

# Solubility of amorphous Th(IV) hydroxide – application of LIBD to determine the solubility product and EXAFS for aqueous speciation

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**Summary.** The solubility of amorphous Th(IV) hydroxide at pH 3.0–13.5 and the aqueous speciation at pH < 4 are investigated in 0.5 M NaCl and 25 °C. The laser-induced breakdown detection (LIBD) is used to monitor the initial formation of thorium hydroxide colloids during the coulometric titration of  $1.2 \times 10^{-2}$ – $1.0 \times 10^{-5}$  M thorium solutions in the pH range of 2.7–4.5. The accurate solubility limit determined by this method is comparable with data measured from undersaturation with an X-ray amorphous solid precipitated at higher pH and dried at room temperature. Based on hydrolysis constants selected from the literature, the solubility product of Th(OH)<sub>4</sub> (am) in 0.5 M NaCl is calculated to be  $\log K'_{sp} = -44.48 \pm 0.24$  and  $\log K_{sp}^{\circ} = -47.8 \pm 0.3$  (converted to  $I = 0$  with the SIT coefficients of the NEA-TDB).

In other solubility studies with amorphous Th(IV) hydroxide or hydrous oxide, considerably higher thorium concentrations are measured at pH 3.5–5. Therefore, solutions of comparable H<sup>+</sup> and thorium concentrations are prepared by careful coulometric titration and examined by ultrafiltration, LIBD and X-ray absorption fine structure (XAFS) spectroscopy. These measurements demonstrate the presence of a large amount of small Th(IV) colloids. The Th L<sub>3</sub> edge EXAFS spectra of these colloidal suspensions are similar to that of the amorphous solid.

## 1. Introduction

The solubility of amorphous Th(IV) precipitates, called either amorphous hydroxides Th(OH)<sub>4</sub> (am) or hydrous oxides ThO<sub>2</sub>·xH<sub>2</sub>O (am), has been investigated by Nabanets and Kudritskaya [1] at 17 °C in 0.1 M NaClO<sub>4</sub>, by Moon [2] at 18 °C in 0.5 M NaClO<sub>4</sub>, and by Rai *et al.* at 22–25 °C in 0.1 M NaClO<sub>4</sub> [3], 0.6 M NaCl and KCl [4, 5] concentrated NaCl and MgCl<sub>2</sub> solutions [5], and in 0.1 M NaCl [6]. In these studies, the amorphous precipitates were not dried or treated at higher temperature but only washed with water. Although relatively widely scattered, the solubilities determined in these studies at pH 3.5–5 are reasonably consistent. Using a precipitate dried at room temperature for one week in a vacuum desiccator, Östhols *et al.* [7] measured the solubility at 25 °C in 0.5 M NaClO<sub>4</sub>. Their results

are 3–4 orders of magnitude lower than those in [1–6] but still about 6 orders of magnitude higher than for crystalline ThO<sub>2</sub> (cr).

The discrepancies in solubility data for X-ray amorphous Th(IV) precipitates may be due to the fact that they do not refer to a well-defined unique solid phase but to hydrated oxyhydroxides ThO<sub>n</sub>(OH)<sub>4–2n</sub> (am) with  $0 < n < 2$ , depending on the preparation method, pretreatment, alteration and temperature [2, 6, 8]. Furthermore, the inclusion of colloids can also explain the large discrepancies in the measured thorium concentrations. The latter effect is investigated in the present study. For this purpose we apply the laser-induced breakdown detection (LIBD), which is capable of detecting actinide colloids of small size [9–11]. In addition, extended X-ray absorption fine structure (EXAFS) spectroscopy at the Th L<sub>3</sub> edge is used for the aqueous speciation of thorium solutions up to pH 4.

Recently, Bundschuh *et al.* [9] developed an alternative method to investigate the solubility of oxides or hydroxides. Coulometric pH titration was combined with the LIBD to detect initial colloid formation as a function of the H<sup>+</sup> and Th(IV) concentration in 0.5 M HCl/NaCl. Considering colloids as small solid particles, their formation indicates that the solubility is just exceeded during the titration. As an unexpected result, the titrations in the pH range 1.5–2.5 led to the formation of small ThO<sub>2</sub> (s) colloids with a mean diameter of 16–23 nm, which subsequently agglomerate to a microcrystalline precipitate [9, 12]. The solubility product for the freshly formed ThO<sub>2</sub> (s) colloids,  $\log K_{sp}^{\circ} = -52.8 \pm 0.3$  [9] and  $-53.2 \pm 0.4$  for the precipitate formed from colloid agglomeration [12], are close to the value calculated for ThO<sub>2</sub> (cr) from thermochemical data,  $\log K_{sp}^{\circ}(\text{ThO}_2(\text{cr})) = -54.2 \pm 1.3$  [13]. The same titration-LIBD method is applied in the present study, however at pH 3–5. In this higher pH range, hydrolysis and polynucleation lead to the formation of amorphous thorium hydroxide colloids [12]. The H<sup>+</sup> and Th(IV) concentrations at the onset of colloid formation define the solubility of Th(OH)<sub>4</sub> (am) excluding colloidal thorium species.

### 1.1 Thermodynamic data for Th(IV) at 25 °C

The hitherto available data on the solubility and hydrolysis of tetravalent actinides have been critically discussed in our recent review [14]. The selected equilibrium constants

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**Table 1.** Thermodynamic constants at  $I = 0$  and ion interaction (SIT) coefficients for Th(IV) species at 25 °C (from Neck and Kim [14]).

Solubility product of Th(OH) <sub>4</sub> (am): $\log K_{sp}^{\circ} = -47.0 \pm 0.8$				
Formation constants $\log \beta_{xy}^{\circ}$ and hydrolysis constants $\log {}^*\beta_{xy}^{\circ}$ for the complexes Th <sub>x</sub> (OH) <sub>y</sub> <sup>4x-y+</sup>				
$\log \beta_{1,1}^{\circ} = 11.8 \pm 0.2$			$\log {}^*\beta_{1,1}^{\circ} = -2.2 \pm 0.2$	
$\log \beta_{1,2}^{\circ} = 22.0 \pm 0.6$			$\log {}^*\beta_{1,2}^{\circ} = -6.0 \pm 0.6$	
$\log \beta_{1,3}^{\circ} = 31.0 \pm 1.0$			$\log {}^*\beta_{1,3}^{\circ} = -11.0 \pm 1.0$	
$\log \beta_{1,4}^{\circ} = 38.5 \pm 1.0$			$\log {}^*\beta_{1,4}^{\circ} = -17.5 \pm 1.0$	
$\log \beta_{2,2}^{\circ} = 22.3$			$\log {}^*\beta_{2,2}^{\circ} = -5.7$	
$\log \beta_{4,8}^{\circ} = 91.6$			$\log {}^*\beta_{4,8}^{\circ} = -20.4$	
$\log \beta_{4,12}^{\circ} = 141.3$			$\log {}^*\beta_{4,12}^{\circ} = -26.7$	
$\log \beta_{6,15}^{\circ} = 176.0$			$\log {}^*\beta_{6,15}^{\circ} = -34.0$	
Ion interaction (SIT) coefficients:				
<i>i</i>	<i>j</i>	$\varepsilon_{ij}$	<i>j</i>	$\varepsilon_{ij}$
H <sup>+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.14 ± 0.02 <sup>b</sup>	Cl <sup>-</sup>	0.12 ± 0.01 <sup>b</sup>
OH <sup>-</sup>	Na <sup>+</sup>	0.04 ± 0.01 <sup>b</sup>		
Th <sup>4+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.67 ± 0.1 <sup>c</sup>	Cl <sup>-</sup>	0.25 ± 0.03 <sup>b</sup>
Th(OH) <sup>3+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.45 ± 0.1 <sup>c</sup>	Cl <sup>-</sup>	0.2 ± 0.1 <sup>c</sup>
Th(OH) <sub>2</sub> <sup>2+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.3 ± 0.1 <sup>c</sup>	Cl <sup>-</sup>	0.1 ± 0.1 <sup>c</sup>
Th(OH) <sub>3</sub> <sup>+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.15 ± 0.1 <sup>c</sup>	Cl <sup>-</sup>	0.05 ± 0.1 <sup>c</sup>
Th(OH) <sub>4</sub> <sup>0</sup>	ClO <sub>4</sub> <sup>-</sup>	0 <sup>b</sup>	Cl <sup>-</sup>	0 <sup>b</sup>
Th(OH) <sub>4</sub> <sup>0</sup>	Na <sup>+</sup>	0 <sup>b</sup>		
Th <sub>2</sub> (OH) <sub>2</sub> <sup>6+</sup>	ClO <sub>4</sub> <sup>-</sup>	1.3 <sup>d</sup>		
Th <sub>4</sub> (OH) <sub>8</sub> <sup>8+</sup>	ClO <sub>4</sub> <sup>-</sup>	1.7 <sup>d</sup>		
Th <sub>4</sub> (OH) <sub>12</sub> <sup>4+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.4 <sup>d</sup>		
Th <sub>6</sub> (OH) <sub>15</sub> <sup>9+</sup>	ClO <sub>4</sub> <sup>-</sup>	5.6 ± 1.9 <sup>d</sup>		

a:  $\log \beta_{xy}^{\circ}$  refers to the reaction:  $x\text{Th}^{4+} + y\text{OH}^{-} \rightleftharpoons \text{Th}_x(\text{OH})_y^{4x-y+}$

$\log {}^*\beta_{xy}^{\circ}$  refers to the reaction:  $x\text{Th}^{4+} + y\text{H}_2\text{O} \rightleftharpoons \text{Th}_x(\text{OH})_y^{4x-y+} + y\text{H}^{+}$ ;

b: from the NEA-TDB [16];

c: Estimated in [14] according to the analogies and systematics pointed out in the NEA-TDB [16];

d: Calculated from the  $\Delta\varepsilon$  values derived in [14] as described in the text.

at  $I = 0$  are summarized in Table 1 together with the SIT coefficients used for ionic strength corrections. The solubility product of amorphous Th(IV) hydroxide or hydrous oxide ( $K'_{sp}$  in a given medium and  $K_{sp}^{\circ}$  at  $I = 0$ ), formation constants of hydroxide complexes  $\text{Th}_x(\text{OH})_y^{4x-y+}$  ( $\beta_{xy}$ ) and corresponding hydrolysis constants ( ${}^*\beta_{xy}$ ) are defined by

$$K'_{sp} = [\text{Th}^{4+}][\text{OH}^{-}]^4 = K_{sp}^{\circ} / \gamma_{\text{Th}}(\gamma_{\text{OH}})^4, \quad (1)$$

$$\beta_{xy} = [\text{Th}_x(\text{OH})_y^{4x-y+}] / [\text{Th}^{4+}]^x [\text{OH}^{-}]^y = \beta_{xy}^{\circ} (\gamma_{\text{Th}})^x (\gamma_{\text{OH}})^y / \gamma_{\text{Th}_x(\text{OH})_y}, \quad (2)$$

$${}^*\beta_{xy} = [\text{Th}_x(\text{OH})_y^{4x-y+}] [\text{H}^{+}]^y / [\text{Th}^{4+}]^x = {}^*\beta_{xy}^{\circ} (\gamma_{\text{Th}})^x (a_w)^y / \gamma_{\text{Th}_x(\text{OH})_y} (\gamma_{\text{H}})^y, \quad (3)$$

where  $[i]$  is the concentration of species  $i$ ,  $\gamma_i$  its activity coefficient and  $a_w$  the activity of water. Activity coefficients are calculated with the specific ion interaction theory (SIT) [15, 16]:

$$\log \gamma_i = -z_i^2 D + \sum \varepsilon_{ij} m_j, \quad (4)$$

where  $z_i$  is the charge of ion  $i$ ,  $m_j$  (mol/kg H<sub>2</sub>O) the molal concentration of ion  $j$  and  $D$  the Debye–Hückel term at 25 °C:  $D = 0.509\sqrt{I}/(1 + \text{B}\hat{a}\sqrt{I})$ , with  $\text{B}\hat{a} = 1.5$ .  $I$  is the molal ionic strength and  $\varepsilon_{ij}$  the ion–ion interaction parameter for a pair of oppositely charged ions.

The hydrolysis constants selected in [14] are mainly based on the potentiometric titration studies of Baes *et al.* [17, 18], Brown *et al.* [19], Grenthe and Lagerman [20], and Ekberg *et al.* [21]. These were usually performed in the pH range 2.5–4 and at thorium concen-

trations of  $10^{-4}$ – $10^{-2}$  mol/l. The most recent study of Ekberg *et al.* [21] includes potentiometric titrations at relatively low thorium concentrations of  $10^{-5}$ – $10^{-4}$  mol/l and solvent extraction experiments with thorium concentrations in the range of  $10^{-7}$ – $10^{-5}$  mol/l. The equilibrium constant for  $\text{Th}(\text{OH})_3^{+}$  is selected from the potentiometric titration and solvent extraction studies in [19, 21, 22] and those selected for  $\text{Th}(\text{OH})_2^{2+}$ ,  $\text{Th}(\text{OH})_3^{+}$ , and  $\text{Th}(\text{OH})_4(\text{aq})$  are close to the values determined in [21]. The SIT is applied to the conditional hydrolysis constants reported for the polynuclear species  $\text{Th}_2(\text{OH})_2^{6+}$  [17, 20],  $\text{Th}_4(\text{OH})_8^{8+}$  [17, 20, 21],  $\text{Th}_4(\text{OH})_{12}^{4+}$  [19, 20] and  $\text{Th}_6(\text{OH})_{15}^{9+}$  [19–21] in 0.1 M KNO<sub>3</sub> [19], 1 M NaClO<sub>4</sub> [17, 21] and 3 M NaClO<sub>4</sub> [20] to evaluate the equilibrium constants at  $I = 0$  [14]:

$$\begin{aligned} \log {}^*\beta_{2,2}^{\circ} &= -5.7 & (\Delta z^2 = 6, \Delta\varepsilon = 0.24), \\ \log {}^*\beta_{4,8}^{\circ} &= -20.4 & (\Delta z^2 = 8, \Delta\varepsilon = 0.13), \\ \log {}^*\beta_{4,12}^{\circ} &= -26.7 & (\Delta z^2 = -36, \Delta\varepsilon = -0.59), \\ \log {}^*\beta_{6,15}^{\circ} &= -34.0 & (\Delta z^2 = 0, \Delta\varepsilon = 3.7 \pm 1.9). \end{aligned}$$

These parameterizations imply unknown uncertainties, because the data refer to hydrolysis schemes with different sets of polynuclear species. Nevertheless, they allow estimation of  $\log {}^*\beta_{xy}^{\circ}$  at  $I = 0.5$  M. This cannot be done for other polynuclear species proposed in the literature, for which  $\log {}^*\beta_{xy}^{\circ}$  is available at only one ion strength. The two  $\log {}^*\beta_{6,15}^{\circ}$  values in 1 M NaClO<sub>4</sub> (from [17] and [21]) are widely discrepant and the resulting  $\varepsilon$  value is unrealistically large. As the complex  $\text{Th}_6(\text{OH})_{15}^{9+}$  is of minor importance at  $[\text{Th}] < 10^{-2}$  mol/l it is disregarded in the present paper.

**Table 2.** Solubility products of Th(OH)<sub>4</sub> (am), calculated from experimental data with the hydrolysis constants and SIT coefficients in Table 1.

Exp. data from	Medium	log $K'_{sp}$	log $K^{\circ}_{sp}$
Nabivanets and Kudritskaya [1]	0.1 M NaClO <sub>4</sub> , 17 °C	-44.7 ± 0.4	-46.8 ± 0.4
Ryan, Rai [3]	0.1 M NaClO <sub>4</sub> , 25 °C	-45.2 ± 0.3	-47.3 ± 0.3
Rai <i>et al.</i> [6]	0.1 M NaCl, 23 °C	-44.1 ± 0.4	-46.2 ± 0.4
Moon [2]	0.5 M NaClO <sub>4</sub> , 18 °C	-43.4 ± 0.4	-46.5 ± 0.4
Östhols <i>et al.</i> [7]	0.5 M NaClO <sub>4</sub> , 25 °C	-45.1 ± 0.3	-48.2 ± 0.3

Solubility data for amorphous Th(IV) hydrous oxides or hydroxides are generally determined at pH > 3, *i.e.* above the onset of hydrolysis. Hence, the total Th(IV) equilibrium concentration is given by

$$\begin{aligned}
 [\text{Th}]_{\text{tot}} &= [\text{Th}^{4+}] + \sum x[\text{Th}_x(\text{OH})_y]^{4x-y} \\
 &= K'_{sp}[\text{OH}^-]^{-4} + \sum x(K'_{sp}[\text{OH}^-]^{-4})^x \beta'_{xy}[\text{OH}^-]^y
 \end{aligned}
 \quad (5)$$

and the calculated solubility product is directly correlated with the hydrolysis constants used in Eq. (5). The solubility products reported in the literature for Th(OH)<sub>4</sub> (am) or ThO<sub>2</sub>·xH<sub>2</sub>O (am) differ by orders of magnitude, even if the experimental solubilities are in reasonable agreement: *e.g.* Rai *et al.* calculated log  $K^{\circ}_{sp} = -45.5$  [4, 5] and -44.9 [6], whereas Nabivanets and Kudritskaya [1] calculated log  $K'_{sp} = -41.1$  in 0.1 M NaClO<sub>4</sub> (corresponding to -43.2 at  $I = 0$ ) and Moon [2] calculated log  $K'_{sp} = -50.52$  in 0.5 M NaClO<sub>4</sub> (corresponding to -53.6 at  $I = 0$ ). The main reason for these discrepant numbers are the different hydrolysis constants applied by the authors. Rai *et al.* [4–6] even neglect hydrolysis. If the solubility products are recalculated from the experimental data at pH < 5 with the hydrolysis constants and SIT coefficients in Table 1, the log  $K^{\circ}_{sp}$  values lie within the rather narrow range of log  $K^{\circ}_{sp} = -46.2$  to -47.3 (cf. Table 2). The considerably lower solubility product of Östhols *et al.* [7], log  $K^{\circ}_{sp} = -48.7$  (based on the hydrolysis constants in [20]), becomes -48.2 if recalculated with the hydrolysis constants in Table 1. In our recent review [14], a mean value of log  $K^{\circ}_{sp} = -47.0 \pm 0.8$  is selected for the solubility product of Th(OH)<sub>4</sub> (am) or ThO<sub>2</sub>·xH<sub>2</sub>O (am). The solubility product calculated from the data in [1–6] is highly correlated with the formation constant of Th<sub>4</sub>(OH)<sub>12</sub><sup>4+</sup>. According to the hydrolysis constants in Table 1, this is the prevailing complex at the reported thorium concentrations in the range pH 3.5–5. For the considerably lower thorium concentrations in the study of Östhols *et al.* [7], polynuclear hydrolysis species are calculated to be negligible.

In the present study LIBD and EXAFS measurements are performed to elucidate, whether the differences between the solubility data of Östhols *et al.* [7] and the higher solubilities in other studies [1–6] are due to chemical differences in the solids or to the inclusion of colloids.

## 2. Experimental

### 2.1 Chemicals and analytical methods

Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (p.a.), NaCl (p.a.) and HCl (ultrapure) are purchased from Merck. For further purification, NaCl

is recrystallized twice. Alkaline solutions are prepared with carbonate-free NaOH (Baker) and stored in an argon glove box. Colloid-free thorium stock solutions for the titration-LIBD experiments are obtained by double filtrations through Amicon 10 kD ultrafilters. All solutions are prepared with ultrapure water from a water purification apparatus (Milli-Q-academic, Millipore). Thorium concentrations > 3 × 10<sup>-7</sup> mol/l are determined photometrically by the arsenazo III method [23]. Lower concentrations are determined by ICP-MS (ELAN 6100, Perkin Elmer). As the background is found to be 0.001 ppb Th and the 0.5 M NaCl aliquots have to be diluted and acidified (4% HNO<sub>3</sub>) for ICP-MS analysis, the detection limit for Th in the original solutions is about 10<sup>-10</sup> mol/l.

Combination pH electrodes (type ROSS, Orion Co.) are used to determine the H<sup>+</sup> concentration in 0.5 M NaCl solution. They are calibrated against standard pH buffers (pH 1–10, Merck) and standard solutions  $x$  M HCl/(0.5– $x$ ) M NaCl with  $x$  in the range 0.001–0.1. The relation between the H<sup>+</sup> concentration and measured pH<sub>exp</sub> is given by:

$$-\log[\text{H}^+] = \text{pH}_{\text{exp}} + A,$$

where  $A = \log \gamma_{\text{H}} + \Delta\text{pH} = 0.00 \pm 0.02$  includes the activity coefficient of the H<sup>+</sup> ion and the term  $\Delta\text{pH}$ , which results from the variation of the liquid junction potential when measuring diluted pH buffer solutions for calibration and 0.5 M NaCl test solutions. In the alkaline solutions with the composition  $x$  M NaOH/(0.5– $x$ ) M NaCl and  $x = 0.002$ –0.5, the H<sup>+</sup> concentration is calculated from the given NaOH concentration and the ion product of water (log  $K'_{\text{w}} = -13.73$  in 0.5 M NaCl [16]).

### 2.2 Solubility measurements

Amorphous Th(IV) hydrous oxide or hydroxide is prepared under an argon atmosphere by slow titration of a thorium nitrate solution with carbonate-free NaOH (Baker) up to pH 10. The precipitate is washed with water and dried at room temperature for one week in a vacuum desiccator. The X-ray powder diffraction pattern does not show any characteristic peaks or broadened bands. Assuming the chemical formula ThO<sub>2</sub>·xH<sub>2</sub>O (am), the water content of  $x \approx 2.4$  is determined by gravimetric analysis, *i.e.*, drying the sample overnight at 800 °C. This preparation method is comparable with that used by Östhols *et al.* [7], yielding a solid which also had a low degree of crystallinity and a water content of  $x \approx 2.5$  [7].

The solubility experiments are performed batchwise in 10–30 ml PFA and glass vials. A weighed amount of the

amorphous solid ( $\approx 0.01$  mol per liter solution) is added to the 0.5 M HCl/NaCl and NaOH/NaCl solutions and the  $H^+$  and Th(IV) concentrations are measured as a function of time after 5–204 days. The acidic solutions are thermostated at 25 °C and Amicon 10 kD ultrafilters (pore size 1.4 nm) are used for phase separation. In the case of near-neutral and alkaline solutions (stored at  $22 \pm 2$  °C in an Ar glove box), the thorium concentrations in filtered aliquots are at the background level of the ICP-MS, even after pre-equilibration of the filters. The results of filtration and ultracentrifugation at different rotation velocities indicate that thorium is sorbed on the filters. Therefore, the thorium concentration in near-neutral and alkaline solutions is determined after ultracentrifugation (Beckman XL-90) for 60 minutes at 90 000 rpm using quick-seal centrifuge tubes (Vol.  $\approx 4$  ml). The mean relative centrifugal force is about  $5 \times 10^5$  g.

### 2.3 Titration experiments

The coulometric titration of  $1.2 \times 10^{-2}$  to  $1.0 \times 10^{-6}$  M thorium nitrate solutions (60 ml) at  $I = 0.5$  M (NaCl) and initial  $H^+$  concentrations in the range  $-\log[H^+] = 2.7$ – $4.1$  is performed in a double-walled titration vessel, thermostated at 25 °C, with the equipment described in [9]. A peristaltic pump is used to pump the titration solution through a flow-through cuvette for simultaneous colloid detection by LIBD. Since titrations performed with a current of 0.3–1 mA lead to local oversaturation, leading to the formation of unstable colloids, the titration velocity is decreased, *i.e.*, the current is reduced to 0.05 mA (corresponding to the addition of  $4.48 \times 10^{-2}$  mmol  $OH^-$  per day to 60 ml solution). As a consequence, the titration of Th(IV) solutions above  $10^{-3}$  M requires titration times up to several weeks. The pH electrode is freshly calibrated before and re-calibrated at the end of each experiment. In the case of titrations lasting more than 2 days, the electrode is re-calibrated after 2–3 days and exchanged against another one. The measured values of  $\log[H^+]$  are corrected for the electrode potential drift (usually below 2 mV per day). In each experiment, the thorium concentration is determined in unfiltered aliquots taken at the beginning and at the end, and in some experiments also during the titration to elucidate sorption effects. In addition, 1 kD filtration (Filtron, pore size *ca.* 1.2 nm) is applied to quantify the fraction of Th(IV) colloids.

### 2.4 Colloid detection by LIBD

The colloid detection by LIBD is based on the plasma generation on colloids in the focal volume of a pulsed laser beam [24, 25]. The experimental setup used in the present study and its calibration with reference colloids have been described previously [9, 10, 26]. The laser pulse energy of the Nd-YAG laser (Continuum, Surelite,  $\lambda_{em} = 532$  nm, repetition rate 20 Hz) is adjusted to a constant value of 0.35 mJ, below the breakdown threshold of water. A CCD camera is used to record the plasma light emission, magnified by a macro-microscope. The breakdown probability, *i.e.*, the number of breakdown events per laser pulse for an adjusted energy threshold, is derived from 3000 laser shots. It is correlated with the mass concentration of colloids of a given particle size and material. The lower limit of colloids detectable by LIBD is estimated to be about 5 nm.

**Table 3.** Composition of the EXAFS samples.

Sample	[Th] (mol/l)	Medium, $H^+$ concentration
A	$5.5 \times 10^{-2}$	1.5 M $HClO_4$
B1	$5.0 \times 10^{-3}$	$-\log[H^+] = 3.02^a$
B2	$4.3 \times 10^{-3}$	$-\log[H^+] = 3.50^a$
C1	$2.2 \times 10^{-2}$	$-\log[H^+] = 3.67^a$
C2	$5.8 \times 10^{-3}$	$-\log[H^+] = 3.62^a$
D	Solid $Th(OH)_4$ (am)	

a: in 0.5 M NaCl.

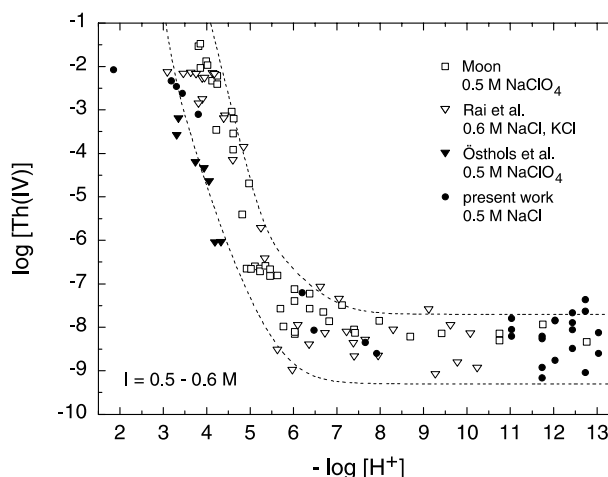
## 2.5 EXAFS study

Thorium  $L_3$  edge X-ray absorption spectra are recorded at the Synchrotronstrahlungslabor HASYLAB, A1-endstation in Hamburg (DESY). The chemical composition, thorium and  $H^+$  concentrations, of the investigated samples are listed in Table 3. Sample A is a reference solution of  $Th^{4+}$  (aq) prepared by dissolving  $Th(OH)_4$  (am) in 1.5 M  $HClO_4$  [27]. Samples B1, B2, C1, and C2 are  $Th(NO_3)_4$  solutions in 0.5 M NaCl. Samples B1 and B2 are taken from experiment LIBD-1, at the beginning and end of the titration, respectively. Sample C1 is prepared by titrating a  $2.2 \times 10^{-2}$  M thorium solution from  $-\log[H^+] = 2.6$  to  $-\log[H^+] = 3.7$ . The presence of colloids is confirmed by LIBD. An attempt to remove the colloids by 1 kD filtration (Filtron, pore size *ca.* 1.2 nm) is not successful. Immediately after filtration, colloids are formed again and, as a consequence, pH is shifted to a lower value. Sample C2 is the suspension after 1 kD filtration. Sample D is the solid  $Th(OH)_4$  (am) used in the present solubility study. The sample preparation, as well as details of the EXAFS measurements and data analysis are given in [12].

## 3. Results and discussion

### 3.1 Solubility of amorphous $Th(OH)_4$ (am)

Fig. 1 shows the solubility data determined with the amorphous Th(IV) precipitate in comparison to literature data



**Fig. 1.** Solubility of amorphous Th(IV) hydroxide or hydrous oxide at  $I = 0.5$ – $0.6$  M and 18–25 °C; comparison of the present results with literature data [2, 4, 5, 7]. The dashed curves represent lower and upper limits calculated with the thermodynamic constants selected in [14],  $\log K_{sp}^{\circ} = -47.0 \pm 0.8$  and the hydrolysis constants given in Table 1.

**Table 4.** Experimental solubility data for Th(OH)<sub>4</sub> (am) at *I* = 0.5 M and 25 °C.

Sample	Acidic and neutral HCl/NaCl solutions		
	time (days)	–log[H <sup>+</sup> ]	log[Th(IV)]
A1	5	1.11	–2.45
	15	1.18	–2.14
	31	1.23	(–2.04) <sup>a</sup>
A2	5	1.46	–2.45
	15	1.55	–2.14
	31	1.72	–2.18
	80	1.84	–2.08
	204	1.86	–2.08
A3	5	2.05	–2.79
	15	2.37	–2.52
	31	2.87	–2.38
	80	3.18	–2.33
	204	3.18	–2.33
A4	5	2.25	–3.04
	15	2.60	–2.67
	31	3.02	–2.55
	80	3.30	–2.46
	204	3.28	–2.45
A5	5	2.63	–3.11
	15	3.05	–2.84
	31	3.34	–2.75
	80	3.48	–2.67
	204	3.45	–2.62
A6	5	3.42	–3.59
	15	3.60	–3.36
	31	3.73	–3.25
	80	3.82	–3.11
	204	3.78	–3.10
A7	15	6.30	–8.22
	211	6.47	–8.06 (–6.35) <sup>b</sup>
A8	15	6.06	–8.37
	211	6.20	–7.20 (–6.20) <sup>b</sup>
A9	15	7.58	–8.52
	211	7.65	–8.35 (–6.08) <sup>b</sup>
A10	15	7.78	–8.67
	211	7.92	–8.60 (–6.67) <sup>b</sup>

determined at comparable ionic strength (*I* = 0.5–0.6 M). The present results in acidic 0.5 M NaCl solutions are comparable with the data determined by Östhols *et al.* [7] in 0.5 M NaClO<sub>4</sub> for a solid prepared in a similar manner. However, a relatively long equilibration time of more than 2 months is needed to obtain constant steady state thorium and H<sup>+</sup> concentrations (cf. Table 4). Dzimitrowicz *et al.* [28] investigated Th(IV) precipitates prepared in a similar way. They were X-ray amorphous. However, as shown by transmission electron microscopy, they included small ThO<sub>2</sub> (cr) crystallites (3–8 nm). Such precipitates probably consist of a non-unique hydrated oxyhydroxide ThO<sub>*n*</sub>(OH)<sub>4–2*n*</sub>·*x*H<sub>2</sub>O (am) with a hydroxide surface layer. The assumption that the amorphous precipitate has a non-unique composition including small ThO<sub>2</sub> (cr) crystallites would also explain that, even after 204 days, a small rest of the solid remains undissolved in sample A2. At –log[H<sup>+</sup>] = 1.85, the Th<sup>4+</sup> (aq) ion is the predominant species in solu-

**Table 4.** Continued.

Sample	Alkaline NaCl/NaOH solutions <sup>d</sup>			
	[NaOH] (mol/l)	time (days)	log[Th(IV)] sample A	log[Th(IV)] sample B
A11	0.002	44		–7.66
		81		–8.20
		122	–7.79 (–7.00) <sup>c</sup>	–8.05 (–6.23) <sup>b</sup>
A12	0.01	44		–7.76
		81		–9.16
		122	–8.25 (–5.80) <sup>b</sup>	–8.92 (–5.88) <sup>b</sup>
A13	0.02	44		–7.67
		81		–7.85
		122	–7.84 (–7.19) <sup>c</sup>	–8.75 (–6.17) <sup>b</sup>
A14	0.05	44		–8.44
		81		–7.66
		122	–8.49 (–6.44) <sup>b</sup>	–7.89 (–6.55) <sup>b</sup>
A15	0.1	44		–8.06
		81		–9.04
		122	–6.22 <sup>c</sup> –7.36 (–6.31) <sup>b</sup>	–7.63 (–6.62) <sup>b</sup>
A16	0.2	44		–8.67
		81		–8.12
		122	–8.60 (–7.12) <sup>c</sup>	–8.18 <sup>c</sup> (–5.85) <sup>b</sup>
A17	0.5	44		–8.53
		81		–8.55
		122	–8.03 –8.32 (–5.94) <sup>b</sup>	–7.85 (–5.98) <sup>b</sup>

a: Solid phase completely dissolved;

b: Measured without phase separation;

c: The high thorium concentration is probably caused by uncautious moving of the centrifuged vial and re-suspension of colloidal particles;

d: log[H<sup>+</sup>] is related to log[OH<sup>–</sup>] in the *x* M NaOH/(0.5 – *x*) M NaCl solutions by the ion product of water: log *K*'<sub>w</sub> = –13.73 [16].

tion and the solubility product calculated from sample A2 (log[Th<sup>4+</sup>] = –2.08 at –log[H<sup>+</sup>] = 1.85), log *K*'<sub>sp</sub> = –49.64 (corresponding to log *K*<sub>sp</sub><sup>o</sup> = –52.9), agrees with the value for microcrystalline ThO<sub>2</sub> (s) [9]. Another possible explanation is the transformation of the amorphous oxyhydroxide “Th(OH)<sub>4</sub> (am)” into a more crystalline oxide, similar to the observation made by Rai *et al.* [6] at 90 °C and pH 1.5–3 in 0.1 M NaCl. In the more acidic sample A1 (initially 0.1 M HCl/0.4 M NaCl), the solid is completely dissolved after 31 days. In this sample the total thorium concentration (log[Th<sup>4+</sup>] = –2.04 at –log[H<sup>+</sup>] = 1.23) is below the solubility limit of ThO<sub>2</sub> (cr).

The present solubility data in alkaline solutions shows no dependence either on pH (cf. Fig. 1) or equilibration time in the range of 44–122 days (cf. Table 4). The large scatter of experimental data is probably due to the variable success in removal of colloids by centrifugation. In some cases essentially higher thorium concentrations are measured (up to 10<sup>–6</sup> mol/l, *i.e.*, close to the values measured without phase separation: log [Th]<sub>tot</sub> = –6.2 ± 0.5). These are likely caused by uncautions handling of the centrifuged vial, leading to re-suspension of colloidal particles. Disregarding these data points, the mean value of the thorium concentrations at

pH > 10 (given with a  $2\sigma$  uncertainty interval),

$$\log[\text{Th}(\text{OH})_4(\text{aq})] = -8.2 \pm 0.9$$

is in reasonable agreement with the value of  $-8.5 \pm 0.6$  selected recently [14] from experimental data in [2–4]. The significantly higher solubilities reported by Nabivanets and Kudritskaya [1] ( $\log[\text{Th}] = -6.3$  at pH = 5.5–7 in 0.1 M NaClO<sub>4</sub>, 17 °C) must be ascribed to insufficient phase separation by centrifugation at only 10 000 rpm. Because of the problems caused by incomplete removal of colloids by centrifugation, we assume that the lower values at  $\log[\text{Th}(\text{IV})] \approx -9$  more likely represent the concentration of mononuclear Th(OH)<sub>4</sub>(aq).

### 3.2 Coulometric pH titration and colloid detection by LIBD

In order to elucidate whether the high thorium concentrations measured at pH = 3.5–5 in [1–6] (cf. Fig. 1) arise from the inclusion of small colloids, coulometric pH titration of colloid-free Th(NO<sub>3</sub>)<sub>4</sub> solutions (0.5 M NaCl, pH ≥ 2.7) is combined with LIBD to determine the onset of colloid formation as a function of the H<sup>+</sup> and thorium concentration. The initial formation of colloids during the titration is recognized by the increase of the breakdown probability (number of breakdown events per laser

pulse). Considering colloids as small solid particles, the H<sup>+</sup> and thorium concentrations at the onset of colloid formation define the solubility of thorium hydroxide excluding colloidal thorium species. The experimental data of the present study, thorium and H<sup>+</sup> concentrations at different stages of the titration experiments, are summarized in Table 5. The formation of appreciable amounts of colloids above the onset of colloid formation determined by LIBD is corroborated by the decrease of the thorium concentration after 1 kD filtration at the end of the titration experiments.

It must be emphasized that the present titration-LIBD experiment, although performed with the same equipment, is not comparable with the previous study of Bundschuh *et al.* [9]. In that previous paper [9], the titration in the range pH = 1.5–2.5 led to the formation of thorium oxide colloids, which subsequently agglomerate and form precipitates after some weeks [12]. At these low pH values, the solid particles are formed in solutions where Th<sup>4+</sup>(aq) is the predominant aqueous species. The present titrations at pH > 3 lead to hydrolysis of the Th<sup>4+</sup>(aq) ion and polynucleation up to the formation of amorphous hydroxide colloids. The chemical and structural differences between the microcrystalline ThO<sub>2</sub> particles formed at pH 1.5–2.5 and the amorphous hydroxide colloids formed at pH 3–4 are explicitly demonstrated and discussed in the EXAFS study of Rothe *et al.* [12].

**Table 5.** Th(IV) and H<sup>+</sup> concentrations at the beginning, at the onset of colloid formation (printed bold) and at the end of the present titration experiments at  $I = 0.5$  M (NaCl) and 25 °C.

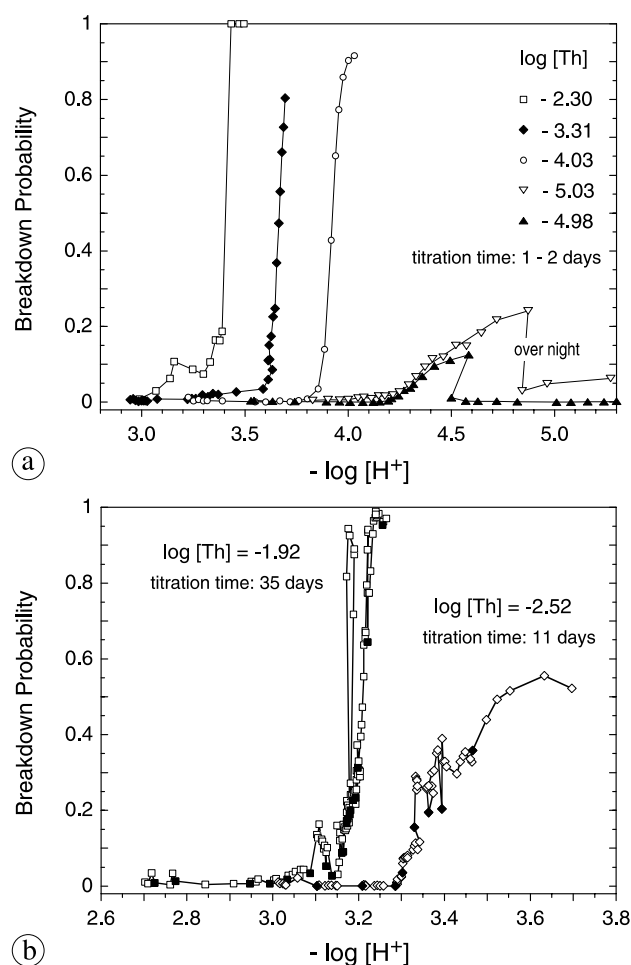
Experiment	log[Th]	–log[H <sup>+</sup> ]	[Th] (mol/l)	
	<b>bold: initial colloid formation</b>		unfiltered	1 kD filtration
LIBD-10		2.70	1.21 × 10 <sup>–2</sup>	
		3.15	1.18 × 10 <sup>–2</sup>	
	<b>–1.93 ± 0.01<sup>a</sup></b>	<b>3.18 ± 0.04</b>		1.04 × 10 <sup>–2</sup>
LIBD-1		3.26	1.15 × 10 <sup>–2</sup>	
		3.02	5.0 × 10 <sup>–3</sup>	
	<b>–2.33 ± 0.04<sup>a</sup></b>	<b>3.37 ± 0.03</b>	4.3 × 10 <sup>–3</sup>	2.7 × 10 <sup>–3</sup>
LIBD-11		3.50	3.0 × 10 <sup>–3</sup>	
		3.01	3.0 × 10 <sup>–3</sup>	
	<b>–2.53 ± 0.02<sup>a</sup></b>	<b>3.32 ± 0.03</b>	2.9 × 10 <sup>–3</sup>	8.9 × 10 <sup>–4</sup>
LIBD-5		3.70	2.9 × 10 <sup>–3</sup>	
		2.94	4.9 × 10 <sup>–4</sup>	
	<b>–3.32 ± 0.02<sup>a</sup></b>	<b>3.61 ± 0.02</b>	4.7 × 10 <sup>–4</sup>	
LIBD-6		3.69	4.7 × 10 <sup>–4</sup>	
		3.23	9.4 × 10 <sup>–5</sup>	
	<b>–4.10 ± 0.08<sup>a</sup></b>	<b>3.86 ± 0.03</b>	6.8 × 10 <sup>–5</sup>	
LIBD-7		4.03	6.8 × 10 <sup>–5</sup>	
		3.53	9.3 × 10 <sup>–6</sup>	
	<b>–5.10 ± 0.10<sup>a</sup></b>	<b>4.19 ± 0.03</b>	1.3 × 10 <sup>–7</sup>	
LIBD-8		5.49	1.3 × 10 <sup>–7</sup>	
		3.83	1.04 × 10 <sup>–5</sup>	
	<b>–5.07 ± 0.10<sup>a</sup></b>	<b>4.22 ± 0.03</b>	6.9 × 10 <sup>–6</sup>	
		4.29	3.2 × 10 <sup>–6</sup>	
		4.87	1.4 × 10 <sup>–7</sup>	
LIBD-9 <sup>b</sup>		5.27	1.4 × 10 <sup>–7</sup>	
		4.06	9.7 × 10 <sup>–7</sup>	
		4.18	7.4 × 10 <sup>–7</sup>	
		4.33	4.5 × 10 <sup>–7</sup>	
		4.60	2.9 × 10 <sup>–7</sup>	
	5.33	1.7 × 10 <sup>–7</sup>		

a: These log[Th] values represent the mean value of the concentrations measured before and after the onset of colloid formation;

b: No significant increase of the breakdown probability.

Fig. 2a shows the breakdown probability measured as a function of the  $H^+$  concentration in a series of  $5.0 \times 10^{-3}$ – $1.0 \times 10^{-5}$  M thorium nitrate solutions. These titrations are performed within 1–2 days. In experiment LIBD-1, at a thorium concentration of  $5.0 \times 10^{-3}$  mol/l, a small increase of the breakdown probability occurs already at  $-\log[H^+] = 3.15$ , *i.e.*, considerably before the formation of a large amount of colloids in the range of  $-\log[H^+] = 3.35$ – $3.40$  leads to a breakdown probability of 100%. In this experiment the coulometric titration is performed with a current of 1 mA (corresponding to the addition of  $3.73 \times 10^{-2}$  mmol  $OH^-$  per hour to 60 ml solution). In several further titration experiments performed with a current of 0.3–1 mA, the breakdown probability of  $1.0 \times 10^{-4}$  M thorium solutions at  $\log[H^+] = 2.8$  to 3.2 increases continuously, starting from the beginning of the titration. As Th(IV) has an extremely high tendency toward polynucleation in this pH range, even a small local oversaturation leads to the formation of unstable colloids already below the solubility limit. However, these colloids re-dissolve within a few days. In the other experiments shown in Fig. 2a, this effect is avoided by decreasing the titration velocity, *i.e.*, by performing the titration with a current of 0.05 mA.

As a consequence of the low titration velocity necessary to avoid colloid formation caused by local pH gradients,



**Fig. 2.** Titration-LIBD experiments at 25 °C: breakdown probability as a function of the  $H^+$  concentration during the coulometric titration of  $1.2 \times 10^{-2}$ – $1.0 \times 10^{-5}$  M thorium nitrate solutions in 0.5 M NaCl.

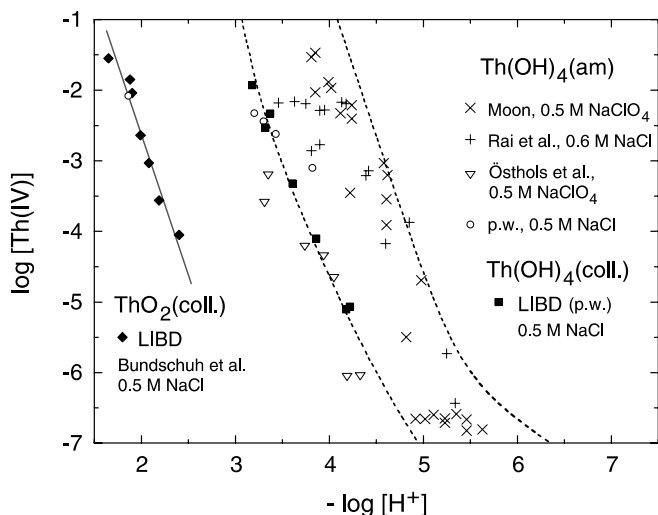
the titration of solutions with high thorium concentrations of  $1.2 \times 10^{-2}$  mol/l (LIBD-10) and  $3.0 \times 10^{-3}$  mol/l (LIBD-11) requires long times of 35 and 11 days, respectively (Fig. 2b). The largest part of the  $OH^-$  ions is consumed by the hydrolysis reactions of thorium and only a small part remains for increasing the pH. Despite the slow titration, the initiation of colloid formation below the solubility limit is not completely avoided at these high thorium concentrations. However, upon stopping the titration or reducing the current to values  $< 0.01$  mA overnight or over the weekend (filled points in Fig. 2b), these unstable colloids re-dissolve. In order to exclude such artefacts, the long-time stability of the thorium colloids present at the end of the titration experiment is ascertained by measuring the breakdown probability in aliquots of the final solutions over a period of 1–3 months. In experiment LIBD-11, the breakdown probability remains at a value of about 50% even after continuing the titration up to  $-\log[H^+] = 3.70$ . However, 1 kD filtration of the final thorium solution shows that 70% of the thorium is present as colloids.

Sorption of thorium onto the glass surface of the reaction vessel is a problem, particularly in the experiments at low thorium concentrations (*cf.* thorium concentration measured in unfiltered aliquots at different stages of the titrations, Table 5). In the experiments at initial thorium concentrations of  $[Th]_{\text{initial}} > 10^{-4}$  mol/l, the observed decrease of the thorium concentrations is less than 20%. However, during the titration experiments at  $[Th]_{\text{initial}} \leq 10^{-5}$  mol/l and  $pH > 4$ , the thorium concentrations decrease to  $10^{-7}$  mol/l. Because of this sorption effect the breakdown probability in the two experiments at  $[Th]_{\text{initial}} = 1 \times 10^{-5}$  mol/l (LIBD-7, LIBD-8) do not reach high values and decrease to the background level when the titration is stopped overnight (Fig. 2a). In experiment LIBD-9, the initial thorium concentration of  $1 \times 10^{-6}$  mol/l decreases continuously from the start of the titration (*cf.* Table 5) and the breakdown probability does not exceed 7%. Therefore, the applicability of the present method and equipment is restricted to thorium concentrations  $\geq 10^{-5}$  mol/l.

The results of the titration-LIBD experiments, *i.e.* the  $H^+$  and Th(IV) concentrations at the onset of colloid formation, are comparable with the solubility data measured by Östhols *et al.* [7] and in the present study with amorphous precipitates dried at room temperature (Fig. 3). This finding gives rise to the conclusion that the high solubilities determined at  $-\log[H^+] = 3.5$ – $5$  with precipitates not dried but only washed with water include large amounts of small colloids, in spite of the fact that Moon [2] and Rai *et al.* [3–6] determined the thorium concentration after filtration at a pore size of about 2 nm. Amorphous precipitates only washed with water may include small particles, which easily become suspended in the solubility experiment, whereas dehydration of the solid by drying may lead to larger agglomerates in the solid and, hence, to less colloids in the solubility experiment.

### Evaluation of the solubility product

The solubility data defined by the onset of colloid formation are used to calculate the solubility product of  $Th(OH)_4$  (am).



**Fig. 3.** Comparison of the present titration-LIBD data at the onset of  $\text{Th}(\text{OH})_4$  (am) colloid formation with classical solubility data for amorphous  $\text{Th}(\text{IV})$  solids at comparable ionic strength (present work and literature studies [2, 4, 5, 7] at  $I = 0.5\text{--}0.6\text{ M}$ ). The lower and upper dashed curves are calculated with  $\log K_{\text{sp}}^{\circ} = -47.8$  and  $-46.2$ , respectively, and the hydrolysis constants in Table 1. According to these constants,  $\text{Th}_4(\text{OH})_{12}^{4+}$  is the prevailing complex along the upper curve. The considerably lower titration-LIBD data of Bundschuh *et al.* [9], for the initial formation of  $\text{ThO}_2$  (colloids) in the pH range 1.5–2.5, are also shown for comparison.

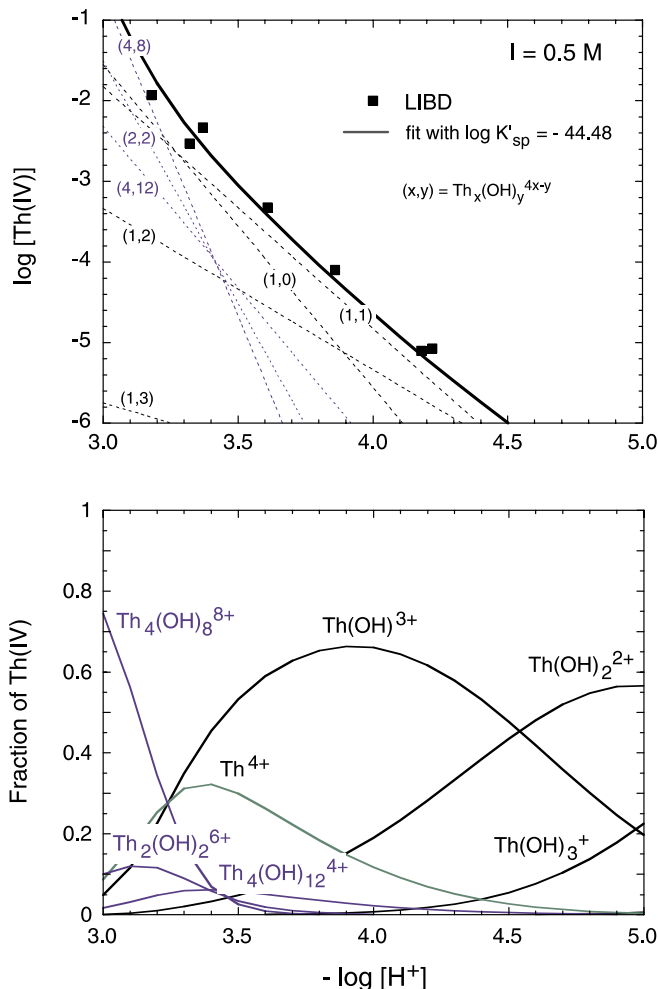
As the experimental data do not allow to determine the solubility product independently of the hydrolysis constants, the  $\log \beta_{xy}^{\circ}$  values in Table 1 are converted to  $I = 0.5\text{ M}$  and used as fixed values in Eq. (5). Considering also the uncertainties in the selected hydrolysis constants, the following solubility product is obtained for  $\text{Th}(\text{OH})_4$  (am):

$$\log K'_{\text{sp}} = -44.48 \pm 0.24 \quad (\text{in } 0.5\text{ M NaCl})$$

and

$$\log K_{\text{sp}}^{\circ} = -47.8 \pm 0.3 \quad (6)$$

after conversion to  $I = 0$  with the SIT coefficients of the NEA-TDB [16]. The calculated solubility curve is shown as a solid line in Fig. 4a. The calculated speciation along this solubility curve predicts  $\text{Th}(\text{OH})^{3+}$  as the predominant complex in the range  $-\log[\text{H}^+] = 3.6\text{--}4.3$  (Fig. 4b). This is consistent with the experimental data, which decrease with a slope of about  $-3$ . At  $-\log[\text{H}^+] < 3.5$  and  $[\text{Th}] > 10^{-3}\text{ mol/l}$ , polynuclear species become predominant. For the titrations at  $[\text{Th}] > 10^{-3}\text{ mol/l}$ , this is confirmed by the balance between the total  $\text{OH}^-$  added coulometrically and the fraction of  $\text{OH}^-$  consumed for increasing the pH. Appreciable amounts of small polynuclear species are formed already prior to the onset of colloid formation. For instance, in experiment LIBD-10 at  $[\text{Th}] = 1.2 \times 10^{-2}\text{ mol/l}$ , an average number of  $n'_{\text{OH}/\text{Th}} = 0.9 \pm 0.1$  mmol  $\text{OH}^-$  ions per mmol thorium are consumed by hydrolysis reactions during the titration from  $-\log[\text{H}^+] = 2.70$  to the onset of colloid formation at  $-\log[\text{H}^+] = 3.18 \pm 0.04$ . This is consistent with the calculated speciation including oligomers. If only mononuclear species are taken into account, the calculated value of  $n_{\text{OH}/\text{Th}} = 0.47$  is significantly too small.



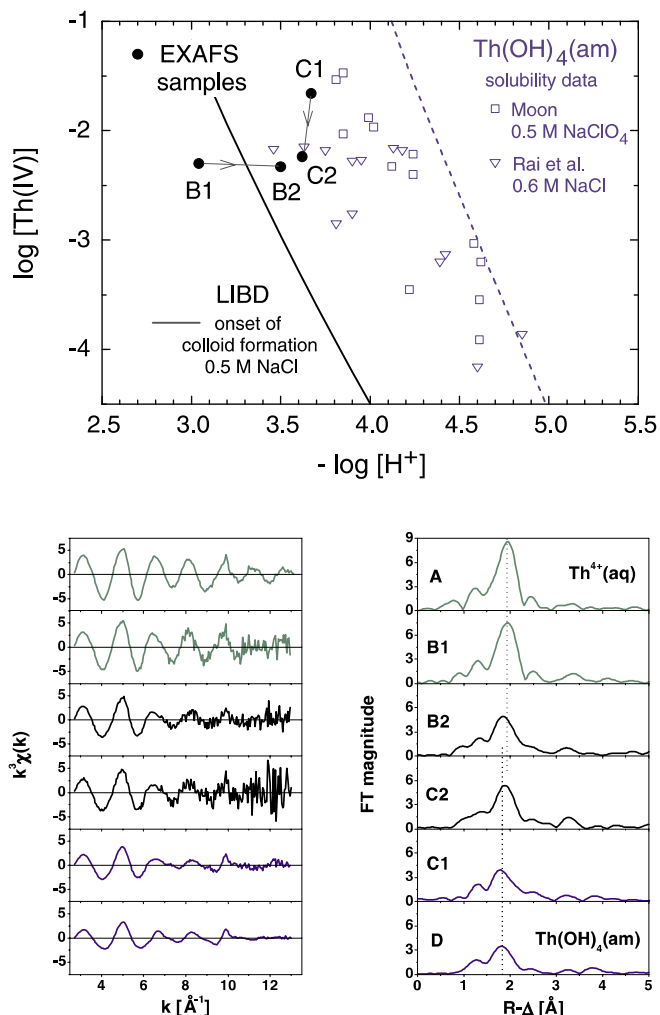
**Fig. 4.** Solubility data determined in the present titration-LIBD study. The solid curve is calculated with  $\log K'_{\text{sp}} = -44.48$  (fit) and the hydrolysis constants in Table 1, converted to  $I = 0.5\text{ M}$ . The  $\text{Th}(\text{IV})$  species distribution along the calculated solubility curve is shown below.

### 3.3 EXAFS study

The conclusions from the LIBD and ultrafiltration data are verified by EXAFS spectra recorded at the  $\text{Th } L_3$  edge for aqueous thorium samples at  $\text{pH} < 4$ , below and above the onset of colloid formation. For easier survey the  $\text{H}^+$  and  $\text{Th}(\text{IV})$  concentrations in the samples investigated are illustrated in Fig. 5a together with the onset of colloid formation determined by LIBD and the solubility data in [2, 4]. It is important to note that no precipitation was observed in any of these colloidal suspensions. In Fig. 5b, the EXAFS spectra of these samples are compared with the spectrum of  $\text{Th}^{4+}$  (aq) in  $1.5\text{ M HClO}_4$  (sample A) and of the amorphous  $\text{Th}(\text{IV})$  solid used in the present solubility study (sample D). Metrical parameters, coordination number ( $N$ ), bond distance ( $R$ ), Debye–Waller factors ( $\sigma^2$ ) and relative shifts in ionization energy ( $\Delta E_0$ ) obtained in theoretical fits to the data are listed in Table 6.

Sample B1 ( $[\text{Th}(\text{IV})] = 5.0 \times 10^{-3}\text{ M}$ ,  $-\log[\text{H}^+] = 3.02$ ) is a solution below the onset of colloid formation. Using the hydrolysis constants in Table 1, the following aqueous speciation is calculated: 59%  $\text{Th}^{4+}$  (aq), 31%  $\text{Th}(\text{OH})^{3+}$  (aq), 1%  $\text{Th}(\text{OH})_2^{2+}$  (aq), 8% dimeric and 1% tetrameric hydrolysis





**Fig. 5.** Speciation by Th- $L_3$  EXAFS:  $\text{Th}^{4+}$  (aq) in 1.5 M  $\text{HClO}_4$  (sample A), aqueous samples B1, B2, C1, and C2 at different pH, and amorphous Th(IV) hydroxide (solid sample D). (a): Composition ( $\text{H}^+$  and Th(IV) concentrations) of the samples B1, B2, C1, and C2 (filled circles) with regard to the onset of colloid formation detected by LIBD (solid line) and to the high solubility data reported in [2, 4, 5]. (b):  $k^3$ -weighted  $\chi(k)$ -functions (left panel) and corresponding Fourier transform magnitudes (right panel).

**Table 6.** Metrical parameters extracted by least squares fitting analysis of EXAFS spectra.

Sample	Shell	$R$ ( $\text{\AA}$ )	$N$	$\sigma^2$ ( $\text{\AA}^2$ )	$\Delta E$ (eV)
A	O	2.45	12.7	0.0072	4.1
B1	O	2.46	11.6	0.0074	3.9
B2	O	2.51	10.6	0.0121 <sup>a</sup>	7.5
C1	O1	2.50	9.4	0.0140 <sup>a</sup>	6.9
	O2	3.09	1.2	0.0007	6.9
	Th	3.99	0.7	0.0032	11.0
C2	O	2.51	10.5	0.0103 <sup>a</sup>	7.5
D	O1	2.46	6.6	0.0106 <sup>a</sup>	6.7
	O2	3.13	4.4	0.0109	15.8
	Th	3.96	1.5	0.0065	8.9

a: Including asymmetry term (3<sup>rd</sup> cumulant).

species. This speciation calculation is consistent with the observed EXAFS spectrum; the spectrum of sample B1 is similar to that of  $\text{Th}^{4+}$  (aq) in 1.5 M  $\text{HClO}_4$  (sample A) and the fit results for both these samples (Table 6) are the

same, to within experimental uncertainty. This is because  $\text{Th}^{4+}$  (aq) is the major solution species in B1. EXAFS is not able to detect the coordinating hydroxyl in the mononuclear hydrolysis species  $\text{Th(OH)}^{3+}$  (aq).

The EXAFS spectra of samples B2, C2 (with similar  $\text{H}^+$  and thorium concentrations, and both above the onset of colloid formation) and particularly sample C1 (with  $\text{H}^+$  and thorium concentrations considerably exceeding the solubility determined by LIBD) are significantly different from that of  $\text{Th}^{4+}$  (aq) and sample B1. The presence of large amounts of polynuclear Th(IV) species or colloids is reflected in highly asymmetric Th–O coordination exhibited by all these samples, *i.e.*, a broad asymmetric Th–O FT peak. This asymmetry required inclusion of an inharmonic correction to the phase [29] in the fits to the Th–O shell. Furthermore, an additional oxygen shell (O2, Table 6) had to be included in the fit to the spectrum of sample C1. This was also necessary in fits to the spectrum of the amorphous solid phase (sample D). In fact, both the EXAFS spectrum of sample C1 and the metrical parameters describing the Th(IV) coordination in this sample are very similar to that of sample D. This indicates that the suspended colloids in sample C1 have a structure similar to the amorphous solid  $\text{ThO}_n(\text{OH})_{4-2n} \cdot x\text{H}_2\text{O}$  (am). The Th–O shell in both these samples has at least two distances and both have Th atoms as nearest neighbors around 4  $\text{\AA}$ . Note that this Th–Th peak in sample C1 disappears in the FT spectrum of sample C2, in which the larger colloids are removed *via* filtration. The  $\text{H}^+$  and thorium concentration and hence the spectrum of sample C2 are more similar to sample B2.

## 4. Conclusions

The present LIBD and EXAFS studies at pH 3–5 demonstrate that the onset of the formation of thorium hydroxide colloids is an accurate function of the  $\text{H}^+$  and Th(IV) concentration. Below this solubility limit, thorium colloids may be formed because of local pH gradients, however they re-dissolve. On the other hand, if this limit is exceeded, thorium colloids are present even after months. They neither re-dissolve nor do they precipitate, indicating that they might be thermodynamically stable species. Solubility data measured in this pH range with X-ray amorphous precipitates dried at room temperature (non-unique oxyhydroxides including small  $\text{ThO}_2$  crystallites) are comparable with the data determined by the titration-LIBD method. Numerous solubility data for amorphous precipitates, not dried but only washed with water, exceed the threshold for colloid formation by 3–4 orders of magnitude. The results are reproducible although small thorium colloids are the prevailing species under such conditions. The same holds for potentiometric titration studies, which are usually performed much faster than in the present study, with high thorium concentrations of  $10^{-4}$ – $10^{-2}$  mol/l, and up to pH 4.

At present, the modelling of solubility data including colloids and the calculated solubility products for Th(IV) hydroxide refer to chemical models, which consider the small colloids as well-defined polynuclear species. The quantification and thermodynamic modelling of the “colloidal solubility” for oxides/hydroxides of highly charged

actinide and other metal ions requires further experiments, *i.e.*, systematic investigation of the equilibrium colloid concentration and size distribution as a function of pH, total metal concentration and time.

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