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Precipitation and Hydrolysis of Thorium in Aqueous Solution. VI. Determination of Formation Constants for Mixed Thorium-Maleate-Hydroxo Complexes and Characterization of Solids *

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Three-component equilibria between thorium(IV), maleic acid ($H_4C_4O_4$) and OH^- were studied by means of coulometric titrations at 25 °C in an ionic medium of 1 M $NaClO_4$ at the range $2.7 \leq -\log[H^+] \leq 7.2$. The total concentrations of thorium, B and maleic acid, C were varied within the limits $2.5 \cdot 10^{-4}$ M $\leq B \leq 1.3 \cdot 10^{-3}$ M and $7.5 \cdot 10^{-3} \leq C \leq 1.3 \cdot 10^{-2}$ M. The ratios C/B varied between $10 < C/B < 30$ to avoid the precipitation of thorium salts. Data can be explained with the mononuclear complexes ThL^{2+}, ThL_2, ThL_3^{2-}, $Th(OH)_2L_2^{2-}$ and $Th(OH)_4L^{2-}$. The dissociation constants of maleic acid were determined for the corresponding ionic strength. Data were analyzed with the least squares computer program LETAGROP-VRID. Three solid phases have been isolated. IR measurements were used to characterize the mode of coordination of the carboxylate ligand. The compounds are: $Na_2Th(OH)_2(C_4H_2O_4)_2 \cdot 4H_2O$, $K_2ThO(C_4H_2O_4)_2 \cdot 2H_2O$ and $Na_2Th(OH)_4(C_4H_2O_4) \cdot 4H_2O$.

Precipitation and complex formation of thorium(IV) has been studied earlier with hydroxide[1] and a number of dicarboxylic acids. *viz.* phthalic,[2,3] maleic,[4] fumaric[4] and oxalic[5] acid. Studies were also performed in a sea water medium where it was suggested that thorium predominates as neutral hydroxo species.[6] Tomat *et al.*[7] have also studied water soluble complexes of thorium with a series of dicarboxylate ligands at I=1 M, but only in acid solutions. Equilibrium constants were not reported for any complex with mixed ligands.

Recently the interest in complexes of thorium, uranium, neptunium and plutonium has increased.[8–12] Thorium is used as a geochemical tracer for sedimentation and bioturbation in the coastal marine environment.[13] According to some authors[14] it seems likely that organic complexes of thorium predominate over inorganic in organic-rich stream waters, soil horizons and water logged recent sediments.

In the present work the complex formation with maleic acid was studied up to the pH range of natural waters. The existence of mixed ligand complexes was confirmed earlier,[4] but their composition and stability have not been determined.

* Experimental work was performed at (a) and computer calculation at (b).
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EXPERIMENTAL

Reagents and Analyses. A stock solution of thorium(IV) was prepared by dissolving thorium nitrate (Merck, *p.a.*) in double distilled water. The concentration of thorium was determined gravimetrically as ThO_2 after being precipitated with oxalic acid and ignited at 600 °C. Maleic acid (Merck, *p.a.*) was dissolved in 1 M sodium perchlorate solution and analyzed potentiometrically. The stock solution of sodium perchlorate was prepared from Na_2CO_3 and $HClO_4$, both of reagent grade, following the procedure described by Biedermann.[15]

Emf titrations. A series of potentiometric titrations was performed where the following cell was used:

R C|equilibrium solution|Glass electrode

where R C is the reference half cell:

R C=1 M $NaClO_4$||1.00 M Na^+, 0.98 M ClO_4^-, 0.02 M Cl^-|AgCl, Ag

The salt bridge was of the "Wilhelm" type.[16] The glass electrode was a Radiometer 6202 C and the Ag, AgCl electrode was prepared according to Brown.[17] The free hydrogen ion concentration, $[H^+]$, was calculated from the measured emf using the relation

$$E=E_o+59.157 \log [H^+]+E_j$$

where E_o is a constant, determined separately in a solution of known $[H^+]$. For the liquid junction potential, E_j, we have used $E_j=-42.0\ [H^+]$ mV.

In each of the different titrations, the total concentration of thorium, B, and maleic acid, C, were kept constant. The following concentration ranges were studied: $2.5 \cdot 10^{-4} \leq B \leq 1.3 \cdot 10^{-3}$ M; $7.5 \cdot 10^{-3} \leq C \leq 1.3 \cdot 10^{-2}$ M covering C/B ratios 10, 15 and 30. $[H^+]$ was decreased coulometrically within the range $2.7 \lesssim -\log [H^+] \lesssim 7.2$. These relatively high C/B ratios and limited pH range were necessary to avoid precipitation in the system, according to Ref. 5. Burette titration with $1 \cdot 10^{-3} < B < 1 \cdot 10^{-2}$ M could not be applied because of precipitation at these thorium concentrations.

The coulometer arrangement was the following one:

(−) Pt|equilibrium solution|1.0 M NaCl|Ag (+)

with the anodic reaction:

$$Ag(s)+Cl^- \Rightarrow AgCl(s)+e^-$$

and the cathodic reaction:

$$H^+ + e^- \Rightarrow \tfrac{1}{2}H_2(g)$$

The instrument used was a Leeds and Northrup Coulometric Analyzer No. 7960 and Radiometer PHM-64.

Usually, the titrations were started in the absence of thorium ($B=0$) and titrated to $-\log [H^+] \approx 3$. In this way, it was possible to obtain a precise determination of C within each titration and precipitation of thorium salts in acid range was avoided. Then thorium was added by a micropipette and the titration was continued.

Preparation of solid thorium hydroxo maleate complexes. Precipitates were isolated from solutions with $B=0.01$ M and $C=0.1$ M, where $-\log [H^+]$ was adjusted with NaOH (compound I and III, *cf.* Table 1) or KOH (compound II) to give the following $-\log [H^+]$ values: 5 (compound I); 2, 3, 5 (compound II); 3.3 (compound III in a mixture with large crystals of $NaH_3C_4O_4$) and 7.2 (compound III). In these solutions the ionic strength was adjusted to 1.0 M by $NaClO_4$. The different precipitates were left to settle, washed with

water and dried in a desiccator over calcium chloride. For chemical analysis a weighted amount of the solid was transferred to a Kjeldahl flask, to which 1 cm^3 of H_2SO_4 was added and the mixture was heated until a clear solution was obtained. After cooling, $-\log [H^+]$ was adjusted to 8 by the addition of dilute ammonia to precipitate thorium hydroxide which was ignited for gravimetric determinations as ThO_2. Sodium and potassium were determined by flame photometry in the filtrate. Quantitative analysis of carbon and hydrogen were also performed. Infrared spectra (4000–200 cm^{-1}) were recorded on Perkin-Elmer Model 580 B infrared spectrophotometer using Nujol mulls and KBr pellets. X-Ray diffraction patterns were recorded on a Philips X-ray diffractometer with a proportional counter using graphite monochromatized CuK_α radiation. Thermogravimetric measurements were carried out on a Cahn RG electromicroanalytical balance with a heating rate of 2 °C/min in air.

Data treatment. In the presence of a tenfold (or more) excess of maleic acid to thorium, binary $Th^{4+}-OH^-$ equilibria were found to be negligible (*cf.* calculations below). Thus, the equilibria which must be considered in the present study are:

(i) the binary maleic acid (H_2L) equilibria

$$H_2L \Leftrightarrow HL^- + H^+;\ \beta_{-101}$$

$$H_2L \Leftrightarrow L^{2-} + 2H^+;\ \beta_{-201}$$

(ii) three component equilibria of the general form

$$pH^+ + qTh^{4+} + rH_2L \Leftrightarrow H_pTh_q(H_2L)_r^{p+4q};\ \beta_{pqr}$$

The mathematical analysis of present data was performed by using the least squares computer program LETAGROPVRID [18] (version ETITR).[19] Triplets p,q,r and corresponding equilibrium constants that "best" fit the experimental data were determined by minimizing the error squares sum $U=\Sigma(Z_{calc}-Z)^2$, where $Z=(h-H-k_w h^{-1})/C$, *i.e.* the average number of OH^- bound or reacted per maleic acid. H denotes the total concentration of protons calculated over the zero level H_2O, Th^{4+}, H_2L. The term $k_w h^{-1}$, where k_w is the ionic product of water, can be neglected in the present study. The standard deviations $\sigma(Z)$ and $3\sigma(\log \beta_{pqr})$ were defined and calculated according to Sillén.[20] The computations were performed on a CD CYBER 730 computer.

DATA, CALCULATIONS AND RESULTS

The data which were used to evaluate the acidity constants of maleic acid comprise 133 experimental points. The analysis of the data ended at $\sigma(Z)=0.007$ giving $\log \beta_{-101} = -1.71\pm0.006$ and $\log \beta_{-201} = -7.29\pm0.012$. The mathematical analysis of the three component data, comprising four titrations with 101 experimental points was started by making Z *vs.* $-\log[H^+]$ and $\bar{n}$ *vs.* $\log[L^{2-}]$ plots, as presented in Figs. 1 and 2, respectively. ($\bar{n}$ is here defined as the average ligand number.) As can be seen from Fig. 1, Z exceeds the value of 2 for the highest $-\log[H^+]$ values studied. This fact shows that binary and/or ternary hydroxo species of thorium are formed. It is also clear from the $\bar{n}$ curves (Fig. 2), that besides a series of ThL_n^{2+} complexes additional species are formed at $\bar{n} \gtrsim 3$. By assuming the formation of ThL^{2+}, ThL_2 and ThL_3^{2-} a calculation based on data with $\bar{n} \lesssim 3$ gave:

$\log \beta_{-211} = -0.80\pm0.08$, $\log \beta_{-412} = -5.27$ (min. value) to -4.58 (max. value) and $\log \beta_{-613} = -7.58\pm0.08$ with $\sigma(Z)=0.006$. The great uncertainty in β_{-412} is mainly due to the fact that this complex is formed in small amounts. Furthermore, the measurements had to be performed with high excess of ligand at low B ($B \leq 0.001$ M) (in order to avoid precipitation of thorium salts) which implies that the effects due to the formation of $Th^{4+}-L^{2-}$ complexes are small compared to the H^+-L^{2-} effects. The search for the composition and stability of

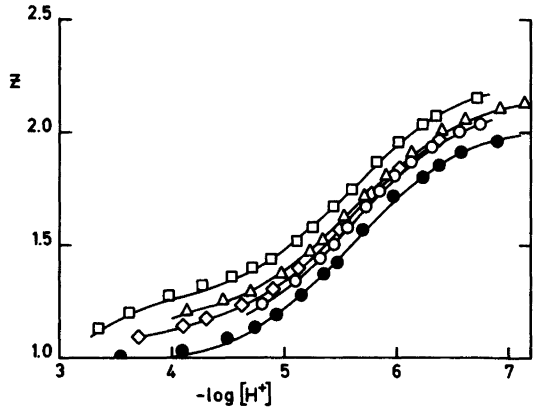

Fig. 1. A part of experimental data plotted as curves $Z(-\log[H^+])$. Filled symbols denote titrations with $B=0$ and $C=0.0122$ M. Open symbols stand for the following values in B and C: ○ 0.00025, 0.0075; △ 0.00064, 0.0101; □ 0.0013, 0.0125; ◇ 0.00064, 0.01254 M resp. Full curves have been calculated using the set of proposed constants in Table 2.

the predominating hydroxo complex was performed as p,q,r analysis (systematic testing of p,q,r combinations) on the whole data material. The strategy was thereby to find that complex which gives the lowest error square sum $U=\Sigma(Z_{calc}-Z)^2$. At the low B values studied, only mononuclear complexes have been tested. The results of this analysis are given in Fig. 3. As can be seen the "best" fit is obtained assuming the $-6,1,2$ species, $Th(OH)_2L_2^{2-}$, with $\log \beta_{-612}=-13.66\pm0.09$ giving $\sigma(Z)=0.010$. This conclusion was supported by the preparation of compound I in Table 1. However, at $-\log[H^+]\geq$, 6.5, systematic deviations in the residuals $[Z_{calc}-Z]$ were found, indicating the existence of additional species. To explain these effects another systematic search was performed. The lowest value in U was now obtained for $Th(OH)_4L^{2-}$. It was also found that the $(-5,1,1)$ and $(-8,1,2)$ species give a fit almost equally well. However, we find these less likely mainly from structural reasons. Our conclusion about the existence of $Th(OH)_4L^{2-}$ ion was also

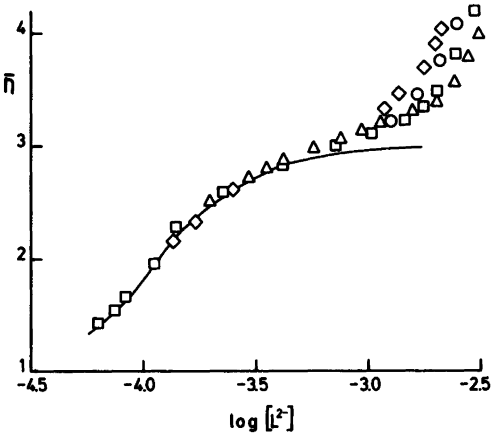

Fig. 2. Curves $(\bar{n}\ \log[L^{2-}])$. The symbols denote the same $B-C$ combinations as in Fig. 1. The full curve has been calculated using log $\beta_{(-2n)1n}$ values $(n=1,2,3)$ given in Table 2.

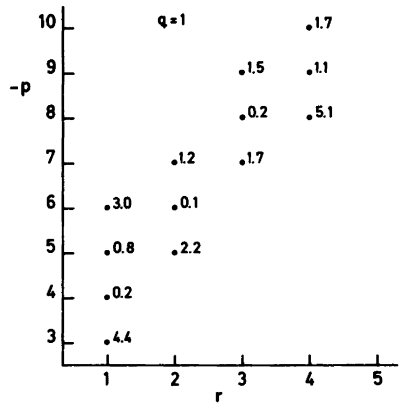

Fig. 3. Results of the first *pqr*-analysis. The diagram gives $U(-pr)\cdot 10^{-5}$ with $q=1$.

supported by the preparation of compound III in Table 1. As a final calculation, β_{-612} and β_{-611} were covaried, giving $\log \beta_{-612}=-13.65\pm0.07$, $\log \beta_{-611}=-23.0\pm0.2$ and $\sigma(Z)=0.007$. Composition and stability of proposed complexes are given in Table 2.

In order to visualize the amounts of the different complexes, the computer program SOLGASWATER[21] equipped with plotting procedures was used to calculate some distribution diagrams, *cf.* Fig. 4. The fraction of thorium complexes is plotted *vs.* $-\log[H^+]$for one typical concentration of thorium and maleate. In the range characteristic for natural waters mixed complexes are by far the most predominating. For better understanding of geochemical cycling of thorium, future studies on mixed ligand complexes of thorium seem to be urgent.

In order to support solubility data, the solid thorium maleate complexes (I–III) were isolated as described in Experimental. The composition of these compounds, decomposition temperature and analytical characteristics are presented in Table 1. All three compounds are white, insoluble in water and common organic solvents. Only compound II shows good crystallinity. Infrared spectra of these compounds are presented in Fig. 5. Major absorption bands have similar position for all three compounds. Some differences will be discussed. The

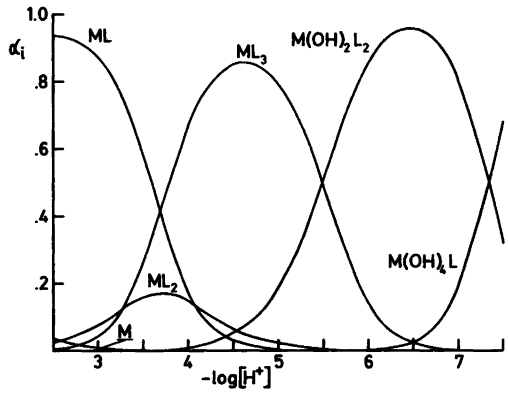

Fig. 4. Distribution diagram $\alpha_i(-\log[H^+])$. The calculation was performed using the constants from Table 2 ($\log \beta_{-412}=-4.58$) with $B=0.001$ and $C=0.010$ M resp. (Charges of the complexes are omitted.)

Table 1. Analytical and some physical data.

Compound	Decomp. temp.[a] (K)	Analysis (%)[b] C	H	Na,K	Th
$Na_2Th(OH)_2(C_4H_2O_4)_2 \cdot 4H_2O$ (I)	315	15.50 (15.69)	2.60 (2.30)	8.05 (7.51)	37.95 (37.90)
$K_2ThO(C_4H_2O_4)_2 \cdot 2H_2O$ (II)	319	16.51 (16.61)	1.23 (1.02)	13.10 (13.25)	39.14 (39.30)
$Na_2Th(OH)_4(C_4H_2O_4) \cdot 4H_2O$ (III)	315	8.69 (9.02)	2.35 (2.65)	8.81 (8.64)	43.46 (43.60)

[a] Obtained from thermogravimetric decomposition curve. [b] Calculated values are given in parentheses.

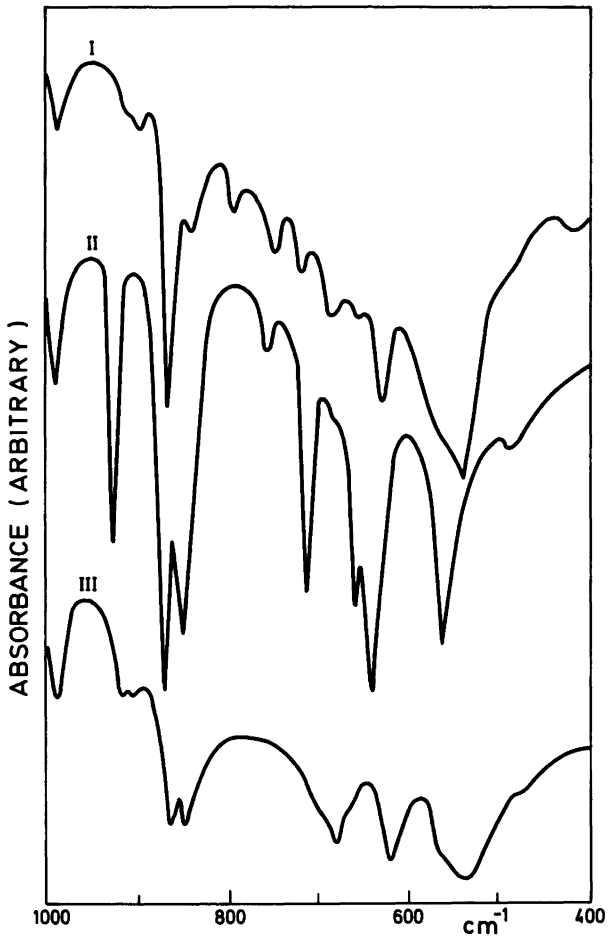

Fig. 5. Infrared spectra of compounds I, II, and III in the wave number range 1000–400 cm^{-1}.

Table 2. Proposed binary and ternary complexes in the $H^+-Th^{4+}-$maleic acid (H_2L) system. The formation constants are defined according to the reaction $pH^+ + qTh^{4+} + rH_2L \Leftrightarrow H_pTh_q(H_2L)_r^{p+4q}$.

$p\ q\ r$	proposed formula	$\log(\beta_{pqr} \pm 3\sigma)$
−1 0 1	HL^-	−1.71±0.006
−2 0 1	L^{2-}	−7.29±0.012
−2 1 1	ThL^{2+}	−0.80±0.08
−4 1 2	ThL_2	−5.27 to −4.58
−6 1 3	ThL_3^{2-}	−7.58±0.08
−6 1 2	$Th(OH)_2L_2^{2-}$	−13.65±0.07
−6 1 1	$Th(OH)_4L^{2-}$	−23.0±0.2

absorption bands present in the region 3200−3700 cm^{-1} originate from O−H stretchings of water molecules and OH^- groups. The broadness of this absorption band, especially observed in compound III indicates the presence of hydrogen bondings. The asymmetric stretching frequency of coordinated COO^- groups appear as a strong absorption band in the region 1600 cm^{-1}. The shift of this absorption band to lower wave numbers in comparison to its position in the free ligand confirms the coordination of both carboxylate groups.[22] The feature of infrared spectra in this region suggests that both carboxylate groups are equivalent and no evidence for free COOH group exists. Such acidic complexes were found earlier with zirconium and some organic acids.[23,24] However, attempts to prepare acidic complexes with thorium and maleate[25] and some other dicarboxylate ligands,[26] were unsuccessful. Very interesting is the appearance of the strong absorption band in compound II at 921 cm^{-1}. As similar band is not present in the spectra of compounds I and III (Fig. 5). Although the oxo species are not common in chemistry of thorium(IV) the position of this absorption band suggests the presence of Th=O bond in compound II. According to the classification of Barraclough *et al.*[27] compound II could be included in the class of oxo-compounds containing one oxygen atom per metal atom where high degree of double bond character is expected. The infrared stretching frequency of metal-oxygen double bond of this class of compounds is observed in the range 900−1100 cm^{-1}.

The infrared spectra of (oxalato)-[28] and (oxydiacetato)thorium(IV)[29] complexes were investigated and since there was no additional absorption band in the region 900−1100 cm^{-1} the presence of Th=O bond was not postulated. This is confirmed by the X-ray crystal structure determination of diaqua(oxydiacetato)sulphatothorium(IV) monohydrate.[30]

The position of the absorption bands in the region below 900 cm^{-1} mostly originating from metal-ligand oscillating vibrations is comparable in all complexes. In addition, it is to expect that some of the water molecules present are coordinated to thorium atom, stabilizing the structure and rising the coordination number of thorium(IV).

CONCLUSION

By using a precise coulometric technique it has become possible to determine a series of mononuclear Th-species. Besides the binary ThL_n^{4-2n}-complexes (n=1,2,3) two mixed hydroxo complexes, $Th(OH)_2L_2^{2-}$ and $Th(OH)_4L^{2-}$, were evaluated. The precision of the stability constants is somewhat high (*cf.* Table 2). This is mainly due to the low solubility of

the different solid phases, which implies that only low B ($B \leq 0.001$ M) could be studied.

The acidity constants for maleic acid are in very good agreement with literature values. For instance, Tomat *et al.*[7] (1 M (Na,H)ClO_4 medium, 20 °C) reported log $\beta_{-101} = -1.66$ and log $\beta_{-201} = -7.29$. Furthermore, they found log $\beta_{-211} = -0.95 \pm 0.03$, which is close to the present value (-0.80 ± 0.08). On the other hand, log $\beta_{-412} = -4.03 \pm 0.06$ is significantly higher than that is found in this study. An explanation to this may be that Tomat *et al.*[7] neglected the formation of a possible ThL_3^{2-}-complex, which leads to an overestimation of β_{-412}. In fact the ThL_2-complex seems to be less significant in comparison with the others (*cf.* Fig. 4). Formation constants for ThL_3^{2-}, $Th(OH)_2L_2^{2-}$ and $Th(OH)_4L^{2-}$ have not been reported earlier.

Three new different thorium maleate solid compounds have been prepared. Of these, compounds I and III support the results from the equilibrium analysis of present titration data. The difference in thorium and zirconium system with the maleate ligand is obvious, as thorium does not form acidic complexes both in solution and in the solid state. Furthermore, the soluble region in the present system is somewhat larger than for the corresponding zirconium system.[4,23] Further research on thorium complexes with other dicarboxylic acids is in progress.

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