Radiochim. Acta **91**, 253–262 (2003)
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Solubility of crystalline thorium dioxide

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(Received July 9, 2002; accepted July 17, 2002)

Thorium dioxide / Crystallinity / Solubility product / Titration / LIBD / Particle size / Irreversible dissolution / Tetravalent actinides

Summary. The solubility of thorium oxides of different crystallinity is investigated at 25 °C by different experimental approaches. The dissolution of bulk crystalline ThO_2(cr) is a very slow process and the Th(IV) concentrations measured after one year at pH 1–3 in 0.1 and 0.5 M HCl-NaCl solutions do not represent equilibrium data. Coulometric titration of thorium nitrate solutions in the low pH range of 1.5–2.5 leads to the formation of microcrystalline $ThO_2 \cdot xH_2O$(mcr) particles which subsequently agglomerate to a precipitate. The solubility of this solid, in equilibrium with Th^{4+}(aq), is measured from the oversaturation direction. The solubility product is determined to be $\log K'_{sp} = -49.9 \pm 0.4$ in 0.5 M NaCl corresponding to $\log K^\circ_{sp} = -53.2 \pm 0.4$ (converted to $I = 0$ with the SIT). It is close to the thermochemical value for ThO_2(cr) and about 6 orders of magnitude lower than that of X-ray amorphous Th(IV) hydroxide or hydrous oxide. The differences in the solubility products are discussed with regard to the particle size and compared with analogous data for U(IV), Np(IV) and Pu(IV).

Above the threshold of hydrolysis of Th^{4+} at pH > 2.5, the dissolution of microcrystalline $ThO_2 \cdot xH_2O$(mcr) is found to be irreversible. In near-neutral to alkaline solutions, the measured thorium concentrations approach those of amorphous $Th(OH)_4$(am). Similar results are obtained with crystalline ThO_2(cr) in 0.5 M NaCl-NaOH solutions. The solubility is not controlled by the bulk crystalline solid but by amorphous fractions on the surface.

1. Introduction

In a recent study [1] we investigated the solubility of amorphous Th(IV) hydroxide or hydrous oxide. Based on a critical discussion of the literature on the hydrolysis of Th(IV) [1, 2], the solubility product was calculated to be $\log K^\circ_{sp}(Th(OH)_4(am)) = -47.0 \pm 0.8$ at 25 °C. As shown by laser-induced breakdown detection (LIBD) and extended X-ray absorption fine structure (EXAFS) spectroscopy [1], the large differences between the lower and higher solubility data are primarily due to the inclusion of polynuclear and colloidal Th(IV) hydrolysis species. As a continuation of these studies, the present work is aimed at the solubility of the thermodynamically stable crystalline ThO_2(cr).

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Rai *et al.* [3, 4] calculated the solubility product of crystalline thorium dioxide as a function of the temperature from known thermochemical data ($\log K^\circ_{sp}(ThO_2(cr)) = -54.2 \pm 1.3$ at 25 °C). Experimental solubility data in acidic solutions, where the hydrolysis of Th(IV) is negligible (pH < 2.5), have been determined at 18 °C in 0.1 M $NaClO_4$ [5] and at 22 °C in 0.1 M NaCl [4]. There are also studies at elevated temperature [4, 6]. Baes *et al.* [6] measured the solubility after adding crystalline ThO_2(cr) to oversaturated acidic Th(IV) solutions in 1 M $NaClO_4$ at 95 °C. Rai *et al.* [4] observed the transformation of an amorphous precipitate into a crystalline solid at 90 °C and pH 1.5–3 in 0.1 M NaCl. They also observed that solubility data for ThO_2(cr) determined from undersaturation after more than two years at 23 °C decreased after storing the samples for two weeks at 90 °C and readjusting them for 1 day at 23 °C. This effect was explained by an increased crystallinity after heating the samples.

Bundschuh *et al.* [7] combined coulometric pH titration with LIBD to determine the onset of colloid formation as a function the H^+ and Th(IV) concentration in 0.5 M HCl-NaCl. Considering colloids as small solid particles, their formation indicates that the solubility limit is just exceeded during the titration. The titrations in the pH range 1.5–2.5 led to the formation of small ThO_2 colloids with a mean diameter of 16–23 nm [7] and to a solubility product of $\log K^\circ_{sp} = -52.8 \pm 0.3$, close to the thermochemical value of bulk ThO_2(cr). In order to verify the reproducibility of these surprising results, some additional titration-LIBD experiments are performed in the present study.

The solubility behaviour in near-neutral and alkaline solutions implies a certain ambiguity. Experimental solubility studies with crystalline thorium dioxide [5, 8–10] yielded solubility data similar to values for amorphous solids. Moon [5] determined the solubility of ThO_2(cr) prepared at 700 °C in the pH range of 2–13 in 0.1 M $NaClO_4$. With increasing pH the solubility data measured with ThO_2(cr) approach those of $Th(OH)_4$(am) ($\log[Th] = -8.2 \pm 0.3$ at pH > 6). Hubert *et al.* [10] used ThO_2(cr) prepared by heating thorium oxalate, hydroxide and nitrate at 900 and 1600 °C. Although the solutions at pH 1–3 did not attain equilibrium after 4 months, the thorium concentrations measured at pH 5.3–7.2 in 0.1 M $NaClO_4$ reached values of 10^{-11} to 10^{-9} mol/l after only 10 days. These experimental observations led to the conclusion that in near-neutral and alkaline solutions, where $Th(OH)_4$(aq) is the predominant

aqueous species, the bulk crystalline solid is covered with an amorphous, more soluble surface layer [2, 9].

As the reported solubility products of $Th(OH)_4$(am) and ThO_2(cr), and also the corresponding values for the other tetravalent actinides [2], differ by about 6 orders of magnitude, the knowledge of the solubility controlling solid or surface properties is of essential importance for the geochemical modelling of tetravalent actinides in natural aquatic systems. Therefore, the redox-stable Th(IV) is used as a surrogate for other tetravalent actinides to elucidate by additional experiments whether performance assessment calculations can take credit of the low solubilities calculated for crystalline dioxides or whether one has to expect values comparable to those for the amorphous phases.

2. Experimental

2.1 Chemicals and analytical methods

Crystalline, anhydrous ThO_2 (99.99%) was obtained from Alfa Aesar and additionally heated at 750 °C for 8 hours. $Th(NO_3)_4 \cdot 5H_2O$ (p.a.), NaCl (p.a.) and HCl (ultrapure) were purchased from Merck. For further purification, NaCl was recristallized twice. Alkaline solutions were prepared with carbonate-free NaOH (Baker) and stored in an argon glove box. Colloid-free thorium stock solutions for the titration-LIBD experiments were obtained by double filtrations through Amicon 10 kD ultrafilter. All solutions were prepared with ultrapure water from a water purification apparatus (Milli-Q-academic, Millipore). Thorium concentrations $> 3 \times 10^{-7}$ mol/l were determined photometrically by the arsenazo III method [11], lower thorium concentrations were determined by ICP-MS (ELAN 6100, Perkin Elmer). As the background was found to be about 0.001 ppb Th and the 0.5 M NaCl aliquots must be diluted and acidified (4% HNO_3) for ICP-MS analysis, the detection limit for thorium in the original solutions is about 10^{-10} mol/l.

Combination pH electrodes (type ROSS, Orion Co.) calibrated as described previously [1, 7] were used to determine the H^+ concentration in the NaCl solutions. The H^+ concentration in the 0.5 M NaOH-NaCl solutions is calculated from the given NaOH concentration and the ion product of water ($\log K'_w = -13.73$ in 0.5 M NaCl [12]).

XRD patterns were recorded with a Bruker D8 diffractometer equipped with a Bruker Si(Li) solid state detector using steps of 0.01° and counting times of 30 sec per step.

2.2 Solubility experiments

The solubility experiments were performed batchwise in PFA or glass vials (Vol. 10–30 ml). An appropriate amount of crystalline, anhydrous ThO_2(cr) (~ 0.01 mol per liter solution) was added to 0.1 or 0.5 M HCl-NaCl and 0.5 M NaOH-NaCl solutions. The acidic solutions were thermostated at 25 °C, while near-neutral and alkaline solutions were stored at 22 ± 2 °C in an Ar glove box. Aliquots of the samples were measured as a function of equilibration time ranging from a few days to several months. Microcrystalline thorium dioxide $ThO_2 \cdot xH_2O$(mcr) precipitated as a result from the agglomeration of ~ 20 nm particles formed by coulometric titration of thorium nitrate solutions at pH = 1.5–2.5 in 0.5 M NaCl. Solubility data for the in-situ formed precipitates were determined from the oversaturation direction, after equilibration times of up to 160 days. In a few additional experiments, small aliquots of these samples were diluted with 0.5 M NaCl to increase pH.

The thorium concentration in acidic samples was determined after filtration through Amicon 10 kD ultrafilter (pore size ~ 1.4 nm). In near-neutral and alkaline samples, sorption onto the filters lead to thorium concentrations at the background level of the ICP-MS. Therefore, ultracentrifugation for 60 minutes at 90 000 rpm (corresponding to a mean relative centrifugal force of about 5×10^5 g) was used for phase separation.

2.3 Coulometric pH titration combined with LIBD

The equipment used for the coulometric pH titration combined with LIBD is the same as that used by Bundschuh *et al.* [7]. The coulometric titration of 7.6×10^{-3}, 5.0×10^{-5} and 3.2×10^{-5} M thorium nitrate solutions (60 ml) at $I = 0.5$ M (HCl-NaCl), using a current of 0.1–1 mA, is performed in a double-walled titration vessel thermostated at 25 °C and equipped as described in [7]. The pH electrode is freshly calibrated before and re-calibrated at the end of each experiment. A peristaltic pump is used to pump the titration solution through a flow-through cuvette for simultaneous colloid detection by LIBD.

The experimental setup of the LIBD apparatus used in the present study and its calibration with reference colloids has been described previously [13, 14]. 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 and 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 is derived from 3000 laser shots.

3. Results and discussion

The discussion of the solubility of ThO_2(cr) is divided into the results for acidic solutions, from which the thermodynamic solubility product is determined, and into the results for near-neutral and alkaline solutions, where the solubility behaviour deviates from predictions based on equilibrium thermodynamics. The experimental data in acidic solutions are based on different experimental methods: classical solubility experiments from undersaturation, solubility data obtained from oversaturation and by applying the titration-LIBD method. Differences in the experimental solubility products are discussed as a possible effect of particle size.

3.1 Solubility study with ThO_2(cr) in acidic solutions

In a classical solubility study from the undersaturation direction, anhydrous ThO_2(cr) was added to 0.1 M and 0.5 M HCl-NaCl solutions and the H^+ and thorium concentration were measured after 79, 169, and 318 days. The values measured after 318 days show no increase compared to those determined after 169 days (c.f. Table A1, Appendix A). However, Fig. 1 clearly demonstrates that no equilibrium state is reached. The thorium concentration in the range of

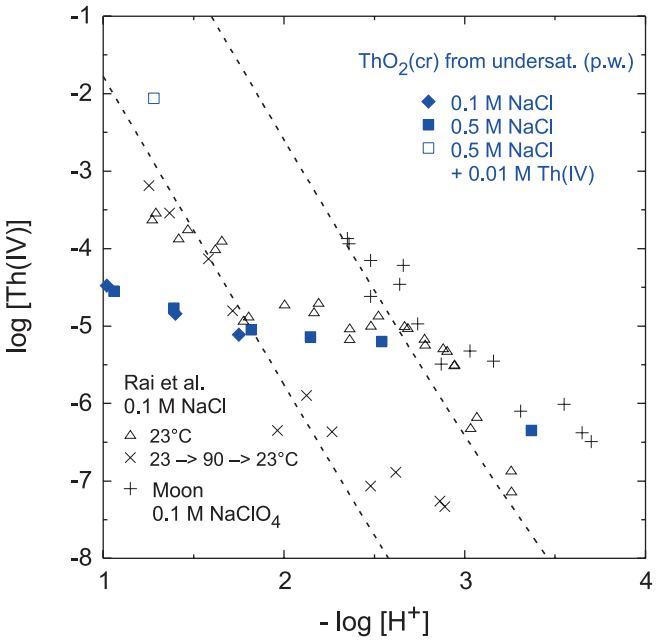


Fig. 1. Solubility data for ThO_2(cr) at 18–25 °C, determined in the present work after 318 days (filled points), by Rai *et al.* [4] and Moon [5]. The calculated dashed lines represent lower and upper limits according to the solubility data of Rai *et al.* [4] in 0.1 M NaCl and the titration-LIBD data of Bundschuh *et al.* [7] in 0.5 M NaCl, respectively.

$-\log[H^+] = 1.0$–2.5 shows only a slight dependence on pH, whereas equilibrium values of log[Th] are expected to decrease with a slope of -4 as indicated by the calculated dashed lines in Fig. 1. The thorium concentration at pH 1 is several orders of magnitude below the calculated equilibrium value.

In sample C10 (open square in Fig. 1) an appreciable amount of solid ThO_2(cr) was added to an initially 0.01 M Th(IV) solution at $-\log[H^+] = 1.23$ (prepared by dissolving $Th(OH)_4$(am) in 0.1 M HCl/0.4 M NaCl). Within 318 days the thorium concentration neither decreased nor increased. Even storing this sample for 14 days at 80 °C did not affect the thorium concentration (c.f. Table A1). The thorium concentration approached from undersaturation (filled squares) at similar acidity, *e.g.* in sample C5 with $-\log[H^+] = 1.35$, is more than two orders of magnitude lower. But in contrast to sample C10, the procedure of storing sample C5 for 14 days at 80 °C and keeping it for 3 further days at room temperature led to a significant increase of the thorium concentration, from 1.7×10^{-5} to 4.7×10^{-5} mol/l.

Our results are comparable to those of Hubert *et al.* [10], who investigated the dissolution kinetics of ThO_2(cr) at 25 °C in 0.1 M $HClO_4$-$NaClO_4$ as a function of the calcination temperature and grain size. Using ThO_2(cr) prepared by heating thorium oxalate, hydroxide and nitrate at 900 and 1600 °C, the thorium concentrations measured after 3 months at pH 1–3 were almost independent of pH. However, depending on the preparation of the solid, the measured value of log[Th] varies from -5.5 to -4.0 and correlates with the surface area of the solid [10]. The slow dissolution kinetics of ThO_2(cr) and its dependence on the preparation and pretreatment of the solid was also observed in 7.5 M HNO_3 [15].

3.2 Coulometric pH titration combined with LIBD

In a recent study Bundschuh *et al.* [7] performed coulometric titrations of 2.8×10^{-2}–8.9×10^{-5} M thorium nitrate solutions in the pH range of 1.5–2.5 up to the formation of thorium colloids. The solubility data determined in this way are defined by the values of log[Th] and $-\log[H^+]$ at the onset of colloid formation when the solubility limit was just exceeded during the titrations. They decrease with a slope of -4. This is consistent with the literature on the hydrolysis of Th(IV), *i.e.*, with negligible hydrolysis at pH < 2.5. The evaluated solubility product of $\log K^\circ_{sp} = -52.8 \pm 0.3$ (data in 0.5 M NaCl converted to $I = 0$ with the SIT and the uncertainty given as standard deviation), is close to the thermochemical value, $\log K^\circ_{sp}(ThO_2(cr)) = -54.2 \pm 1.3$ [3]. Accordingly the experimental results were ascribed to microcrystalline thorium dioxide colloids (mean particles size ~ 16–23 nm) in equilibrium with Th^{4+}(aq) [7].

The same titration-LIBD method and equipment is used in the present study to verify the reproducibility of these surprising results of Bundschuh *et al.* [7]. Three additional titration experiments are performed at thorium concentrations of 7.6×10^{-3}, 5.0×10^{-5} and 3.2×10^{-5} mol/l. The results are shown in Fig. 2. The solubility data derived from the onset of colloid formation (Table A3) confirm the findings of Bundschuh *et al.* [7]. The mean value of the solubility product calculated from the data determined in both the previous and the present work is found to be $\log K'_{sp} = -49.6 \pm 0.5 (2\sigma)$ in 0.5 M NaCl. Using the specific ion interaction theory (SIT) and the ion interaction coefficients $\varepsilon_{Th\text{-}Cl} = (0.25 \pm 0.03)$ mol/kg and $\varepsilon_{Na\text{-}OH} = (0.04 \pm 0.01)$ mol/kg [12] the solubility product at $I = 0$ is calculated to be

$$\log K^\circ_{sp} = -52.9 \pm 0.5 \,.$$

EXAFS measurements [16] have shown that the thorium dioxide colloids formed in this acidic pH range and the precipitates formed by subsequent agglomeration (see below) are chemically different from the long-time stable colloids

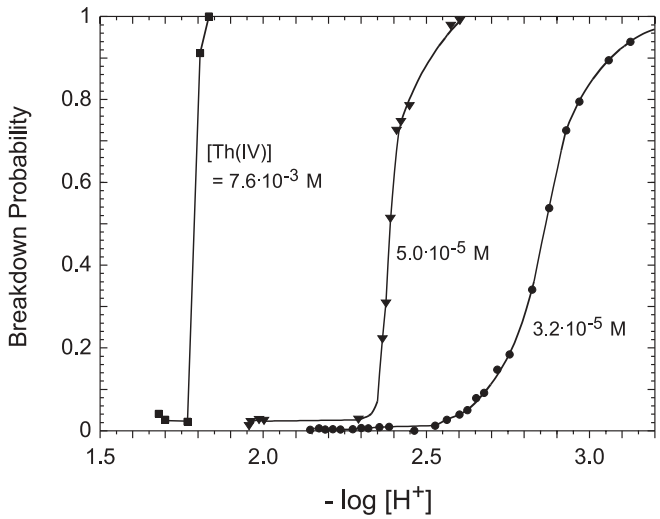


Fig. 2. Titration-LIBD experiments at 25 °C: breakdown probability as a function of the H^+ concentration during the coulometric titration of 7.6×10^{-3}, 5.0×10^{-5} and 3.2×10^{-5} M thorium nitrate solutions in 0.5 M NaCl. The onset of colloid formation is indicated by the steep increase of the breakdown probability.

formed at pH > 3 by chemical condensation reactions and polynucleation of hydrolysed Th(IV) species.

3.3 Precipitation of microcrystalline $ThO_2 \cdot xH_2O$(mcr) and solubility determined from oversaturation

In some of the colloidal ThO_2 suspensions produced in the titration-LIBD experiments of Bundschuh *et al.* [7], the formation of small amounts of a visible precipitate has been noticed after 1–4 weeks. (We cannot exclude that the precipitation occurred earlier, because after having finished the titration experiments, the clear colloid containing solutions were stored and not further observed.) The thorium concentrations measured after 100 and 160 days in the solutions above the precipitates are summarized in Table A4. The titration experiment performed in the present study at $[Th] = 7.6 \times 10^{-3}$ mol/l (LIBD-10) led to spontaneous precipitation a few hours after the solubility limit at $-\log[H^+] = 1.8$ was exceeded. The solubility measured after 19 and 36 days is comparable to the values obtained in the previous experiments. These solubility data determined from the oversaturation direction decrease with a slope of -4 (Fig. 3), indicating that the experimental data actually refer to the equilibrium between $ThO_2 \cdot xH_2O$(mcr) and Th^{4+}(aq). They are somewhat lower than the data obtained by the titration-LIBD method and lead to a solubility product of $\log K'_{sp} = -49.9 \pm 0.4$ in 0.5 M NaCl (uncertainty given as 2σ) corresponding to

$$\log K^\circ_{sp} = -53.2 \pm 0.4 \,.$$

The precipitates obtained at pH 1.5–2.5 consist of a fine white powder, which settles to the bottom of the solution, quite different from the gelatinous thorium hydroxide precipitates formed in neutral and alkaline solutions. The small amounts of solid (about 1 mg) formed in the experiments LIBD-3 and LIBD-4 were separated from the solutions and investigated by XAFS (Rothe *et al.* [16]). The Th-L3 EXAFS spectrum of $ThO_2 \cdot xH_2O$(mcr) was found to be clearly different from that of an amorphous Th(IV) precipitate prepared at pH 10 and dried at room temperature, but also from that of anhydrous ThO_2(cr). The first Th−O neighbour appears more ordered compared to the amorphous compound, but less ordered than ThO_2(cr); details are given in [16]. The somewhat larger amount of solid precipitate obtained in the titration-LIBD experiment at $[Th] = 7.6 \times 10^{-3}$ mol/l was used for characterisation by X-ray diffraction. An amount of about 20 mg was centrifuged and washed with water to remove the background electrolyte NaCl. The aqueous suspension was pipetted on an oriented quartz slide and dried at room temperature. The microcrystalline thorium dioxide structure is confirmed by weak broad bands at diffraction angles where the XRD pattern of the bulk ThO_2(cr) shows sharp peaks (Fig. 4).

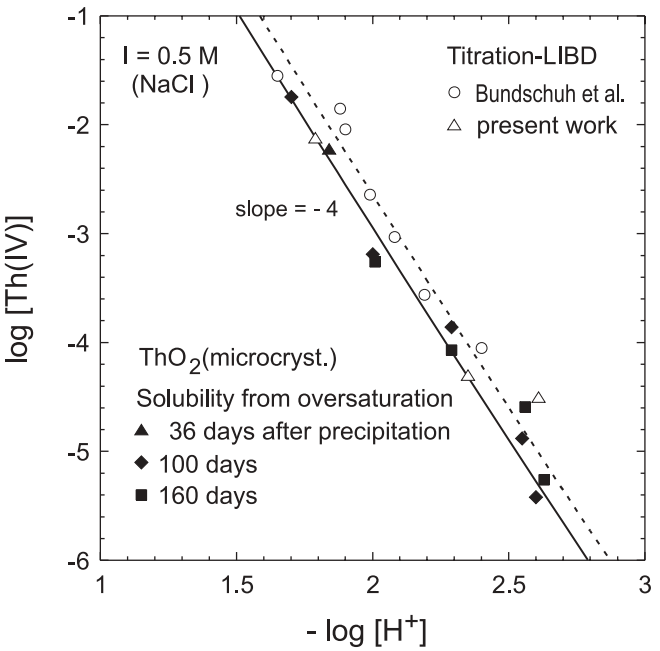


Fig. 3. Solubility of microcrystalline $ThO_2 \cdot xH_2O$(mcr) in 0.5 M NaCl at 25 °C. Open symbols refer to data determined by titration-LIBD, filled symbols to data determined in equilibrium with the solid precipitates.

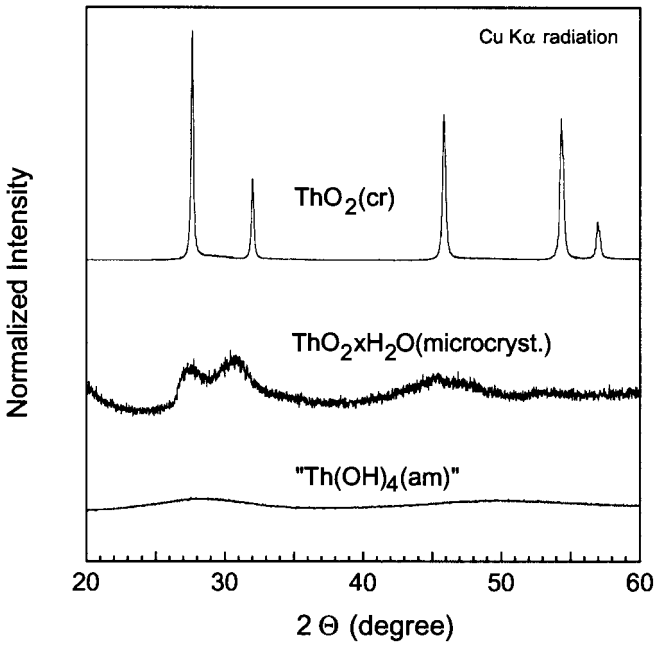


Fig. 4. X-ray diffraction patterns of anhydrous ThO_2(cr) and microcrystalline $ThO_2 \cdot xH_2O$(mcr) precipitated at $-\log[H^+] = 1.8$. The pattern for amorphous "$Th(OH)_4$(am)" used in [1] (prepared at pH 10 and dried at room temperature) is shown for comparison.

3.4 Solubility product and particle size effect

Rai *et al.* [3] used critically evaluated thermochemical data $\Delta_f H^\circ_m$ (ThO_2(cr)), S°_m (ThO_2(cr)), S°_m (Th(cr)), $\Delta_f G^\circ_m$ (Th^{4+}(aq)) from [17–19], and S°_m (O_2(g)), $\Delta_f G^\circ_m$ (OH^-(aq)), $\Delta_f G^\circ_m$ (H_2O(l)) from [20] to calculate the solubility product of crystalline thorium dioxide at 25 °C:

$$\log K^\circ_{sp}\,(ThO_2(cr)) = -54.2 \pm 1.3 \,.$$

Slightly different values of $\log K^\circ_{sp}(ThO_2(cr)) = -54.13$ and -54.32 ± 1.13 are obtained using the data selected by Wagman *et al.* [20] ($\Delta_f G^\circ_m(ThO_2(cr)) = -1168.77$ kJ/mol and $\Delta_f G^\circ_m(Th^{4+}(aq)) = -705.1$ kJ/mol, given without uncertainty limits) or if CODATA [21] ($\Delta_f G^\circ_m(ThO_2(cr)) =$

$-(1169.2 \pm 3.5)$ kJ/mol) is used in combination with $\Delta_f G^\circ_m(Th^{4+}(aq)) = -(704.6 \pm 5.4)$ kJ/mol [19].

The solubility products derived from the titration-LIBD experiments and from the solubility data measured after precipitation of microcrystalline $ThO_2 \cdot xH_2O$(mcr), $\log K^\circ_{sp} = -52.9 \pm 0.5$ and -53.2 ± 0.4, respectively, may be considered as upper limits for ThO_2(cr). The solubility data determined by Rai *et al.* [4] at 23 °C after an equilibration time of more than two years and those after additional heating for 14 days at 90 °C and re-adjusting the samples for one day at 23 °C (Fig. 1) represent a lower limit of $\log K'_{sp} \geq -52.9$ in 0.1 M NaCl and $\log K^\circ_{sp} \geq -55.0$, if converted to $I = 0$ with the SIT (c.f. remarks on ionic strength corrections, Appendix B). These upper and lower limits are in accord with the thermochemical value of $\log K^\circ_{sp}(ThO_2(cr)) = -54.2 \pm 1.3$ [3].

According to the equations of Schindler [22] the solubility product of oxide and hydroxide particles < 300 nm depends noticably on the particle size, because of the difference in Gibbs energy when either small solid particles or large crystals with negligible molar surface are suspended in water. For approximately spherical ThO_2 particles with diameter d, the difference between the solubility product of small ThO_2 particles and $\log K^\circ_{sp}(S \to 0) = -54.2$ for a large crystal of ThO_2(cr) is given by [7]:

$$\log K^\circ_{sp} \text{ (particle size } d) = -54.2 + 23/d \text{ (nm)} . \qquad (1)$$

From the titration-LIBD experiments at pH = 1.5–2.5 the solubility product of small thorium dioxide colloids is determined to be $\log K^\circ_{sp} = -52.9 \pm 0.5$. Application of Schindler's equation to estimate the particle size from the experimental solubility product yields $d = 13$–29 nm, which is in excellent agreement with the value of 16–23 nm, based on optical particle size determination by LIBD [7]. The solubility product after agglomeration and precipitation of microcrystalline $ThO_2 \cdot xH_2O$(mcr), $\log K^\circ_{sp} = -53.2 \pm 0.4$, corresponds to a calculated particle size of 16–58 nm, while the experimental particle size was found to be about 50 nm (optical particle size determination by LIBD) up to > 1 μm as observed by photon correlation spectroscopy (PCS). Obviously, the crystallite size is the decisive parameter in Eq. (1) and not the larger size after agglomeration of smaller particles.

Transmission electron microscopy (TEM) investigations on X-ray amorphous Th(IV) precipitates dried at room temperature indicate the inclusion of small ThO_2(cr) crystallites in the range of 3–8 nm [23]. Applying Eq. (1) to the solubility product of amorphous precipitates, $\log K^\circ_{sp}$ ("$Th(OH)_4$(am)") $= -47.0 \pm 0.8$ [1, 2], indeed leads to a calculated particle size of 3–4 nm. Accordingly all experimental solubility data for Th(IV) oxides/hydroxides could be ascribed to ThO_2(cr) as the only solid phase with the differences in $\log K^\circ_{sp}$ arising from the particle size. However, such small particles have a relatively large hydrated surface with OH-groups, which probably determines the chemical properties. The hitherto available experimental solubility data exhibit a gap of more than 5 orders of magnitude between the upper limit for the solubility product of ThO_2(cr), *i.e.*, $\log K^\circ_{sp} = -53.2 \pm 0.4$ determined for microcrystalline thorium dioxide, and the lower limit of $\log K^\circ_{sp} = -47.8$ for X-ray amorphous solids. This large gap requires to distinguish between the thermodynamic data for crystalline ThO_2(cr) and amorphous $ThO_n(OH)_{4-2n} \cdot xH_2O$(am), which may be called "$Th(OH)_4$(am)", "$ThO_2 \cdot xH_2O$(am)" or "ThO_2(am, hyd)".

Table 1. Solubility products $\log K^\circ_{sp}$ for $An(OH)_4$(am) and AnO_2(cr) at 25 °C.

An	$An(OH)_4$(am)	AnO_2(cr)
Th	-47.0 ± 0.8 [a]	-54.2 ± 1.3 [c]
	-47.8 ± 0.3 [b]	-53.2 ± 0.4 [e]
U	-54.5 ± 1.0 [a]	-60.6 ± 0.5 [c]
		-60.9 ± 0.4 [d]
Np	-56.7 ± 0.5 [a]	-63.7 ± 1.8 [c]
		-65.8 ± 1.1 [d]
Pu	-58.5 ± 0.7 [a]	-64.1 ± 0.7 [c]
		-64.0 ± 0.5 [d]
Am		-65.4 ± 1.7 [d]

a: Review of Neck and Kim [2];
b: Exp. value excluding colloidal contributions [1];
c: Calculated by Rai *et al.* [3] using thermochemical data from [17–20];
d: Calculated using thermochemical data from the NEA-TDB [12, 25, 26];
e: Present work, exp. value for microcrystalline $ThO_2 \cdot xH_2O$(mcr).

Similar differences as for the solubility products of ThO_2(cr) and ThO_2(am, hyd) are known for the other tetravalent actinides (Table 1). The variation of the solubility products for the amorphous An(IV) oxides, $\log K^\circ_{sp}$ (AnO_2(am, hyd)) in the series Th, U, Np, Pu follows

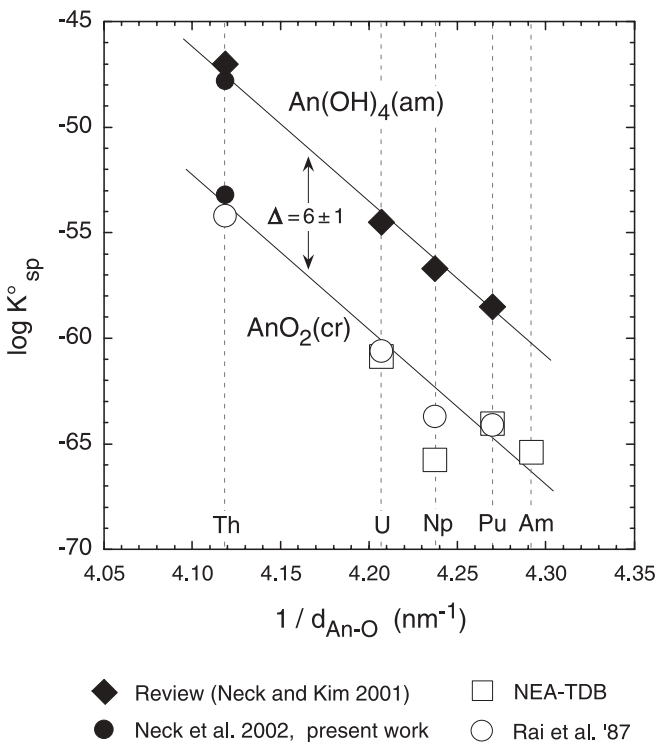


Fig. 5. Solubility products of $An(OH)_4$(am) and AnO_2(cr) as a function of the distance d_{An-O} (sum of crystal radii of An^{4+} and O^{2-} in the fluorite structure [27]). Filled symbols represent $\log K^\circ_{sp}$ values derived from experimental solubility studies (review of Neck and Kim [2], exp. values determined in [1] and present work), open symbols represent values calculated values from thermochemical data (Rai *et al.* [3] and NEA-TDB [12, 25, 26]).

a smooth trend as a function of the crystal ionic radii (Fig. 5). The same trend is observed for the solubility products of the crystalline dioxides $\log K^\circ_{sp}$ (AnO_2(cr)) calculated from thermochemical data for Th, U, Np, Pu and Am. A noticeable deviation is observed for the value of $\log K^\circ_{sp}(NpO_2(cr)) = -65.75 \pm 1.07$ calculated with $\Delta_f G^\circ_m(NpO_2(cr)) = -(1021.7 \pm 2.5)$ kJ/mol and $\Delta_f G^\circ_m(Np^{4+}(aq)) = -(491.8 \pm 5.6)$ kJ/mol from the NEA-TDB [26]. The latter value differs from $\Delta_f G^\circ_m(Np^{4+}(aq)) = -(502.9 \pm 7.5)$ kJ/mol [19] used by Rai *et al.* [3].

3.5 Solubility of ThO_2(cr) and $ThO_2 \cdot xH_2O$(mcr) in near-neutral and alkaline solutions

In the previous section the thermochemical value for the solubility product of ThO_2(cr) was found to be consistent with experimental solubilities in acidic solutions. According to the known hydrolysis constants of Th(IV), the complex $Th(OH)_4$(aq) is the predominant specie in in near-neutral and alkaline solution. By combining $\log K^\circ_{sp}(ThO_2(cr)) = -54.2 \pm 1.3$ and $\log \beta^\circ_4 = 38.5 \pm 1.0$ [1, 2], the equilibrium thorium concentration is calculated to be $\log[Th(OH)_4(aq)] = -15.7 \pm 1.6$, which is far below the detection limit of ICP-MS. Contrary to the predicted solubility, the present experimental data for crystalline ThO_2(cr), determined from the undersaturation direction in 0.5 M NaOH-NaCl solutions ($-\log[H^+] = 11.0$–13.5), is clearly above the analytical detection limit given by the background level ($\leq 10^{-10}$ mol/l). The thorium concentrations measured after 71 and 122 days are summarized in Table A2. They show no dependence on pH and the mean value (given with an uncertainty of $\pm 2\sigma$):

$$\log[Th] = -9.3 \pm 0.8$$

is close to the solubility of $Th(OH)_4$(am), $\log K^\circ_{s,4} = -8.5 \pm 0.6$. Fig. 6 shows a comparison of the present experimental data with the theoretical solubility curve for ThO_2(cr) and the experimental and calculated solubility of amorphous Th(IV) precipitates.

In a few additional experiments, the solubility study with microcrystalline thorium dioxide precipitated in the pH range of 1.5–2.5 was extended to pH 3.0–6.6 (c.f. Table A4).

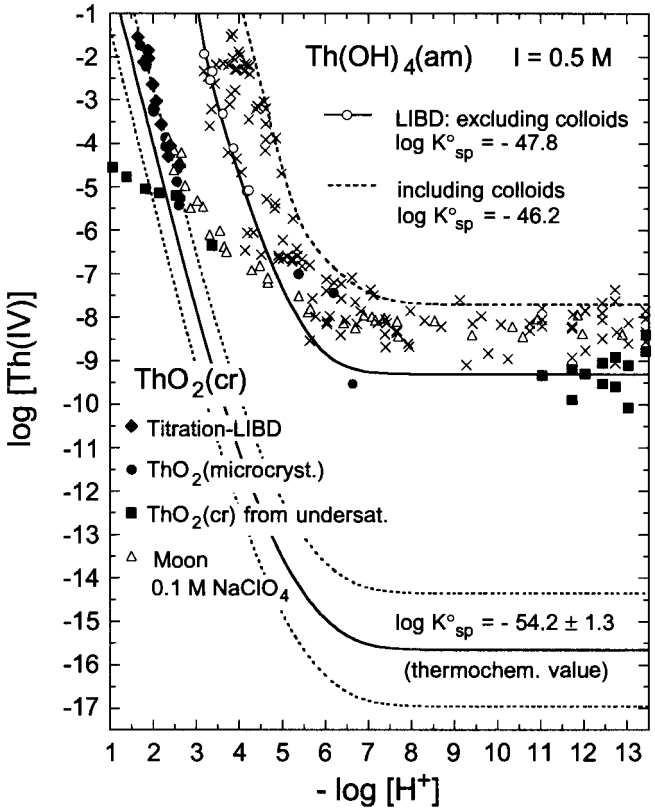


Fig. 6. Experimental and calculated solubility of ThO_2(cr) and $Th(OH)_4$(am) at $I = 0.5$ M and 25 °C. The solubility data for ThO_2(cr) are determined in the present study (filled symbols) from under- and oversaturation and by titration-LIBD in 0.5 M NaCl and by Moon [5] in 0.1 M $NaClO_4$ at 18 °C (open triangles). The solubility data for amorphous precipitates (×) are taken from [1, 5, 28–30] (all data at $I = 0.5$–0.6 M and 18–25 °C). The lines are calculated for $I = 0.5$ M with the hydrolysis constants selected in [1], $\log K^\circ_{sp}(ThO_2(cr)) = -54.2 \pm 1.3$ [3] and $\log K^\circ_{sp}(Th(OH)_4(am)) = -47.0 \pm 0.8$ [1, 2].

For this purpose, small aliquots of the acidic samples were diluted with 0.5 M NaCl and stored for 242 days in an argon box. Similar as in the study of Moon [5] (open triangles in Fig. 6), the measured thorium concentrations (filled circles in Fig. 6) do not follow the calculated solubility curve but approach the values for amorphous precipitates. Solid-liquid equilibrium data for microcrystalline $ThO_2 \cdot xH_2O$(mcr) are

Table 2. Solubility data for ThO_2(cr) in near-neutral and alkaline solutions.

Authors	Solid	Medium	Temperature	log[Th]
Hubert *et al.* [10]	ThO_2(cr) prepared at 900 and 1600 °C	0.1 M $NaClO_4$, pH 5.3–7.2	room temp.	
	a) from hydroxide			-10.3 ± 0.2 [a]
	b) from nitrate			-9.6 ± 0.4 [a]
	c) from oxalate			-10.6 ± 0.6 [a]
Fourest *et al.* [9]	ThO_2(cr) pellets sintered at 1450 °C	synthetic granite waters, pH 6.6–9.2	25 °C	-10.3 ± 0.7
			90 °C	-8.3 ± 0.4
Moon [5]	ThO_2(cr) prepared at 700 °C from oxalate	0.1 M $NaClO_4$, pH 6–13	18 °C	-8.2 ± 0.3
Wierczinski *et al.* [8]	ThO_2 (microcryst.)	cement pore water, pH 12.5 and 13.1	22 °C	-9.6 ± 0.4
			55 °C	-10.0 ± 0.1
present work	ThO_2(cr) from Alfa Aesar	0.1 M NaCl-NaOH, pH 11–13.5	22 °C	-9.3 ± 0.8

a: Measured after only 10 days, while the data of [8] and [9] were measured after 25 and 31 days, respectively, and those of the present work after 71 and 112 days.

obtained only at pH < 2.5, where the Th^{4+} aquo ion is the predominant aqueous specie, suggesting that there is no reversible equilibrium between ThO_2(cr) and Th(IV) hydrolysis species. This conclusion is supported by further experimental observations. Precipitation of microcrystalline thorium dioxide particles does not occur in solutions above pH 3, where the aqueous speciation of Th(IV) is dominated by hydroxide complexes. For instance, 10^{-2}–10^{-4} M thorium nitrate solutions at pH ≈ 3 (as used for the titration experiments in [1]) are more than 5 orders of magnitude oversaturated with regard to the solubility of ThO_2(cr), but they are stable towards colloid formation or precipitation. On the contrary, in an aliquot containing small amounts of microcrystalline thorium dioxide, the solid particles re-dissolved when the acidity was decreased from $-\log[H^+] = 2.5$ to 3.0 by dilution with 0.5 M NaCl (c.f. Table A4). The final thorium concentration of $\log[Th] = -4.24$ considerably exceeds the calculated solubility of ThO_2(cr) but remains below that of "$Th(OH)_4$(am)".

The present solubility values in near-neutral and alkaline solutions are consistent with those of other authors [5, 8–10], who also measured thorium concentrations much higher than calculated for crystalline ThO_2(cr) (c.f. Table 2).

4. Conclusions

Solubility experiments with well-crystallized ThO_2(cr) are related to the problem of very slow dissolution kinetics [10, 15]. The present experiments did not reach equilibrium after a period of one year. Dissolution experiments from undersaturation direction give only a lower limit for the solubility of ThO_2(cr) in acidic solutions. However, equilibrium between ThO_2(cr) and Th^{4+}(aq) can be reached from oversaturation as shown in the present study at 25 °C and in literature studies at 90–95 °C [4, 6].

The experimental solubility data determined for ThO_2(cr) in near-neutral and alkaline solutions exceed the thermodynamic calculation by many orders of magnitude and approach those of the amorphous solid. (Similar observations in solubility studies with UO_2(cr) [31, 32] have been discussed in [2].) These experimental findings may simply be caused by the dissolution of small amounts of amorphous parts present in the crystalline solid, which remain dissolved as hydrolysed species $An_x(OH)_y^{4x-y}$(aq). This can be explained as a result of irreversible dissolution reactions.

At low pH, the dissolution of AnO_2(cr) may lead to an equilibrium with An^{4+}(aq). However, at pH values above the the onset of hydrolysis, the sorption or precipitation of monomeric or polynuclear hydroxide complexes $An_x(OH)_y^{4x-y}$(aq) on the surface of crystalline AnO_2(cr) will result in an amorphous surface layer. As a consequence, the slow dissolution of AnO_2(cr) followed by the very fast hydrolysis reactions of the An^{4+} ions might result in an irreversible dissolution reaction until the concentration of the hydroxide complexes $An_x(OH)_y^{4x-y}$(aq) reach the solubility limit of "$An(OH)_4$(am)":

$$AnO_2(cr) \rightarrow An_x(OH)_y^{4x-y}(aq) \Leftrightarrow An(OH)_4(am)\,. \qquad (2)$$

Of course there is a thermodynamic driving force for the transformation of the "$An(OH)_4$(am)" on the surface into the more stable AnO_2(cr), a process which is enhanced by increased temperature, but solid transformations are usually slow compared to hydrolysis and solid-liquid interface reactions.

The conclusions derived from the solubility of thorium dioxide are considered to hold as well for the other tetravalent actinides. However, concerning the irreversible dissolution reaction $AnO_2(cr) \rightarrow An_x(OH)_y^{4x-y}(aq)$ it is to note that the threshold for the hydrolysis of the Th^{4+} ion is in the pH range of 2.5–3 [33, 34]. It is about one pH-unit lower for U^{4+} [12] and already at pH 0–1 for Np^{4+} and Pu^{4+} [35–37]. Both the experimental observations and the possible explanation in terms of irreversible dissolution of AnO_2(cr) lead to the conclusion that conservative performance assessment calculations on the long-time behaviour of tetravalent actinides in natural systems must not take credit of the extremely low solubilities resulting from thermodynamic calculations for the crystalline An(IV) dioxides.

Appendix A: Tables of experimental solubility data

Table A1. Solubility data for ThO_2(cr) in acidic solutions at $I = 0.1$ M and 0.5 M (HCl/NaCl) and 25 °C.

Sample	time (days)	$-\log[H^+]$	$\log[Th]$
$I = 0.1$ M (HCl/NaCl)			
C1	79	1.00	−4.57
	169	1.01	−4.52
	318	1.02	−4.48
C2	79	1.32	−4.89
	169	1.39	−4.83
	318	1.40	−4.84
C3	79	1.71	−5.13
	169	1.74	−5.09
	318	1.75	−5.11
$I = 0.5$ M (HCl/NaCl)			
C4	79	1.03	−4.60
	169	1.05	−4.56
	318	1.06	−4.55
C5	79	1.35	−4.73
	169	1.39	−4.74
	318	1.39	−4.77
	335[a]	1.40	−4.33
C6	79	1.79	−5.14
	169	1.84	−5.06
	318	1.82	−5.05
C7	79	2.12	−5.22
	169	2.15	−5.13
	318	2.15	−5.14
C8	79	2.54	−5.29
	169	2.54	−5.18
	318	2.54	−5.20
C9	79	3.39	−6.72
	169	3.36	−6.86
	318	3.37	−6.35
C10[b]	0	1.23	−2.04
	79	1.24	−2.06
	169	1.26	−2.04
	318	1.28	−2.05
	335[a]	1.28	−2.06

a: 318 days at RT, 14 days at 80 °C and again 3 days at RT;
b: $Th(OH)_4$(am) dissolved in 0.1 M HCl/0.4 M NaCl + addition of ThO_2(cr).

Table A2. Solubility data for ThO_2(cr) in alkaline solutions at $I = 0.5$ M (NaCl/NaOH) and (22 ± 1) °C.

Sample	[NaOH] (mol l^{-1})	$-\log[H^+]^a$	time (days)	log[Th]
C11	0.002	11.03	71	−9.33
			112	−9.32
C12	0.01	11.73	71	−9.89
			112	−9.19
C13	0.02	12.03	71	−9.29
			112	−9.29
C14	0.05	12.43	71	−9.52
			112	−9.04
C15	0.1	12.73	71	−8.90
			112	−9.59
C16	0.2	13.03	71	−10.06
			112	−9.09
C17	0.5	13.43	71	−8.77
			112	−8.39

a: The H^+ concentration is calculated from the given OH^- concentration in the solutions of the composition x M NaOH/$(0.5 - x)$ M NaCl and $\log K'_w = -13.73$ in 0.5 M NaCl.

Table A3. The H^+ concentration for the incitement of $ThO_2 \cdot xH_2O$(mcr) colloid formation during the titration of thorium nitrate solutions in 0.5 M HCl/NaCl at 25 °C.

	log [Th]	$-\log[H^+]_{coll}$
LIBD-1	-2.04 ± 0.02	1.90 ± 0.02
LIBD-2	-2.64 ± 0.02	1.99 ± 0.02
LIBD-3	-3.03 ± 0.02	2.08 ± 0.02
LIBD-4	-3.56 ± 0.02	2.19 ± 0.03
LIBD-5	-4.05 ± 0.02	2.40 ± 0.03
LIBD-6	-1.55 ± 0.02	1.65 ± 0.02
LIBD-7	-1.85 ± 0.02	1.88 ± 0.02
LIBD-8[a]	-4.30 ± 0.02	2.35 ± 0.04
LIBD-9[a]	-4.50 ± 0.02	2.60 ± 0.04
LIBD-10[a]	-2.12 ± 0.02	1.79 ± 0.02

a: Present work, all other data are from [7].

Table A4. Solubility data for microcrystalline $ThO_2 \cdot xH_2O$(mcr) at $I = 0.5$ M (HCl/NaCl) and 25 °C.

Solubility data measured after noticing visible precipitates in the colloid containing solutions[a]

Sample	time (days)	$-\log[H^+]$	log [Th]
LIBD-3	100	2.00	−3.19
	160	2.01	−3.26
LIBD-4	100	2.29	−3.86
	160	2.29	−4.07
LIBD-5	100	2.55	−4.88
	160	2.56	−4.59
LIBD-6	100	1.70	−1.74
	160	1.72	(−1.60)[b]
LIBD-8	100	2.60	−5.42
	160	2.63	−5.26
LIBD-10	1	1.83	−2.20
	19	1.82	−2.26
	36	1.84	−2.22

Table A4. Continued

Solubility data measured after diluting solid phase containing aliquots of the samples LIBD-5 and LIBD-8 with 0.5 M NaCl

Sample	time (days)	$-\log[H^+]$	log [Th]
LIBD-5a	242	3.01	(−4.24)[b]
LIBD-8a	242	3.03	−4.65
LIBD-5b	242	5.37	−7.00
LIBD-5c	242	6.18	−7.43
LIBD-8b	242	6.63	−9.52

a: Precipitation could not occur in the solutions of experiments LIBD-1, LIBD-2 and LIBD-7, because they were acidified after having finished the titration;
b: No visible solid present.

Appendix B: Remarks on ionic strength corrections

Throughout the present paper the SIT and the ion interaction coefficients of the NEA-TDB [12] are used for the calculation of activity coefficients γ_i, *i.e.*, to convert conditional solubility products $K'_{sp} = [Th^{4+}][OH^-]^4$ in a given medium into K°_{sp} at $I = 0$:

$$K^\circ_{sp} = [Th^{4+}][OH^-]^4 \gamma_{Th^{4+}} (\gamma_{OH^-})^4 . \quad \text{(B1)}$$

It is to note that considerably lower $\log K^\circ_{sp}$ values are calculated from the experimental solubility products at $I = 0.1$ or 0.5 M, if the set of Pitzer parameters proposed by Rai *et al.* [4, 29] (Table B1) is used to calculate the activity coefficients. For instance the values of $\log \left\{\gamma_{Th^{4+}} (\gamma_{OH^-})^4\right\} = -4.05$ in 0.10 m NaCl and −5.13 in 0.506 m NaCl calculated with the Pitzer parameters from [29] are about two orders of magnitude lower than those calculated with the SIT: −2.14 and −3.30, respectively. The binary pa-

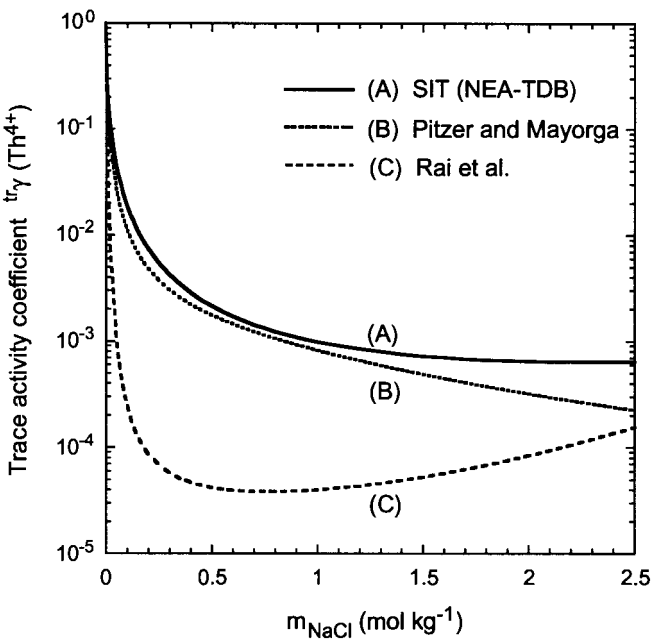


Fig. B1. Trace activity coefficients of Th^{4+} in NaCl solution at 25 °C, calculated with the SIT using ion interaction coefficients from the NEA-TDB [12] and with different sets of the Pitzer parameters reported by Pitzer and Mayorga [39] and Rai *et al.* [29].

Table B1. Ion interaction Pitzer parameters for Th^{4+} at 25 °C.

Binary interaction parameters Th^{4+}-Cl^-					
$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{Φ}	data source	Reference
1.014	13.33		−0.1034	*a*	Pitzer, Mayorga [39]
1.092	13.7 ($\alpha_1 = 2$)	−160 ($\alpha_2 = 12$)	−0.112	*b*	Roy *et al*. [38], Rai *et al*. [29]
Ternary interaction parameters					
$\theta_{Th^{4+}/H^+} = 0.60$		$\Psi_{Th^{4+}/H^+/Cl^-} = 0.37$		*b*	Roy *et al*. [38]
$\theta_{Th^{4+}/Na^+} = 0.42$		$\Psi_{Th^{4+}/Na^+/Cl^-} = 0.21$		*c*	Rai *et al*. [29]
$\theta_{Th^{4+}/Mg^{2+}} = 0.60$		$\Psi_{Th^{4+}/Mg^{2+}/Cl^-} = 0.21$		*c*	Rai *et al*. [29]

a: Isopiestic data of Robinson [40];
b: HCl activities in aqueous HCl-$ThCl_4$ mixtures [38];
c: Solubility data for $Th(OH)_4$(am) in NaCl and $MgCl_2$ solutions of pH 3–5, in combination with the binary parameters of Roy *et al*. [38].

rameters used by Rai *et al*. [4, 29] lead to $\gamma_{Th^{4+}}$ values which considerably deviate from the Debye–Hückel law at low ionic strength (Fig. B1). They were derived by Roy *et al*. [38], who performed emf (a_{HCl}) measurements in aqueous HCl-$ThCl_4$ mixtures of various composition at 25 °C, including data at low H^+ concentrations (pH ≥ 3) where hydrolysis of the Th^{4+} is not negligible as assumed in [38]. The ternary parameters reported in [29] for the systems Na-Th-Cl and Mg-Th-Cl were derived from the solubility of amorphous Th(IV) hydrous oxide at pH 3.5–5.5 in NaCl and $MgCl_2$ solutions, where Th(IV) is strongly hydrolysed. The binary parameters of Pitzer and Mayorga [39] were calculated from Robinson's isopiestic data for $ThCl_4$ [40]. These data were also used by Ciavatta [24] to derive the SIT coefficient $\varepsilon_{Th\text{-}Cl} = (0.25 \pm 0.03)$ kg/mol adopted in the NEA-TDB [12]. The proposed sets of interaction coefficients include an unknown uncertainty, because they are derived under experimental conditions where thorium is not a trace component. Therefore it is not clear whether they properly describe the Th^{4+} trace activity coefficients needed in Eq. (B1).

Acknowledgment. The present work was partially supported by ANDRA (contract No. 008790) and by the European commission, in the frame of the ACTAF program within the 5th R&D framework program (contract No. FIKW-CT-2000-00035).

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