute.

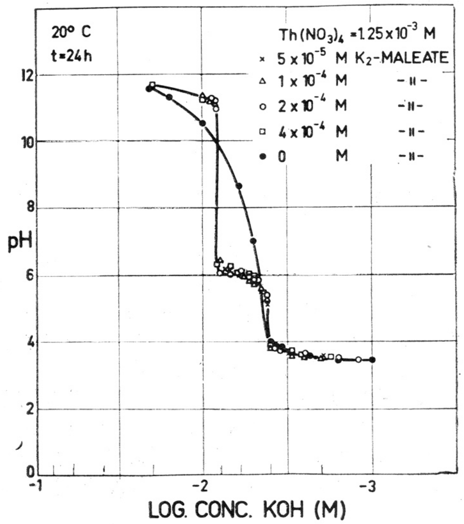

Fig. 6. The *p*H curve of the soluble complex of thorium maleate formed in excess of thorium in region 3 (Fig. 2) compared with the *p*H curve of thorium hydroxide.

Several series of systems were prepared at the molar ratio of precipitation components $(\mathrm{Th})_{\mathrm{tot}} : (\mathrm{Maleate})_{\mathrm{tot}} > 1$. The pH was measured and plotted against log. concentration of potassium hydroxide. For comparison the pH curve taken from our earlier work on pure thorium hydroxide[10] is plotted in Fig. 6. In the presence of small amounts of maleate, the pH curve has two steps. At $p\mathrm{H} = 3.5$ thorium hydroxide starts to precipitate. The horizontal part of the pH curve near $p\mathrm{H} = 6$ denotes the existence of soluble thorium maleato complexes (formed in region 4, Fig. 3). By the addition of very small amounts of potassium hydroxide, the pH rapidly increases and thorium hydroxide is precipitated.

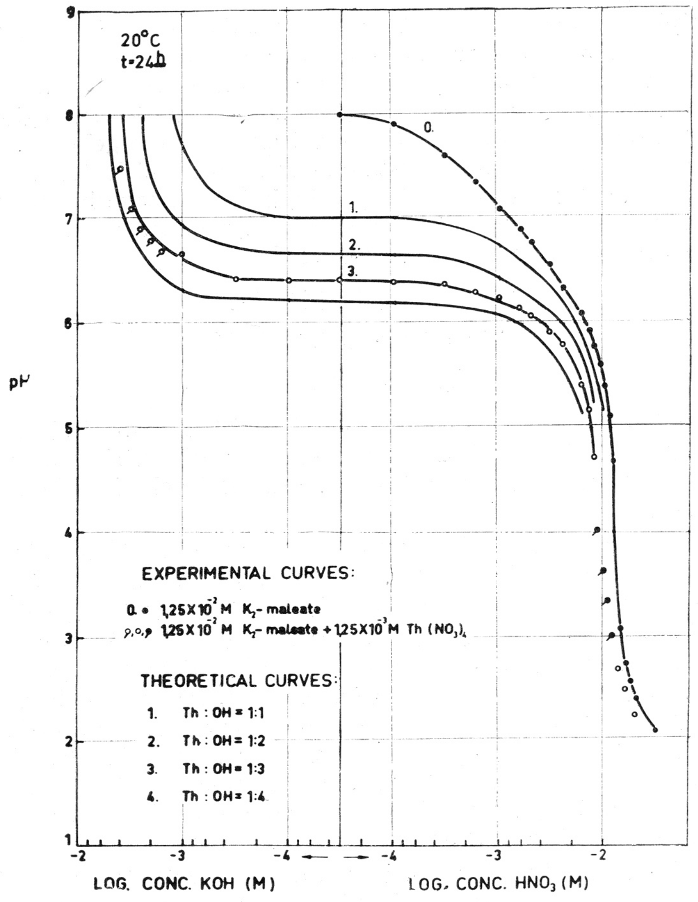

Fig. 7. The pH curve of 0.0125 M potassium maleate solution after the addition of nitric acid and potassium hydroxide (curve 0) Curves 1—4 are theoretical and calculated for different ratios (1 : 1, 1 : 2, 1 : 3 and 1 : 4) of hydroxyl to thorium in the soluble complex.

In region 3 (Fig. 3) a soluble mixed hydroxo-maleato complex is formed. The number of hydroxyl ions bound per thorium in the soluble complex was determined by the method described in the earlier paper[6].

Curve 0 (Fig. 7) presents the *p*H as a function of the total added amount of nitric acid and potassium hydroxide to the 12.5 m*M* potassium maleate. This curve may be called the »titration curve« of 12.5 m*M* maleate. Curves 1—4 are calculated for mixtures of 12.5 m*M* maleate and 1.25 m*M* thorium nitrate under the assumption that one (curve 1), two (curve 2), three (curve 3) or four (curve 4) hydroxyl ions are bound to one thorium in the soluble thorium complex and that the H^+ consumption of the maleate is that given by curve 0. The experimental values for such a mixture on adding H^+ or OH^- coincide with curve 3.

DISCUSSION

The precipitation diagram (Fig. 1) shows that the two different precipitates of thorium are formed at various concentrations of sodium fumarate and various *p*H. It was not possible to obtain reproducible results when fumarate was added to thorium. The reason can be that the species in region 2 must be very slow in reverting to those in region 1 and that the gelatinous material is slow in converting into the crystalline material which turns out to be significant. Many analyses were made in vain, before discovering the fact.

According to the results of the analyses of thorium fumarate (Table I) the following brutto formulas can be assumed:

$$\mathrm{Th(Fumarate)_2 \times 7\ H_2O} \qquad \mathrm{I}$$

$$\mathrm{Th(H\text{-}fumarate)_2(OH)_2 \times 5\ H_2O} \qquad \mathrm{II}$$

$$\mathrm{ThO(H\text{-}fumarate)_2 \times 6\ H_2O} \qquad \mathrm{III}$$

all of them having the same molecular weight, and the theoretical composition: 39.6% Th, 16.39% C, 3.07% H. Comparing the experimental results (Table I) and the theoretical ones, a satisfactory agreement is obtained especially for the TGA results.

The DTA diagram of thorium fumarate shows two dehydration maxima which correspond at least to two kinds of water, or to OH and H_2O groups.

In this paper the IR spectra were measured but not studied in detail, except for some characteristic maxima which will be discussed. The IR spectrum of thorium fumarate shows a maximum existing between 2700 and 3700 cm.$^{-1}$ which is characteristic for OH vibrations. There is a sharp intensive maximum at 1200 cm.$^{-1}$, characteristic for acid salts and an additional maximum at 960 cm.$^{-1}$ Analogous maxima were found by Haritonov, Bochkarev and Zajcev in the spectrum of acid tetraoxalato zirconate[11]. According to these authors it is possible to attribute these two maxima to the deformation of the OH vibration from the COOH groups.

Because the intensity of the maximum appearing at 960 cm.$^{-1}$ is too weak to correspond to the Th = 0 bond, the IR results suggest formula II as the most probable.

The precipitation diagram (Fig. 3) shows that thorium maleate is formed only in a narrow range of maleate concentration (region 1). It could be detected only by a systematic change of the maleate concentration and of the *p*H. Füredi[2] found that thorium can be precipitated with thorium maleate, but the *p*H was not varied and the precipitate was not analysed. Cerkovnickaja and Charikov[3] studied the behaviour of thorium ion in the presence of maleate at only one high concentration where only the soluble complex exists and is in equilibrium with thorium hydroxide. On the basis of the above finding they concluded that thorium and maleate do not form the precipitate.

The precipitate of thorium maleate is gelatinous and is formed in very small amounts in region 1. It was difficult to separate it from the mother liquor. Theoretical values for the monomer of the brutto formula $Th(OH)_2$ Maleate $\times$ H_2O (58.3% Th, 12.1% C, 1.5% H) show great disagreement regarding the experimentally obtained value for the carbon percentage (Table II). However, the theoretical values for the polymer Th_5 (Maleate)$_4$ $(H_2O)_{12}$ are in much better agreement, especially with the TGA results. If, instead of the ratio [Th] : [Maleate] : $[H_2O]$ = 1.25 : 1 : 3.05, obtained by TGA measurements, the ratio with integer numbers [Th] : [Maleate] : $[H_2O]$ = 5 :4 : 12 is taken into account, good agreement is obtained for formulas I and II:

$$[O = Th^{OH}_{OH}\ (Mal\ Th^{OH}_{OH})_3\ Mal\ Th = O] \times 8\ H_2O \qquad \text{I}$$

theoretical values: 58.0% Th, 9.6% C and 1.60% H.

$$\left[{}^{HO}_{HO}Th^{OH}_{OH}(Mal\ Th\ {}^{OH}_{OH})_4\right] \times 6\ H_2O \qquad \text{II}$$

theoretical values: 60.1% Th, 9.94% C and 1.66% H.

A similar structure containing $Th(OH)_2$- chains was found by X-ray analysis by Lundgren and Sillén[12] for crystals of $Th(OH)_2CrO_4 \times H_2O$. The chain structure in the proposed formulae I and II is in good agreement with a very broad range of dehydration shown in the DTA and TGA experiments.

The IR spectrum of thorium maleate shows a very broad maximum between 2300 and 3700 cm.$^{-1}$, indicating strong hydrogen bonding. There is no maximum at 1200 cm.$^{-1}$ which indicates that the COOH group is not present. After heating to 205° C thorium maleate is completely dehydrated. The IR spectrum does not show intensive bands for Th = O and Th—O—Th bonds. According to these result formula II seems to be more probable.

Little information only about soluble thorium maleato complexes are obtained as yet. From the stability constants of maleic acid[13] ($K_1 = 1.42 \times 10^{-2}$ and $K_2 = 8.5 \times 10^{-7}$) it is evident that above $pH = 7$ almost all maleate ions are completely dissociated. The observed lowering of the pH of the maleate solution on adding thorium nitrate is due to the formation of mixed hydroxo maleato complexes only, similar as in the case of phthalate[6] and different from that of oxalate nonhydrolysed complex[7]. In order to determine the number of maleate ions bound to thorium in the complex, some other precise techniques should be used.

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IZVOD

Taloženje i hidroliza torija u vodenoj otopini. IV. Kompleksi torija s fumarnom i maleinskom kiselinom

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Ispitano je taloženje iz vodene otopine torijeva nitrata 1,25 m*M* s natrijevim fumaratom i kalijevim maleatom u širokom području koncentracija i *p*H. Osim torijeva hidroksida, koji nastaje kod visokih *p*H vrijednosti kada je organski ligand prisutan u velikom suvišku, nastaju i talozi kojih je najvjerojatniji sastav: $\mathrm{Th(H\text{-}fumarat)_2(OH)_2} \times 5\,\mathrm{H_2O}$ i $[\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}}\mathrm{Th}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}}(\mathrm{Mal\ Th}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}})_4] \times 6\,\mathrm{H_2O}$. U suvišku fumarat iona, torij ne stvara topljive komplekse. U suvišku maleata stvara se međutim topljivi miješani hidrokso-maleato torijev kompleks koji vjerojatno sadrži 3 OH vezana na torij. Taj je kompleks u heterogenoj ravnoteži s torijevim hidroksidom.

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