

Solubility of $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ and the formation of ternary Th(IV) hydroxide-carbonate complexes in NaHCO_3 - Na_2CO_3 solutions containing 0–4 M NaCl

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Thermodynamic modelling / Ionic strength / SIT*

Summary. The solubility of $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ is studied at $I = 0.1$ – 4.0 M (NaHCO_3 - Na_2CO_3 -NaCl) and 22°C . Several sets of closed system experiments are performed at total carbonate concentrations of $C_{\text{tot}} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 0.02$ and 0.1 M in the range $\text{pH}_c = 8$ – 11 . In our recent study at $I = 0.5$ M, the simultaneous evaluation of solubility data at widely varied pH_c and carbonate concentrations has shown that $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$, $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$ and $\text{Th}(\text{OH})_4(\text{CO}_3)_2^{2-}$ are the most important ternary complexes. The present results at $I = 0.1$ – 4.0 M are used to describe the ionic strength dependence of the equilibrium constants $\log K_{s,1yz}$ (for the reactions $\text{Th}(\text{OH})_4(\text{am}) + z\text{CO}_3^{2-} \rightleftharpoons \text{Th}(\text{OH})_y(\text{CO}_3)_z^{4-y-2z} + (4-y)\text{OH}^-$) with the SIT. EXAFS measurements in 0.1 and 1.0 M carbonate solutions support the calculated speciation. They show clearly different spectra for the predominant species $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ and $\text{Th}(\text{CO}_3)_5^{6-}$, respectively.

1. Introduction

In carbonate containing solutions the $\text{Th}^{4+}(\text{aq})$ ion can form complexes with high coordination numbers and because of competing hydrolysis reactions about 20 different binary and ternary complexes $\text{Th}(\text{OH})_y(\text{CO}_3)_z^{4-y-2z} = (1yz)$ are theoretically possible [1]. Their charge can vary from $+2$ to -6 and hence the effect of ionic strength can be extremely different. Therefore, it is difficult to identify unequivocally the complexes formed at different pH, carbonate concentration and ionic strength. A comprehensive investigation of the predominant species in system Th(IV)-OH- CO_3 requires the variation of the OH^- and CO_3^{2-} concentrations over wide ranges, preferentially at constant ionic strength. This was done recently [1] at $I = 0.5$ M (NaHCO_3 - Na_2CO_3 -NaOH-NaCl). The solubility of $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ at $\text{pH}_c = 4.5$ – 13.5 , either under CO_2 partial pressures of 1.0 and 0.1 bar (open system) or at total carbonate concentrations of $C_{\text{tot}} = 0.1$, 0.04 and 0.015 M (closed sys-

tem) [1] was discussed together with similar results in 0.5 M NaHCO_3 - Na_2CO_3 -NaClO₄ [2] and data in NaHCO_3 and Na_2CO_3 -NaOH solutions of variable ionic strength [3, 4]. The simultaneous evaluation of the different sets of solubility data has shown that only a few complexes contribute to the Th concentration in these studies. $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$, $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$ and $\text{Th}(\text{OH})_4(\text{CO}_3)_2^{2-}$ were found to be the predominant complexes with minor contributions coming from $\text{Th}(\text{OH})_2(\text{CO}_3)(\text{aq})$ and $\text{Th}(\text{OH})_3(\text{CO}_3)^-$. Other ternary and binary carbonate complexes have no effect in these studies. The pentacarbonate complex $\text{Th}(\text{CO}_3)_5^{6-}$ is formed at carbonate concentrations above 0.1 M and $\text{pH}_c < 11$ as confirmed by EXAFS studies [4], but at higher pH_c values mixed hydroxide-carbonate complexes are formed, even at CO_3^{2-} concentrations of 1 – 2 M [1]. In order to test the model evaluated in [1] EXAFS measurements are also performed in the present paper.

In our recent study [1] the equilibrium constants at $I = 0.5$ M were converted to $I = 0$ with the specific ion interaction theory (SIT) [5–7]. The unknown ion interaction coefficients $\varepsilon(\text{Na}^+, \text{Th}(\text{OH})_y(\text{CO}_3)_z^{4-y-2z})$ were estimated according to known values for actinide hydroxide and carbonate complexes of the same charge: 0.1 , 0.05 , 0 , -0.05 , -0.1 , -0.15 , -0.2 , -0.25 and -0.3 kg/mol for Th(IV) complexes of charge 2 , 1 , 0 , -1 , -2 , -3 , -4 , -5 and -6 , respectively. Model calculations with the evaluated equilibrium constants and these estimated SIT coefficients were also consistent with solubility data in Na_2CO_3 -NaOH mixtures of higher ionic strength. The concentrations calculated for the complexes $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ and $\text{Th}(\text{OH})_4(\text{CO}_3)_2^{2-}$ reproduce well the experimental data in 1 M Na_2CO_3 containing 0.01 – 0.5 M NaOH and in 0.1 M NaOH containing 0.001 – 2 M Na_2CO_3 [1, 3, 4]. However, a systematic study of the ionic strength dependence is necessary to test the reliability of these ion interaction coefficients, in particular with regard to their application to analogous complexes of U(IV), Np(IV) and Pu(IV). This is the objective of the present work.

2. Experimental

$\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (p.a.), NaCl (p.a.), NaHCO_3 (p.a.), Na_2CO_3 (p.a.) and HCl (ultrapure) were obtained from Merck,

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carbonate-free NaOH solutions from Baker. All solutions were prepared with ultrapure water purified with a Milli-Q-academic (Millipore) apparatus. Thorium concentrations were determined by ICP-MS (ELAN 6100, Perkin Elmer) as described recently [1]. The determination of $\text{pH}_c = -\log[\text{H}^+]$ with combination pH electrodes (type ROSS, Orion Co.) calibrated against H^+ concentrations in NaCl solutions of the corresponding ionic strength is described in detail in [8, 9]. The concentrations $\log[\text{OH}^-]$, $\log[\text{HCO}_3^-]$ and $\log[\text{CO}_3^{2-}]$ are calculated from $\log[\text{H}^+]$ and $C_{\text{tot}} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ (closed systems) by using NEA-TDB auxiliary data for the dissociation constants of water and carbonic acid in NaCl solution: $\log K_w^\circ = -14.00$, $\log K_2^\circ = -(10.33 \pm 0.02)$, water activities and SIT coefficients of $\varepsilon(\text{H}^+, \text{Cl}^-) = (0.12 \pm 0.01)$, $\varepsilon(\text{Na}^+, \text{OH}^-) = (0.04 \pm 0.01)$, $\varepsilon(\text{Na}^+, \text{HCO}_3^-) = (0.00 \pm 0.02)$, and $\varepsilon(\text{Na}^+, \text{CO}_3^{2-}) = -(0.08 \pm 0.03)$ kg/mol [7].

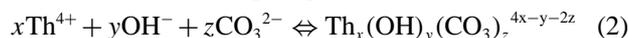
Solubility experiments were performed with amorphous $\text{Th}(\text{OH})_4(\text{am})$ or $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ with $x \sim 2.4\text{--}2.5$ [2, 10] prepared by slow titration of a thorium nitrate solution with carbonate-free NaOH up to pH 10. The precipitate was washed with water and stored as aqueous suspension. The samples for the solubility studies were prepared in polyethylene vials (20–50 mL) and an appropriate amount of precipitate was added (*ca.* 0.003 mol Th per liter solution). The sealed vials were stored in an Ar glove box at $(22 \pm 2)^\circ\text{C}$. Four sets of experiments were performed at a total carbonate concentration of $C_{\text{tot}} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 0.02$ M and strictly constant ionic strengths of $I = 0.1, 0.5, 2.0$ and 4.0 M ($\text{NaHCO}_3\text{--Na}_2\text{CO}_3\text{--NaCl}$) with H^+ concentrations in the range $\text{pH}_c = 8.4\text{--}10.6$. An additional set of experiments was performed in 0.1 M $\text{NaHCO}_3\text{--Na}_2\text{CO}_3$ solutions ($C_{\text{tot}} = 0.1$ M). The Th concentration was determined after ultrafiltration using Filtron polyether sulfone membrane filters (Microsept TM 10 kD, pore size *ca.* 1.5 nm) to remove colloidal Th(IV) species. A few samples at low Th concentrations were measured in parallel after ultracentrifugation for 60 minutes at 90 000 rpm (*ca.* 5×10^5 g) and consistent results were obtained. The constant H^+ and Th concentrations after 8 and 14 days indicated that solid-liquid equilibria were reached.

Th L3 XAFS measurements with a 1.5×10^{-3} M Th solution in 1.0 M $\text{Na}_2\text{CO}_3\text{--}0.1$ M NaHCO_3 and a 1.2×10^{-3} M Th sample taken from the solubility study at $C_{\text{tot}} = 0.1$ M and $\text{pH}_c = 9.14$ in 0.5 M $\text{NaHCO}_3\text{--Na}_2\text{CO}_3\text{--NaCl}$ are performed at the Angströmquelle Karlsruhe (ANKA), Forschungszentrum Karlsruhe, Germany at the ANKA-XAS endstation. A Si(311) ($2d = 3.274 \text{ \AA}$) crystal pair is used in the fixed-exit DCM. The beam spot size is $(8 \times 1) \text{ mm}^2$. Higher harmonic radiation in the incident beam is suppressed by detuning the parallel alignment of the DCM crystals to 60% of photon flux peak intensity. Spectra are recorded in fluorescence mode by registering the normalized Th $L_{\alpha 1,2}$ fluorescence radiation as a function of the incident photon energy using a 5-pixel energy dispersive solid state Ge detector (Canberra LEGe) and an Ar filled ionization chamber for I_0 . Extended X-ray absorption fine structure (EXAFS) data analysis is based on standard least square fit techniques using the UWXAFS [11, 12] program package. Metrical parameters, coordination number (N), bond distance (R), Debye–Waller factors (σ^2) and relative shifts in

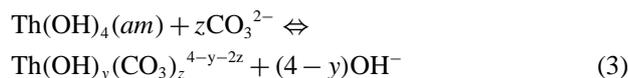
ionization energy (ΔE_0) are obtained using the *feffit* code (v2.98) and FEFF8.2 [13, 14] calculations.

3. Results and discussion

The solubility of amorphous Th(IV) hydroxide or hydrous oxide in carbonate solution is given by the equilibrium constants for the dissolution of the solid (solubility product $\log K_{\text{sp}}$) and the formation constants $\log \beta_{xyz}$ of the complexes $\text{Th}_x(\text{OH})_y(\text{CO}_3)_z^{4x-y-2z}$:



The solubility studies in carbonate solution [1–4] clearly show that the formation of a solubility limiting Th(IV) carbonate solid or carbonate containing surface layer can be ruled out [1]. In addition, the solubilities obtained with a fresh precipitate did not differ noticeably from those for dried $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ [1]. As the present solubility data were determined after 10 kD ultrafiltration, contributions from colloids or large polynuclear Th(IV) hydroxide-carbonate species are excluded. In this case data can be well described considering only mononuclear species [1]. The evaluation of solubility data ($[\text{Th}]_{\text{tot}} = \sum [\text{Th}(\text{OH})_y(\text{CO}_3)_z^{4-y-2z}]$) yields conditional solubility constants $\log K'_{s,1yz} = (\log K'_{\text{sp}} + \log \beta'_{1yz})$ for the reactions



Our recent solubility study at $I = 0.5$ M ($\text{NaHCO}_3\text{--Na}_2\text{CO}_3\text{--NaOH--NaCl}$), *i.e.*, two sets of open system experiments under $p_{\text{CO}_2(\text{g})} = 1.0$ and 0.1 bar at $\text{pH}_c = 4.5\text{--}7.5$ and three sets of closed system experiments at $C_{\text{tot}} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 0.1, 0.04$ and 0.015 M and $\text{pH}_c = 8.5\text{--}13.5$ [1], was evaluated together with a similar study of Östhols *et al.* [2] at $I = 0.5$ M ($\text{NaHCO}_3\text{--Na}_2\text{CO}_3\text{--NaClO}_4$) and solubility data measured by Rai *et al.* [3, 4] in NaHCO_3 and $\text{Na}_2\text{CO}_3\text{--NaOH}$ solutions of variable ionic strength. In order to identify the complexes formed in these solubility experiments, in a first step, an upper limit was calculated for each possible complex (1yz) by increasing $\log K'_{s,1yz}$ until the calculated species concentration line exceeds one of the different data sets at any pH value. In a second step, a least square fit program was used considering simultaneously all experimental data at $I = 0.5$ M. A model including only the unequivocally identified complexes was extended step by step by adding successively other possible complexes (1yz) and repeating the optimization procedure. This evaluation procedure clearly showed that $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ and $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$ are the predominant complexes in the open system studies (with minor contributions from $\text{Th}(\text{OH})_2(\text{CO}_3)(\text{aq})$ and $\text{Th}(\text{OH})_3(\text{CO}_3)^-$) and that $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ is the predominant complex in the closed system experiments (with certain contributions of $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$ at $\text{pH}_c < 9$ and $C_{\text{tot}} < 0.02$ M and of $\text{Th}(\text{OH})_4(\text{CO}_3)_2^{2-}$ at $\text{pH} > 11$ and $C_{\text{tot}} = 0.1$ M). The sensitivity analysis gave no significant values for other ternary complexes (1yz) and binary carbonate complexes ($10z$). At

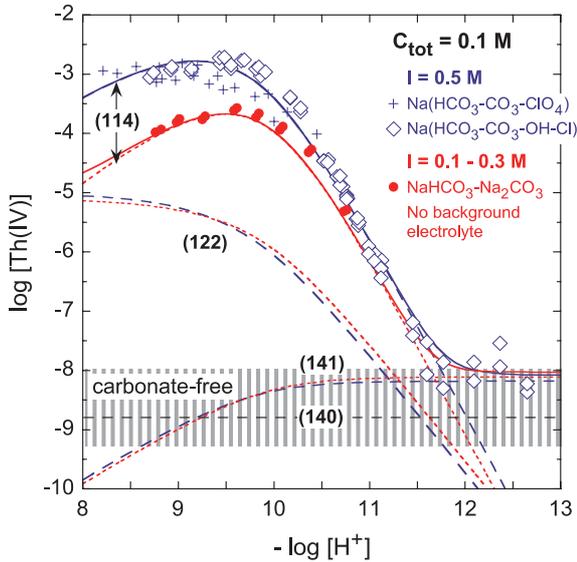


Fig. 1. Solubility of $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ at $C_{\text{tot}} = 0.1 \text{ M}$: Comparison of experimental data at $I = 0.5 \text{ M}$ ($\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-NaOH-NaCl}$ [1] or $\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-NaClO}_4$ [2]) and at $I = 0.1\text{-}0.3 \text{ M}$ ($0.1 \text{ M NaHCO}_3\text{-Na}_2\text{CO}_3$ without additional background electrolyte). The concentrations of the complexes (114), (122) and (141), dashed lines for $I = 0.5 \text{ M}$, dotted lines for $I = 0.1\text{-}0.3 \text{ M}$, are calculated with the equilibrium constants and SIT coefficients reported in [1] (c.f., Table 1).

$C_{\text{tot}} = 0.1 \text{ M}$ where the solubility maximum reaches values above 10^{-3} M (Fig. 1), the Th speciation is not caused by the pentacarbonate complex $\text{Th}(\text{CO}_3)_5^{6-}$ as assumed by Östholms *et al.* [2] but by the complex $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$. Neither the limiting carbonate complex $\text{Th}(\text{CO}_3)_5^{6-}$ nor any other complex or combination of other complexes can reproduce the data at pH_c 8–11. The formation of $\text{Th}(\text{CO}_3)_5^{6-}$ requires carbonate concentrations significantly above 0.1 M . This result of the model calculations (c.f., discussion in [1]) is additionally confirmed by EXAFS measurements performed in the present work (c.f., Sect. 3.3.).

In the NEA-TDB [6, 7], our previous [1] and present studies the ionic strength dependence of the solubility constants ($\log K'_{s,1yz}$ in a given electrolyte medium and $\log K^\circ_{s,1yz}$ at $I = 0$):

$$K'_{s,1yz} = \frac{[\text{Th}(\text{OH})_y(\text{CO}_3)_z]^{4-y-2z} [\text{OH}^-]^{4-y}}{[\text{CO}_3^{2-}]^z} = \frac{K_{s,1yz}^\circ (\gamma_{\text{CO}_3^{2-}})^z}{\gamma_{(1yz)} (\gamma_{\text{OH}^-})^{4-y}} \quad (4)$$

is described with the specific ion interaction theory (SIT) [5–7]. Accordingly, activity coefficients γ_i are given by Eq. (5) and $\log K^\circ_{s,1yz}$ for negatively charged complexes (1yz) is related to the conditional solubility constants $\log K'_{s,1yz}$ by Eq. (6):

$$\log \gamma_i = -z_i^2 D + \sum \varepsilon_{ij} m_j \quad (5)$$

$$\log K^\circ_{s,1yz} = \log K'_{s,1yz} - \Delta z^2 D + \Delta \varepsilon m_{\text{Na}^+} \quad (6)$$

where z_i is the charge of ion i , ε_{ij} is the interaction parameter for ion i and an oppositely charged ion j , m_j (mol/kg H_2O) is the molal concentration of ion j , D is the Debye-Hückel term at 25°C : $D = 0.509 \sqrt{I}/(1 + B\hat{a}\sqrt{I})$, with $B\hat{a} = 1.5$ and I (mol/kg H_2O) is the molal ionic

Table 1. Ion-interaction (SIT) coefficients and equilibrium constants or upper limits for the formation of $\text{Th}(\text{OH})_y(\text{CO}_3)_z^{4-y-2z} = (1yz)$ at $I = 0$ (25°C). Data from Altmaier *et al.* [1] except otherwise stated.

Complex/charge	$\varepsilon((1yz), \text{Cl}^-)$ or $\varepsilon(\text{Na}^+, (1yz))^a$	$\log K^\circ_{s,1yz}$	$\log \beta^\circ_{1yz}^b$
Hydroxide complexes			
(100) 4+	0.25 ± 0.03^c	-47.8 ± 0.3^c	0
(110) 3+	0.20 ± 0.1^d		11.8 ± 0.2^d
(120) 2+	0.10 ± 0.1^d		21.4 ± 0.2^d
(130) 1+	0.05 ± 0.1^d		30.6 ± 1.0^d
(140) 0	0	-8.8 ± 0.6^d	39.0 ± 0.5^d
Carbonate complexes			
(101) 2+	0.20	< -35.8	< 12.0
(102) 0	0	< -26.8	< 21.0
(103) 2-	-0.10	< -20.6	< 27.2
(104) 4-	-0.20	< -17.6	< 30.2
(105) 6-	-0.30 ± 0.15^c	< -16.6	< 31.2
		-18.4^e	29.4
Ternary hydroxide-carbonate complexes			
(111) 1+	0.05	< -26.2	< 21.6
(112) 1-	-0.05	< -18.4	< 29.4
(113) 3-	-0.15	< -14.0	< 33.8
(114) 5-	-0.25	-12.0 ± 0.2	35.8 ± 0.3
(121) 0	0	-17.1 ± 0.3	30.7 ± 0.4
(122) 2-	-0.10	-10.8 ± 0.2	37.0 ± 0.4
(123) 4-	-0.20	< -9.9	< 37.9
(124) 6-	-0.30	≤ -13.3	≤ 34.5
(131) 1-	-0.05	-9.3 ± 0.5	38.5 ± 0.6
(132) 3-	-0.15	< -8.4	< 39.4
(133) 5-	-0.25	< -10.9	< 36.9
(141) 2-	-0.10	-7.2 ± 0.3	40.6 ± 0.5
(142) 4-	-0.20	< -9.1	< 38.7

a: Uncertainties of the estimated SIT coefficients are expected to be smaller than ± 0.2 [1];

b: Formation constants $\log \beta^\circ_{1yz}$ are related to $\log K^\circ_{sp} = -(47.8 \pm 0.3)$ [1, 10]. Uncertainties are given as 2σ ;

c: NEA-TDB [7], $\varepsilon(\text{Na}^+, \text{Th}(\text{CO}_3)_5^{6-}) = \varepsilon(\text{Na}^+, \text{U}(\text{CO}_3)_5^{6-}) = -(0.30 \pm 0.15) \text{ kg/mol}$ [7];

d: Neck *et al.* [10]; e: Felmy *et al.* [4].

strength. The ion interaction coefficients $\varepsilon(\text{Na}^+, \text{OH}^-) = (0.04 \pm 0.01)$ and $\varepsilon(\text{Na}^+, \text{CO}_3^{2-}) = -(0.08 \pm 0.03) \text{ kg/mol}$ are given in the NEA-TDB [7] and the unknown values $\varepsilon(\text{Na}^+, \text{Th}(\text{OH})_y(\text{CO}_3)_z^{4-y-2z})$ can be estimated according to known values derived for actinide hydroxide and carbonate complexes of analogous charge from experimental data in NaCl solution [1, 6, 7].

The equilibrium constants and upper limits of $\log K^\circ_{s,1yz}$ and the SIT coefficients from our previous study [1] are summarized in Table 1. The formation constants $\log \beta^\circ_{1yz}$ refer to the solubility product of $\log K^\circ_{sp} = -(47.8 \pm 0.3)$ [10] appropriate for $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in carbonate solution [1]. These results are now extended by a systematic study of the ionic strength dependence of the Th(IV) solubility and the equilibrium constants $\log K_{s,1yz}$ for the predominant ternary complexes.

3.1 Closed system solubility experiments

**at $C_{\text{tot}} = 0.1 \text{ M}$: Comparison of data
at $I = 0.5 \text{ M}$ ($\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-NaCl}$)
and at $I = 0.1\text{-}0.3 \text{ M}$ ($\text{NaHCO}_3\text{-Na}_2\text{CO}_3$)**

For comparison with previous solubility data at $C_{\text{tot}} = 0.1 \text{ M}$ and $I = 0.5 \text{ M}$ ($\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-NaCl}$ [1] or $\text{NaHCO}_3\text{-}$

$\text{Na}_2\text{CO}_3\text{-NaClO}_4$ [2]), an additional set of experiments at $C_{\text{tot}} = 0.1 \text{ M}$ was performed in the same pH_c range, *i.e.*, at the same OH^- and CO_3^{2-} concentrations, but with the slight difference that no background electrolyte was added to the $0.1 \text{ M NaHCO}_3\text{-Na}_2\text{CO}_3$ solutions. Accordingly, ionic strength varies with pH_c : $I = [\text{NaHCO}_3] + 3[\text{Na}_2\text{CO}_3] = 0.1\text{--}0.3 \text{ M}$, *e.g.*, $I = 0.2 \text{ M}$ at $\text{pH}_c = \text{p}K'_2 = 9.80$ in $0.5 \text{ M NaHCO}_3/0.5 \text{ M Na}_2\text{CO}_3$. The results are shown in Fig. 1. In order to illustrate the effect of 0.1 M carbonate, the scattered Th concentrations measured in neutral and alkaline carbonate-free solutions after ultrafiltration or ultracentrifugation [10] are shown as hatched area. The high solubility at $\text{pH}_c = 8\text{--}10$, followed by a steep decrease at $\text{pH}_c > 10$, is well described by the complex $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$.

The Th(IV) equilibrium concentrations in $0.1 \text{ M NaHCO}_3\text{-Na}_2\text{CO}_3$ differ considerably (up to an order of magnitude at $\text{pH}_c < 10$) from those determined in our previous study [1] and by Östhols *et al.* [2] where the ionic strength was kept constant at $I = 0.5 \text{ M}$ by adding NaCl or NaClO_4 background electrolyte. However, this difference is perfectly consistent with the ionic strength dependence of $\log K_{s,114}$ predicted by the equilibrium constants and SIT coefficients in Table 1. The concentration lines in Fig. 1 are calculated with these parameters taking into account the variation of ionic strength and hence of $\text{p}K'_2$ and $\log K'_{s,1yz}$. Contrary to the highly charged complex $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ ($\Delta z^2 = 12$ for $\log K_{s,114}$) the calculated concentrations of $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$ and $\text{Th}(\text{OH})_4(\text{CO}_3)_2^{2-}$ are not significant under these conditions and according to their charge, the variation of $\log K_{s,122}$ ($\Delta z^2 = -2$) and $\log K_{s,141}$ ($\Delta z^2 = 0$) from $I = 0.1\text{--}0.3$ to 0.5 is rather small.

3.2 Closed system solubility experiments at $C_{\text{tot}} = 0.02 \text{ M}$ and $I = 0.1\text{--}4.0 \text{ M}$

The strong increase of the $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ concentration with increasing ionic strength is studied at $C_{\text{tot}} = [\text{HCO}_3^-] +$

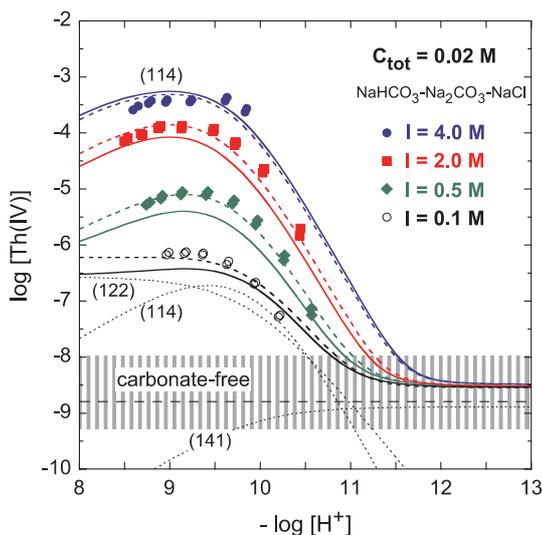


Fig. 2. Solubility of $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ at $C_{\text{tot}} = 0.02 \text{ M}$ and $I = 0.1, 0.5, 2.0$ and 4.0 M ($\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-NaCl}$). Experimental data in comparison with model predictions (solid lines and dotted speciation lines for $I = 0.1 \text{ M}$) based on the equilibrium constants and SIT coefficients from [1]. The dashed lines represent best fits to the data at different ionic strengths.

Table 2. Conditional equilibrium constants $\log K'_{s,114}$ and $\log K'_{s,122}$ (molal scale) fitted to the experimental solubility data at the different ionic strengths.

I (mol/kgH ₂ O)	$\log K'_{s,114}$	$\log K'_{s,122}$
0.10	-10.7 ± 0.3	-10.7 ± 0.2
0.20 ^a	-10.3 ± 0.1^a	
0.51 ^b	-10.0 ± 0.2^b	$-11.2 \pm 0.1^{b,c}$
0.51	-9.7 ± 0.1	
2.09	-9.4 ± 0.2	
4.37	-9.8 ± 0.3	

a: Value at $\text{pH}_c = \text{p}K_2 = 9.80$ from the set at $C_{\text{tot}} = 0.1 \text{ M}$ ($0.1 \text{ M NaHCO}_3\text{-Na}_2\text{CO}_3$);

b: From our previous study at $I = 0.5 \text{ M}$ [1];

c: Derived from open system experiments under $p\text{CO}_2(\text{g}) = 1.0$ and 0.1 bar [1].

$[\text{CO}_3^{2-}] = 0.02 \text{ M}$ and strictly constant ionic strengths of $I = 0.1, 0.5, 2.0$ and 4.0 M ($\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-NaCl}$). Fig. 2 shows the experimental solubility data in the range $\text{pH}_c = 8.4\text{--}10.6$ which agree well with the model predictions (solid lines). According to the $\log K_{s,1yz}^\circ$ values and upper limits in Table 1, the measured Th concentrations are almost exclusively caused by the complex (114). No other complex has a significant contribution under these conditions, except for the solubility at the lowest ionic strength. At $I = 0.1 \text{ M}$ and $\text{pH}_c < 9.5$ the complex (122) becomes predominant (*c.f.*, dotted speciation lines in Fig. 2). The four sets of solubility data at $C_{\text{tot}} = 0.02 \text{ M}$ are fitted best (dashed curves in Fig. 2) with the conditional equilibrium constants $\log K'_{s,114}$ at $I = 0.1, 0.5, 2.0$ and 4.0 M and $\log K'_{s,122}$ at $I = 0.1 \text{ M}$ given in Table 2. Similar as in the case of the solubility curve at $C_{\text{tot}} = 0.1 \text{ M}$ and $I = 0.5 \text{ M}$ [1] one has to take into account that the high $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ concentrations at $C_{\text{tot}} = 0.02 \text{ M}$ and $I = 4.0 \text{ M}$ leads to a slight decrease of the free carbonate concentration ($[\text{CO}_3^{2-}] = C_{\text{tot}} - [\text{HCO}_3^-] - 4[\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}]$).

Applying the linear SIT regression ($\log K'_{s,1yz} - \Delta z^2 D = \log K_{s,1yz}^\circ - \Delta \varepsilon m_{\text{Na}^+}$) to the $\log K'_{s,114}$ values fitted to the data at different ionic strengths (Fig. 3) yields

$$\log K_{s,114}^\circ = -(11.9 \pm 0.2)$$

$$\Delta \varepsilon = (0.22 \pm 0.05) \text{ kg/mol}$$

and

$$\varepsilon(\text{Na}^+, \text{Th}(\text{OH})(\text{CO}_3)_4^{5-}) = -(0.22 \pm 0.13) \text{ kg/mol}.$$

These values are consistent with $\log K_{s,114}^\circ = -(12.0 \pm 0.2)$ derived in our study at $I = 0.5 \text{ M}$ with an estimated SIT coefficient of $\varepsilon(\text{Na}^+, \text{Th}(\text{OH})(\text{CO}_3)_4^{5-}) = -0.25 \text{ kg/mol}$ [1].

Since increasing ionic strength strongly enhances the formation of the highly charged complex $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$, the equilibrium constant $\log K'_{s,122}$ for the complex $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$ can only be determined at low ionic strength. The present result of $\log K'_{s,122} = -(10.7 \pm 0.2)$ at $I = 0.1 \text{ M}$, corresponding to $\log K_{s,122}^\circ = -(10.5 \pm 0.2)$ at $I = 0$, is reasonably consistent with the value of $\log K_{s,122}^\circ = -(10.8 \pm 0.2)$ [1] derived recently from open system experiments under $p\text{CO}_2(\text{g}) = 1.0$ and 0.1 bar at $I = 0.5 \text{ M}$, where

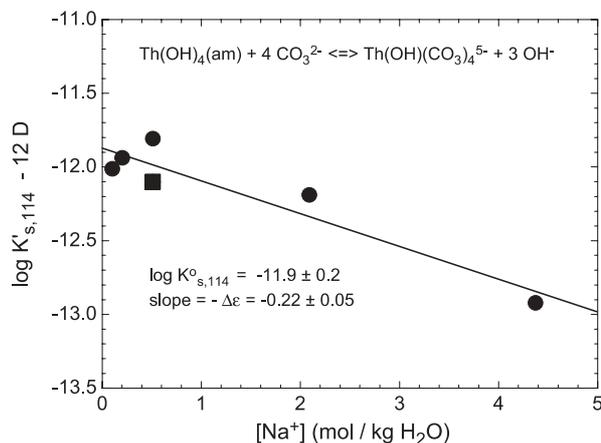


Fig. 3. Application of the linear SIT regression to the conditional equilibrium constants $\log K'_{s,114}$ (best fit values from Table 2) at 0.1–4.0 M (square at $I = 0.5$ M from [1]).

$\log K'_{s,122} = -(11.2 \pm 0.1)$ was converted to $I = 0$ using an estimate of $\varepsilon(\text{Na}^+, \text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}) = -0.10$ kg/mol. With regard to the possible uncertainties, only two $\log K'_{s,122}$ values at $I = 0.1$ and 0.5 M do not allow to calculate reliable SIT coefficients by linear regression.

The complex $\text{Th}(\text{OH})_4(\text{CO}_3)^{2-}$ becomes significant at $\text{pH} > 12$ and $C_{\text{tot}} > 0.02$ M. The equilibrium constant $\log K^o_{s,141} = -(7.2 \pm 0.3)$ is practically independent of ionic strength ($\Delta z^2 = 0$ and $\Delta \varepsilon \approx 0$). The validity of these parameters up to high ionic strength has already been demonstrated recently [1]. They reproduce well the increase of experimental solubility data in 0.1 M NaOH containing 0.01 – 0.5 M Na_2CO_3 and in 1 M Na_2CO_3 containing NaOH concentrations above 0.5 M [1, 3], where $\text{Th}(\text{OH})_4(\text{CO}_3)^{2-}$ is the major species.

3.3 Speciation by EXAFS

EXAFS studies of thorium in carbonate solutions were reported by Felmy *et al.* [4] who recorded spectra in 0.1 – 1.0 M NaHCO_3 and 1.0 M Na_2CO_3 – 0.1 M NaOH solutions. (The composition given for the sample Th 15 in 1.0 M Na_2CO_3 [4] is probably a misprint, because the addition of 0.1 M NaOH decreases the solubility to values below 10^{-5} M [1, 3, 4] which is much too low for XAFS analysis). Consistent spectra at carbonate concentrations above 0.2 M indicate the presence of the limiting carbonate complex $\text{Th}(\text{CO}_3)_5^{6-}$ [4].

In order to demonstrate that $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ is the predominant complex at $C_{\text{tot}} = 0.1$ M (not $\text{Th}(\text{CO}_3)_5^{6-}$ as assumed in [2, 4]), a saturated sample from the solubility study in 0.5 M NaHCO_3 – Na_2CO_3 – NaCl ($C_{\text{tot}} = 0.1$ M, $\text{pH}_c = 9.14$, $[\text{Th}] = 1.2 \times 10^{-3}$ M) was analysed by EXAFS and compared with a 1.5×10^{-3} M Th solution in 1.0 M Na_2CO_3 – 0.1 M NaHCO_3 ($\text{pH}_c = 10.5$) where $\text{Th}(\text{CO}_3)_5^{6-}$ is the predominant complex. The spectrum of this $\text{Th}(\text{CO}_3)_5^{6-}$ reference solution (solid line in Fig. 4) is identical to those reported by Felmy *et al.* [4] in 0.5 – 1.0 M NaHCO_3 and 1.0 M Na_2CO_3 . The spectrum exhibits a distance of $R(\text{Th}-\text{O}) = (2.50 \pm 0.02)$ Å and a distinct scattering along the $\text{Th}-\text{C}-\text{O}_{\text{dis}}$ path. The spectrum of the sample taken from the solubility study at $C_{\text{tot}} = 0.1$ M and $\text{pH}_c = 9.14$

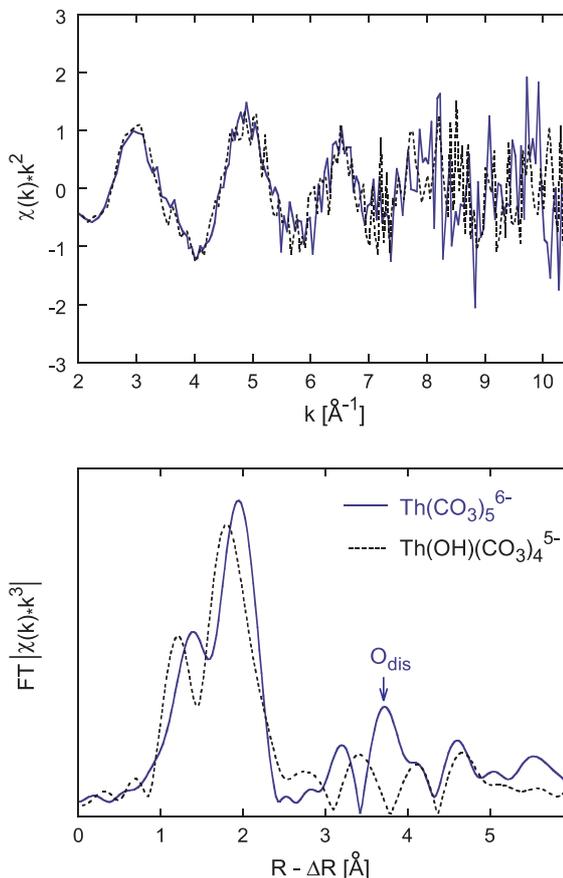


Fig. 4. Th L3 EXAFS of Th(IV) in carbonate solution: k^3 -weighted $\chi(k)$ -functions (above) and corresponding Fourier transform magnitudes (below). The solid line refers to $\text{Th}(\text{CO}_3)_5^{6-}$ in 1.0 M Na_2CO_3 /0.1 M NaHCO_3 ($\text{pH}_c = 10.5$), the dotted line to $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ in a sample from the solubility study at $C_{\text{tot}} = 0.1$ M and $\text{pH}_c = 9.14$ in 0.5 M NaHCO_3 – Na_2CO_3 – NaCl .

in 0.5 M NaHCO_3 – Na_2CO_3 – NaCl (dotted line in Fig. 4) is clearly different. This observation is consistent with the evaluation of the comprehensive sets of solubility data at $I = 0.5$ M [1] which unequivocally showed that $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ is the predominant species in the second EXAFS sample. The Th–O shell shows a bond distance decrease of about 0.03 Å ($R(\text{Th}-\text{O}) = (2.47 \pm 0.03)$ Å) compared to that of $\text{Th}(\text{CO}_3)_5^{6-}$. The calculated coordination numbers N are in the expected range of (10 ± 2) . The limited k -range available and the data quality does not allow to model any distances beyond the first oxygen coordination shell and to confirm the exact number of CO_3^{2-} ligands. However, this is generally difficult as can be seen from the detailed discussion of Felmy *et al.* [4], where the calculated numbers of C and distal O atoms have uncertainties of ± 1 .

Conclusions

The present investigation of the ionic strength dependence of the Th(IV) solubility in carbonate solution and the formation constants of the most important hydroxide-carbonate complexes, $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$, $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$ and $\text{Th}(\text{OH})_4(\text{CO}_3)^{2-}$, confirms the equilibrium constants evaluated in our recent comprehensive study at $I = 0.5$ M [1] and the SIT coefficients estimated from charge type analogs.

The evaluated data set is appropriate to model the solubility of $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ over wide ranges of pH, carbonate concentration and ionic strength. In addition, the results in the system $\text{Th}(\text{IV})\text{-OH-CO}_3$ are considered as qualitative analogs for other tetravalent actinides, helpful to sort out discrepancies pointed out in the NEA-TDB reviews [6, 7] of the speciation models and equilibrium constants proposed in the literature for $\text{U}(\text{IV})$, $\text{Np}(\text{IV})$ and $\text{Pu}(\text{IV})$ in carbonate solution.

References

1. Altmaier, M., Neck, V., Müller, R., Fanghänel, Th.: Solubility of $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in carbonate solution and the formation of ternary $\text{Th}(\text{IV})$ hydroxide-carbonate complexes. *Radiochim. Acta* **93**, 83 (2005).
2. Östholms, E., Bruno, J., Grenthe, I.: On the influence of carbonate on mineral dissolution: III. The solubility of microcrystalline ThO_2 in $\text{CO}_2\text{-H}_2\text{O}$ media. *Geochim. Cosmochim. Acta* **58**, 613 (1994).
3. Rai, D., Felmy, A. R., Moore, D.A., Mason, M. J.: The solubility of $\text{Th}(\text{IV})$ and $\text{U}(\text{IV})$ hydrous oxides in concentrated NaHCO_3 and Na_2CO_3 solutions. *Mat. Res. Soc. Symp. Proc.* **353**, 1143 (1995).
4. Felmy, A. R., Rai, D., Sterner, S. M., Mason, M. J., Hess, N. J., Conradson, S. D.: Thermodynamic models for highly charged aqueous species: Solubility of $\text{Th}(\text{IV})$ hydrous oxide in concentrated NaHCO_3 and Na_2CO_3 solutions. *J. Solut. Chem.* **26**, 399 (1997).
5. Ciavatta, L., The specific interaction theory in evaluating ionic equilibria. *Ann. Chim. (Rome)* **70**, 551 (1980).
6. Lemire, R. J., Fuger, J., Nitsche, H., Potter, P., Rand, M. H., Rydberg, J., Spahiu, K., Sullivan, J. C., Ullman, W. J., Vitorge, P., Wanner, H. (OECD, NEA-TDB): *Chemical Thermodynamics Vol. 4. Chemical Thermodynamics of Neptunium and Plutonium*. Elsevier, North-Holland, Amsterdam (2001).
7. Guillaumont, R., Fanghänel, Th., Fuger, J., Grenthe, I., Neck, V., Palmer, D. A., Rand, M. H. (OECD, NEA-TDB): *Chemical Thermodynamics Vol. 5. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*. Elsevier, North-Holland, Amsterdam (2003).
8. Fanghänel, Th., Neck, V., Kim, J. I., The ion product of H_2O , dissociation constants of H_2CO_3 and Pitzer parameters in the system $\text{Na}^+/\text{H}^+/\text{OH}^-/\text{HCO}_3^-/\text{CO}_3^{2-}/\text{ClO}_4^-/\text{H}_2\text{O}$ at 25 °C. *J. Solut. Chem.* **25**, 327 (1996).
9. Altmaier, M., Metz, V., Neck, V., Müller, R., Fanghänel, Th.: Solid-liquid equilibria of $\text{Mg}(\text{OH})_2(\text{cr})$ and $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}(\text{cr})$ in the system $\text{Mg-Na-H-OH-Cl-H}_2\text{O}$ at 25 °C. *Geochim. Cosmochim. Acta* **67**, 3595 (2003).
10. Neck, V., Müller, R., Bouby, M., Altmaier, M., Rothe, J., Dennecke, M. A., Kim, J. I.: Solubility of amorphous $\text{Th}(\text{IV})$ hydroxide – application of LIBD to determine the solubility product and EXAFS for aqueous speciation. *Radiochim. Acta* **90**, 485 (2002).
11. Sayer, D. E., Bunker, B. A.: In: *X-Ray Absorption: Techniques of EXAFS, SEXAFS and XANES*. (Koningsberger, D. C., Prins, R., eds.) Wiley, New York (1988) p. 211.
12. Stern, E. A., Newville, M., Ravel, B., Yacoby, Y., Haskel, D.: The UWXAFD analysis package: Philosophy and details. *Physica B* **208/209**, 117 (1995).
13. Ankudinov, A. L., Rehr, J. J.: Relativistic calculations of spin-dependent X-ray absorption spectra. *Phys. Rev. B* **56**, 1712 (1997).
14. Ankudinov, A. L., Ravel, B., Rehr, J. J., Conradson, S. D.: Real-space multiple-scattering calculation and interpretation of X-ray absorption near-edge structure. *Phys. Rev. B* **58**, 7565 (1998).