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# Solubility and hydrolysis of tetravalent actinides

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*Thorium(IV)* / *Uranium(IV)* / *Neptunium(IV)* / *Plutonium(IV)* / *Hydrolysis* / *Solubility* / *Oxides* / *Hydroxides*

**Summary.** The solubility and hydrolysis of Th(IV), U(IV), Np(IV), and Pu(IV) are critically reviewed and a comprehensive set of thermodynamic constants at I = 0 and 25 °C is presented. The hydrolysis constants are selected preferentially from experimental studies at actinide trace concentrations, where the interference of colloid formation can be excluded. Unknown formation constants of mononuclear complexes $An(OH)_n^{4-n}$ are estimated by applying a semi-empirical electrostatic model and an empirical correlation with the known constants of other actinide ions. Based on the known and estimated hydrolysis constants, the solubility products of $An(OH)_4$(am) or $AnO_2 \cdot xH_2O$(am) are calculated from experimental solubility data available in the literature. The SIT is used for ionic strength corrections.

The solubilities of U(IV), Np(IV), and Pu(IV) hydroxides or hydrous oxides can be calculated by accounting only for mononuclear hydrolysis species. The considerably higher solubilities of amorphous Th(IV) precipitates at pH $<5$ include major contributions of polynuclear species. The solubility data in acidic solutions depend strongly on the preparation and crystallinity of the solid phase. In neutral and alkaline solutions, where $An(OH)_4$(aq) are the predominant aqueous species, the solubilities of $AnO_2$(cr) become equal to those of the amorphous solids. This indicates that the crystalline dioxides are covered by amorphous hydroxide layers.

## 1. Introduction

Because of their high electric charge, tetravalent actinide ions have a strong tendency toward hydrolysis in aqueous solution and undergo polynucleation or further to colloid formation [1−3]. As the solubilities of An(IV) hydroxides or oxides are low, the possibility to investigate the aqueous speciation by spectroscopic methods is rather poor. Moreover, U(IV), Np(IV), and Pu(IV) are easily oxidized. Such problems complicate the experimental investigation and thermodynamic evaluation of the hydrolysis constants and solubility products. In particular the solubility products reported for amorphous or microcrystalline $An(OH)_4$(am) or $AnO_2xH_2O$(s) show considerable discrepancies. In many cases the data do not refer to a well-defined unique solid phase, because the degree of crystallinity, particle size, content of crystal water and hence the molar Gibbs energy of formation depend on the preparation method, pretreatment, alteration during the experiment, and temperature [3−7]. As the $An^{4+}$ ions hydrolyze even at low pH, there are no solubility data for amorphous An(IV) hydrous oxides or hydroxides with $An^{4+}$ as a predominant equilibrium aqueous species. The solubility products evaluated from experimental solubilities depend directly on the hydrolysis constants applied to calculate the $An^{4+}$ concentration from the total An(IV) concentration determined experimentally. The pH-dependent solubility of An(IV) oxides or hydroxides is often described by simplified chemical models, neglecting many of the hydrolysis species, e.g. polynuclear species, the mononuclear species $An(OH)_2^{2+}$, $An(OH)_3^{+}$, and partly even $An(OH)^{3+}$ [8−11]. As a consequence, the calculated $An^{4+}$ concentrations and solubility products may be considerably overestimated. Despite these ambiguities such models are useful for the estimation of solubilities, even in concentrated chloride brines, where the hydrolysis equilibria are not known and possibly complicated by the formation of ternary hydroxide-chloride complexes at low pH.

The objective of the present work is the evaluation of a comprehensive set of thermodynamic data at I = 0 and 25 °C for the hydrous oxides or hydroxides and aqueous hydrolysis species of tetravalent actinides. As the knowledge of the hydrolysis constants is an indispensable prerequisite for the evaluation of correct solubility products, the known hydrolysis constants are critically selected from the literature. Unknown formation constants of mononuclear hydrolysis species are estimated by applying well founded models, correlations or analogies [12−16]. Based on a chemical model which includes all mononuclear species $An(OH)_n^{4-n}$ up to n = 4 and, if necessary, polynuclear species proposed in the literature, the solubility products are then calculated from the available solubility data. In order to minimize uncertainties arising from ionic strength corrections, the present calculations are restricted to data $I \leq 1$ mol/l.

## 2. Hydrolysis of tetravalent actinides

The hydrolysis reactions of the $An^{4+}$ ions, i.e. the formation of hydroxide complexes $An_x(OH)_y^{4x-y}$, are usually written as

$$x\ An^{4+} + y\ H_2O \leftrightarrow An_x(OH)_y^{4x-y} + yH^+$$

or

$$x\ An^{4+} + y\ OH^- \leftrightarrow An_x(OH)_y^{4x-y}\ .$$

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**Table 1.** Ion interaction (SIT) coefficients at 25 °C used in the present paper (from the NEA-TDB [7, 18], except otherwise stated).

| i | j | $\varepsilon_{ij}$ | | | |
|---|---|---|---|---|---|
| $H^+$ | $ClO_4^-$ | $0.14 \pm 0.02$ | | | |
| $H^+$ | $Cl^-$ | $0.12 \pm 0.01$ | | | |
| $OH^-$ | $Na^+$ | $0.04 \pm 0.01$ | | | |
| | | Th(IV) | U(IV) | Np(IV) | Pu(IV) |
| $An^{4+}$ | $ClO_4^-$ | $0.67 \pm 0.1^a$ | $0.76 \pm 0.06$ | $0.82 \pm 0.05$ | $0.83 \pm 0.1^b$ |
| $An(OH)^{3+}$ | $ClO_4^-$ | $0.45 \pm 0.1^a$ | $0.48 \pm 0.08$ | $0.5 \pm 0.1^a$ | $0.5 \pm 0.1^a$ |
| $An(OH)_2^{2+}$ | $ClO_4^-$ | $0.3 \pm 0.1^a$ | $0.3 \pm 0.1^a$ | $0.3 \pm 0.1^a$ | $0.3 \pm 0.1^a$ |
| $An(OH)_3^+$ | $ClO_4^-$ | $0.15 \pm 0.1^a$ | $0.15 \pm 0.1^a$ | $0.15 \pm 0.1^a$ | $0.15 \pm 0.1^a$ |
| $An^{4+}$ | $Cl^-$ | $0.25 \pm 0.03$ | $0.36 \pm 0.1^a$ | $0.4 \pm 0.1^a$ | $0.4 \pm 0.1^a$ |
| $An(OH)^{3+}$ | $Cl^-$ | $0.2 \pm 0.1^a$ | $0.2 \pm 0.1^a$ | $0.2 \pm 0.1^a$ | $0.2 \pm 0.1^a$ |
| $An(OH)_2^{2+}$ | $Cl^-$ | $0.1 \pm 0.1^a$ | $0.1 \pm 0.1^a$ | $0.1 \pm 0.1^a$ | $0.1 \pm 0.1^a$ |
| $An(OH)_3^+$ | $Cl^-$ | $0.05 \pm 0.1^a$ | $0.05 \pm 0.1^a$ | $0.05 \pm 0.1^a$ | $0.05 \pm 0.1^a$ |
| $An(OH)_4^\circ$ | j | 0 | 0 | 0 | 0 |

a: Estimated according to analogies and systematics as outlined in the text.
b: Capdevila and Vitorge [69] report two independently determined values: $0.85 \pm 0.20$ and $0.82 \pm 0.07$. The former value from Vitorge et al ($1.03 \pm 0.05$) given in the NEA-TDB [7, 18] is revised.

The hydrolysis constants $K'_{xy}$ (in a given medium) and $K^\circ_{xy}$ (at infinite dilution), and the corresponding formation constants $\beta'_{xy}$ and $\beta^\circ_{xy}$ are defined by

$$K'_{xy} = [An_x(OH)_y^{(4x-y)}][H^+]^y/[An^{4+}]^x \quad (1)$$

$$K^\circ_{xy} = K'_{xy}\,(\gamma_{An_x(OH)_y})(\gamma_H)^y/(\gamma_{An})^x\,(a_w)^y \quad (2)$$

and

$$\beta'_{xy} = [An_x(OH)_y^{4x-y}]/[An^{4+}]^x\,[OH^-]^y \quad (3)$$

$$\beta^\circ_{xy} = \beta'_{xy}\,(\gamma_{An_x(OH)_y})/(\gamma_{An})^x\,(\gamma_{OH})^y \quad (4)$$

respectively. [i] denotes the concentration of species i, $\gamma_i$ its activity coefficient and $a_w$ the activity of water. The hydrolysis constants log $K_{xy}$ are related to log $\beta_{xy}$ by the ion product of water (log $K^\circ_w = -14.00 \pm 0.01$ [7]).

In the present work the specific ion interaction theory (SIT) [7, 17, 18] is applied for the calculation of activity coefficients. The simple SIT equation is preferred to the more elaborate Pitzer approach [19], because the hitherto available data for An(IV) hydrolysis species are not sufficient to evaluate all necessary ion interaction coefficients. Some uncertainties arising from the estimation of SIT coefficients have no significant effect on the calculation of activity coefficients at $I \leq 0.1$ mol/kg, whereas an estimated Pitzer coefficient $\beta^{(1)}$ has a considerable effect even at low ionic strength, in particular for ions of high charge. As the influence of the SIT coefficients increases with the ionic strength, the present calculations are restricted to data at $I \leq 1$ mol/kg. According to the SIT, the conditional equilibrium constant K′ is related to K° at $I = 0$ by

$$\log K' = \log K^\circ + \Delta z^2 D - \Delta\varepsilon \cdot I \quad (5)$$

with $\Delta z^2 = \Sigma\, z_i^2$(products) $- \Sigma\, z_i^2$(educts) and $\Delta\varepsilon = \Sigma\, \varepsilon_{ij}$(products) $- \Sigma\, \varepsilon_{ij}$(educts); $z_i$ is the charge of ion i, $m_j$ (mol/kg $H_2O$) the molal concentration of ion j, D is the Debye-Hückel term at 25 °C: $D = 0.509\,\sqrt{I}/(1 + Bå\,\sqrt{I})$, with Bå = 1.5. I is the molal ionic strength, and $\varepsilon_{ij}$ is the interaction parameter for a pair of oppositely charged ions. The ion interaction coefficients used in the present study are summarized in Table 1. As far as available, they are taken from the NEA-TDB [7, 18]. Unknown interaction coefficients are estimated according to known values for analog ions of equal charge, similar size and structure, systematics in the series of tetravalent actinides, and differences between the interaction coefficients $\varepsilon(M^{x+}/Cl^-)$ and $\varepsilon(M^{x+}/ClO_4^-)$ (cf. $\varepsilon_{ij}$ values given in the NEA reviews [7, 18]).

## 2.1 Discussion of literature data

### Thorium(IV)

The hydrolysis behaviour of Th(IV) has been investigated by numerous potentiometric titration experiments in the pH range 2.5–4. At thorium concentrations of $10^{-4}$–$10^{-2}$ mol/l, mononuclear species are usually found to be of minor importance or even negligible compared to the polynuclear species $Th_x(OH)_y^{4x-y}$ (cf. summaries in [1, 20]). On the other hand, the dimeric, trimeric, tetrameric, hexameric, and decameric species proposed in the literature [1, 20–24] are the result of curve fitting procedures. They are not ascertained by spectroscopic or other methods. In addition it is shown by laser-induced breakdown detection (LIBD) [25, 26] that, under the conditions usually applied in potentiometric titration studies ([Th] = $10^{-4}$–$10^{-2}$ mol/l, pH = 2.5–4), a considerable amount of Th(IV) colloids is formed. Accordingly it is not surprising that potentiometric titration studies performed by different authors, in different media, at different ionic strength and temperature or at different total thorium concentrations are interpreted with different sets of species. The published stability constants for the polynuclear species cannot be compared directly, and it is difficult to decide, which set of species and hydrolysis constants is the most realistic. The frequently accepted data of Baes *et al.* [1, 21], Brown *et al.* [20] and Grenthe and Lagerman [23] are listed in Table 2, together with the most recent results of Ekberg *et al.* [24], who performed potentiometric titrations at 15, 25 and 35 °C with relatively low thorium concentrations of $10^{-5}$–$10^{-4}$ mol/l and in addition solvent extraction experiments with thorium concentrations in the range of $10^{-7}$–$10^{-5}$ mol/l.

The first mononuclear hydrolysis constant of Baes *et al.* [21] (log $K^\circ_{11} = -3.0$) and Grenthe *et al.* [23, 30]

**Table 2.** Hydrolysis constants log $K'_{xy}$ proposed for Th(IV) at 25 °C. The constants at I = 0 (log $K^\circ_{xy}$ values in brackets) are calculated with the SIT coefficients in Table 1.

| Authors (Medium) | Brown *et al.* [20] (0.1 M $KNO_3$) | Ekberg *et al.* [24] (1 M $NaClO_4$) | Baes *et al.* [1, 21] (1 M $NaClO_4$) | Grenthe and Lagerman [23] (3 M $NaClO_4$) |
|---|---|---|---|---|
| Mononuclear species | | | | |
| $Th(OH)^{3+}$ | −2.98 | −3.3 ± 0.1 | −4.12[b] | −4.35 ± 0.09 |
| | (−2.3 ± 0.1) | (−2.1 ± 0.2) | (−3.0 ± 0.2) | (−3.1 ± 0.3) |
| $Th(OH)_2^{2+}$ | | −8.6 ± 0.1 | −7.81[b] | |
| | | (−6.6 ± 0.2) | (−5.8 ± 0.2) | |
| $Th(OH)_3^{+}$ | | −13.8[a] | | −12.3 ± 0.2 |
| | | (−11.4) | (< −11.7)[c] | (−9.3 ± 0.4) |
| $Th(OH)_4$(aq) | | −19.4 ± 0.5 | | −16.65 ± 0.04 |
| | | (−17.0 ± 0.5) | (−15.9 ± 0.3)[c] | (−13.6 ± 0.4) |
| Polynuclear species[d] | | | | |
| $Th_2(OH)_2^{6+}$ | | | −4.61[b] | −5.10 ± 0.17 |
| $Th_2(OH)_3^{5+}$ | | | | −7.87 ± 0.05 |
| $Th_4(OH)_8^{8+}$ | | −19.1 ± 0.1 | −19.01[b] | −19.6 ± 0.2 |
| $Th_4(OH)_{12}^{4+}$ | −30.55 | | | −34.86 ± 0.05 |
| $Th_6(OH)_{14}^{10+}$ | | | | −33.67 ± 0.05 |
| $Th_6(OH)_{15}^{9+}$ | −34.41 | −39.5 ± 0.2 | −36.76[b] | |
| $Th_6(OH)_{16}^{8+}$ | | | | −42.9 ± 0.4 |

a: Interpolated from the values at 15 and 35 °C.
b: Calculated by Baes *et al.* [21] from data of Kraus and Holmberg [22].
c: Evaluated by Baes and Mesmer [1] from the solubility data of Nabivanets and Kudritskaya [28].
d: Application of the SIT equation ($\log K^\circ_{xy} = \log K'_{xy} - y \log a_w - \Delta z^2 D + \Delta\varepsilon\, I$) to the polynuclear hydrolysis constants listed in this table leads to the following constants at I = 0 and $\Delta\varepsilon$ values in $NaClO_4$ solution:
$Th_2(OH)_2^{6+}$ ($\Delta z^2 = 6$): $\log K^\circ_{2,2} = -5.7$, $\Delta\varepsilon = 0.24$
$Th_4(OH)_8^{8+}$ ($\Delta z^2 = 8$): $\log K^\circ_{4,8} = -20.4$, $\Delta\varepsilon = 0.13$
$Th_4(OH)_{12}^{4+}$ ($\Delta z^2 = -36$): $\log K^\circ_{4,12} = -26.7$, $\Delta\varepsilon = -0.59$
$Th_6(OH)_{15}^{9+}$ ($\Delta z^2 = 0$): $\log K^\circ_{6,15} = -34.0$, $\Delta\varepsilon = 3.7 \pm 1.9$.

($\log K^\circ_{11} = -3.1$) are in good agreement, but several orders of magnitude lower than the corresponding constants for the other $An^{4+}$ ions. Brown *et al.* [20] and Ekberg et al. [24] found more significant contributions of the species $Th(OH)^{3+}$ and the hydrolysis constants $K_{11}$ reported by these authors are about one order of magnitude greater ($\log K'_{11} = -2.98$ in 0.1 M $KNO_3$ [20] and −3.3 in 1 M $NaClO_4$ [24], corresponding to $\log K^\circ_{11} = -2.3$ and −2.1, respectively.) Nakashima and Zimmer [27] determined a comparable value of $\log K'_{11} = -3.28$ in 0.5 M $KNO_3$ ($\log K^\circ_{11} = -2.2$) by solvent extraction with TBP at pH = 1.5−2.7 and thorium concentrations of $10^{-2}$ mol/l. The hydrolysis constants reported for $Th(OH)_2^{2+}$, $Th(OH)_3^{+}$, and $Th(OH)_4$(aq) differ several orders of magnitude. The $\log K^\circ_{13}$ and $\log K^\circ_{14}$ values reported by Baes and Mesmer [1] are based on solubility data from Nabivanets and Kudritskaya [28], which are conflicting with solubility data published later by other authors (cf. discussion in section 3.1).

## Uranium(IV)

The formation of $U(OH)^{3+}$ has been investigated by numerous authors in different media, preferentially by absorption spectroscopy in the pH range of 0−2. The thermodynamic constants selected in the comprehensive reviews of the NEA and IAEA ($\log K^\circ_{11} = -0.54 \pm 0.06$ [7] and −0.34 ± 0.20 [32], respectively) are in reasonable agreement. Attempts to calculate $\log K_{12}$, $\log K_{13}$ or $\log K_{14}$ from solubility data include the uncertainties in the solid phase and in the redundance of the hydrolysis constants and solubility product. They lead to values, which are not considered as reliable [7]. The only data reported for polynuclear species is based on a potentiometric titration study in 3 M $NaClO_4$ [33], which is interpreted with the formation of $U_6(OH)_{15}^{9+}$ [1, 7] and $\log K'_{6,15} = -16.9 \pm 0.6$.

## Neptunium(IV) and Plutonium(IV)

The initial mononuclear hydrolysis of Np(IV) and Pu(IV) has also been investigated by means of absorption spectroscopy [34−40] (cf. Tables 3 and 4). However, the concentrations used in these studies ([Np(IV)] = $1 \cdot 10^{-3}$−$7 \cdot 10^{-3}$ M, [Pu(IV)] = $1.3 \cdot 10^{-4}$−$2 \cdot 10^{-3}$ M) considerably exceed the solubility limit of the Np(IV) and Pu(IV) hydrous oxides at pH = 1−2 (cf. Figs. 8 and 9 in section 3). The same holds for the studies on the Pu(III)/Pu(IV) redox couples [41, 42]. As demonstrated in the filtration and LIBD study of Knopp *et al.* [45], the formation of Pu(IV) colloids, which remain in solution without precipitation, is the predominant reaction when the concentration exceeds the solubility limit. The interference of colloid formation may have led to misinterpretation and hence to erroneous data in all these studies. This source of error is excluded in the solvent extraction studies of Guillaumont *et al.* [43, 44]. The reported stepwise hydrolysis constants are determined using Np-239 and Pu-238 trace concentrations at I = 1.0 mol/l ($HClO_4$/$LiClO_4$): $\log {}^*K'_1 = -0.45$, $\log {}^*K'_2 = -0.75$, $\log {}^*K'_3 = -3.3$, $\log {}^*K'_4 = -6.3$ for Pu(IV) [43] and $\log {}^*K'_1 = -0.5$, $\log {}^*K'_2 = -1.0$ for Np(IV) [44].

**Table 3.** Formation constants of Np(IV) hydrolysis species at 20−25 °C.

| Medium/Species | log $K'_{1y}$ | log $K^\circ_{1y}$ | log $\beta^\circ_{1y}$ | Method[a] | Ref. |
|---|---|---|---|---|---|
| 1.0 M $HClO_4/LiClO_4$, room temp., $10^{-3}-1$ M $H^+$, $^{239}Np(IV)$ trace conc. | | | | extr | [44] |
| $Np(OH)^{3+}$ | −0.5 | 0.55 | $14.55 \pm 0.2$ | | |
| $Np(OH)_2^{2+}$ | −1.5 | 0.35 | $28.35 \pm 0.3$ | | |
| Other data for $Np(OH)^{3+}$ | | | | | |
| 2.0 M $HClO_4/NaClO_4$, 25 °C 0.01−0.1 M $H^+$, $(1.4-2.7) \cdot 10^{-3}$ M Np(IV) | −2.30 | −1.25 | 12.75 | spec | [34] |
| 1.0 M $HClO_4/NaClO_4$, 25 °C 0.01−0.2 M $H^+$, $7.5 \cdot 10^{-3}$ M Np(IV) | −1.90 | −0.84 | 13.16 | spec | [35] |
| 1.0 M $HClO_4/NaClO_4$, 25 °C | −2.25 | −1.19 | 12.81 | spec | [36] |

a: extr = solvent extraction, spec = spectroscopy.

In our recent paper [45] it is shown that the solubility of $Pu(OH)_4$(am) in the range pH = 0−12 agrees well with the pH-dependence predicted by the hydrolysis constants of Metivier and Guillaumont [43]. The hydrolysis constants of Guillaumont *et al.* [43, 44], with the log $K^\circ_{11}$ values more than an order of magnitude greater than those reported in the other studies, are therefore considered to be the most reliable values among the published data for Np(IV) and Pu(IV). As experimental uncertainties are not given in these papers [43, 44], they are estimated to be about $\pm 0.2$ log units for each hydrolysis step.

## 2.2. Estimation of unknown constants

In order to obtain a complete set of formation constants for mononuclear species $An(OH)_n^{4-n}$, the unknown constants are estimated by applying two different methods. The first method is based on the empirical intercorrelation between hydrolysis constants of actinide ions at different oxidation states. For the second method our recent semi-empirical approach [16] is applied, in which the decrease of stepwise complexation constants for a given metal-ligand system is related to the increasing electrostatic repulsion between the ligands.

### Estimation method (A)

Complexation and hydrolysis constants of metal ions with comparable electronic configuration are known to correlate with the electrostatic interaction energy between the metal and ligand ions [1, 12−15]:

**Table 4.** Formation constants of Pu(IV) hydrolysis species at 20−25 °C.

| Medium/Species | log $K'_{1y}$ | log $K^\circ_{1y}$ | log $\beta^\circ_{1y}$ | Method[a] | Ref. |
|---|---|---|---|---|---|
| 1.0 M $HClO_4/LiClO_4$, room temp., $10^{-8}-1$ M $H^+$, $10^{-8}$ M $^{238}Pu(IV)$ | | | | extr | [43] |
| $Pu(OH)^{3+}$ | −0.45 | 0.60 | $14.6 \pm 0.2$ | | |
| $Pu(OH)_2^{2+}$ | −1.2 | 0.63 | $28.6 \pm 0.3$ | | |
| $Pu(OH)_3^+$ | −4.5 | −2.25 | $39.7 \pm 0.4$ | | |
| $Pu(OH)_4$(aq) | −10.8 | −8.54 | $47.5 \pm 0.5$ | | |
| Other data for $Pu(OH)^{3+}$ | log $K'_{11}$ | log $K^\circ_{11}$ | log $\beta^\circ_{11}$ | | |
| 0.5 M HCl/NaCl, 25 °C 0.01−0.5 M $H^+$, $7.2 \cdot 10^{-4}$ M Pu(IV) | −1.65 | −0.63 | 13.37 | spec | [37] |
| 0.5 M $HClO_4/NaClO_4$, 25 °C 0.01−0.5 M $H^+$, $7.2 \cdot 10^{-4}$ M Pu(IV) | −1.60 | −0.64 | 13.36 | spec | [37] |
| 2.0 M $HClO_4/NaClO_4$, 25 °C 0.01−2.0 M $H^+$, $10^{-3}$ M Pu(IV) | −1.73 | −0.70 | 13.30 | spec | [38] |
| 0.19 M $HClO_4$, 23 °C $1.8 \cdot 10^{-3}$ M Pu(IV) | −1.96 | −1.19 | 12.81 | spec | [39] |
| 0.06 M $HClO_4$, 23 °C $1.6 \cdot 10^{-3}$ M Pu(IV) | −1.48 | −0.94 | 13.06 | spec | [39] |
| 0.5 M $HClO_4/NaClO_4$, 25 °C 0.03−0.5 M $H^+$, $1.3 \cdot 10^{-4}$ M Pu(IV) | −1.57 | −0.611 | 3.39 | spec | [40] |
| 1.0 M $HClO_4/NaClO_4$, 25 °C 0.1−0.2 M $H^+$, $10^{-3}$ M Pu(IV) | −1.51 | −0.45 | 13.55 | redox | [41] |
| 2.0 M $HClO_4/LiClO_4$, 25 °C 0.1−2.0 M $H^+$,$8 \cdot 10^{-3}$ M Pu(IV) | −1.27 | −0.24 | 13.76 | redox | [42] |

a: extr = solvent extraction, spec = spectroscopy, redox = Pu(III)/Pu(IV) redox potential.

**Table 5.** Distances $d_{M\text{-}OH_2}$ and effective radii of actinide ions.

| Md | $_{M\text{-}OH_2}$ (Å)[a] | Effective ionic radius $r_M$ (Å) | |
|---|---|---|---|
| | | in aqueous solution[b] | Crystal radius[c] |
| $Pu^{3+}$ | 2.50 ± 0.01 | 1.12 ± 0.02 | 1.12 (CN = 8) |
| $Am^{3+}$ | | | 1.10 (CN = 8) |
| $Cm^{3+}$ | | | 1.09 (CN = 8) |
| $Th^{4+}$ | 2.46 ± 0.02 | 1.08 ± 0.02 | 1.09 (CN = 9) |
| $U^{4+}$ | 2.42 ± 0.02 | 1.04 ± 0.02 | 1.05 (CN = 9) |
| $Np^{4+}$ | 2.40 ± 0.01 | 1.02 ± 0.02 | 1.03 (CN = 9) |
| $Pu^{4+}$ | 2.39 ± 0.01 | 1.01 ± 0.02 | 1.01 (CN = 9) |
| $NpO_2^+$ | 2.50 ± 0.02 | 1.12 ± 0.02 | |
| $UO_2^{2+}$ | 2.42 ± 0.01 | 1.04 ± 0.02 | |
| $PuO_2^{2+}$ | 2.40 ± 0.01 | 1.02 ± 0.02 | |

a: From the recent compilation of XRD and EXAFS data in aqueous solution [16].
b: Calculated according to $r_M = d_{M\text{-}OH_2} - r_{H_2O}$ with $r_{H_2O} = 1.38 \pm 0.02$ Å [75].
c: Crystal radii at given coordination number (CN) from Refs. [12, 76].

$$\log \beta^\circ_{(M)} \propto {}^{el}E_{M\text{-}L} \propto (z_M/d_{M\text{-}L}) \,. \tag{6}$$

$z_M$ is the charge of the metal ion and $d_{M\text{-}L}$ the distance between the centers of metal and ligand ions. This empirical linear correlation is usually applied to the first complexation constant, as used by Choppin [12, 13] to derive effective charges of $z_M = 2.3 \pm 0.1$ and $3.2 \pm 0.1$ for the penta- and hexavalent actinide ions $AnO_2^+$ and $AnO_2^{2+}$, respectively. The distances $d_{An\text{-}OH}$, i.e. the sum of the effective radii of the actinide and $OH^-$ ions (the latter is assumed to be equal to that of a $H_2O$ molecule) are given in Table 5. Fig. 1 shows the application of this correlation to the known hydrolysis constants for Am(III) and Cm(III) [18, 46, 47], Np(IV) [44], Pu(IV) [43], $NpO_2^+$ [48] and $UO_2^{2+}$ [7, 49]. Since the quotient $z_M/d_{M\text{-}OH}$ increases slightly in the series: Th(IV) < U(IV) < Np(IV) < Pu(IV), a corresponding increase is expected for the constants log $\beta^\circ_{ln}$. This assumption holds quite well for log $\beta^\circ_{11}$ of U(IV), Np(IV), and Pu(IV). The correlation may be used to estimate the unknown constants log $\beta^\circ_{ln}$ for U(IV) and Np(IV). However, as shown in Fig. 1 for the data of Ekberg *et al.* [24], the hydrolysis constants of Th(IV) are significantly lower than the expected values from this correlation. The large differences between the hydrolysis constants of Th(IV) and those of other tetravalent actinides cannot be explained by differences in the size of $An^{4+}$ ions.

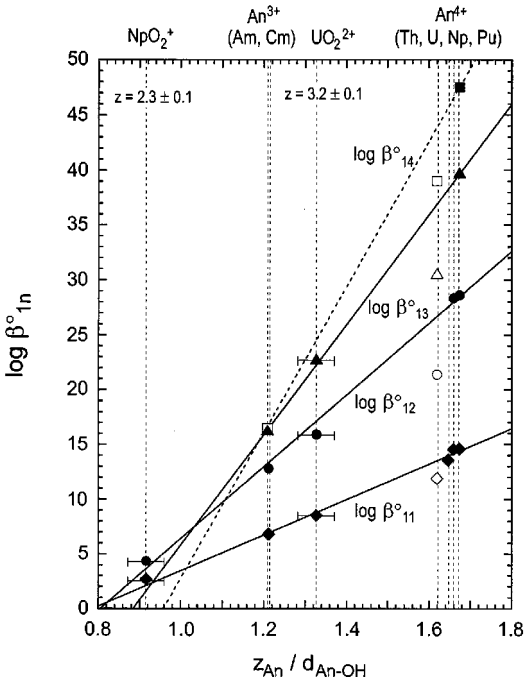


**Fig. 1.** Correlation of the formation constants log $\beta^\circ_{ln}$ of actinide hydroxide complexes with the electrostatic interaction energy ${}^{el}E_{An\text{-}OH}$ between the actinide and $OH^-$ ions.

## Estimation method (B)

The second estimation method applies an electrostatic approach (Neck and Kim [16]), which correlates the mononuclear complexation constants log $\beta^\circ_{ln}$ for a given actinide ion with an inter-ligand electrostatic repulsion energy term:

$$\log \beta^\circ_{ln} = n \log \beta^\circ_{11} - {}^{rep}E_L/RT \ln 10 \,. \tag{7}$$

The Coulomb repulsion energy term ${}^{rep}E_L$ is calculated from the charge and inter-distance of the ligands involved in a given complex and their angular distribution:

$${}^{rep}E_L = N_A\, e^2 \cdot (1/2) \sum_L \frac{z_L\, z_{L'}}{d_{L\text{-}L'}\, \varepsilon_{L\text{-}L'}} \,. \tag{8}$$

$N_A$ is Avogadro's number, e the elementary charge, $z_L$ and $z_{L'}$ the formal charge number of ligand ions (−1 for $OH^-$). The distance $d_{L\text{-}L'}$ between the centers of the ligands L and L′ is calculated from the distance $d_{M\text{-}L} = r_M + r_L$ and the angle $\Theta_{L\text{-}M\text{-}L'}$ between L, M and L′:

$$d_{L\text{-}L'} = \{(d_{M\text{-}L})^2 + (d_{M\text{-}L'})^2 - 2d_{M\text{-}L}\, d_{M\text{-}L'} \cos \Theta_{L\text{-}M\text{-}L'}\}^{1/2} \,. \tag{9}$$

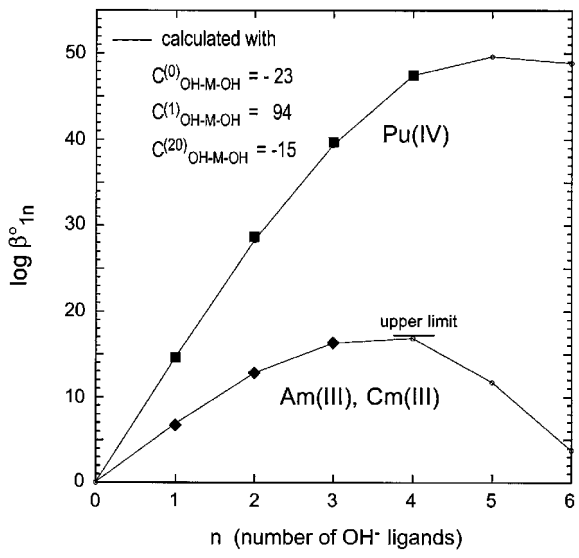


**Fig. 2.** Application of the electrostatic ligand repulsion approach of Neck and Kim [16] to actinide hydroxide complexes. Evaluation of the shielding coefficients $C^{(n)}_{OH\text{-}M\text{-}OH}$ from the known hydrolysis constants of Am(III) and Cm(III) (as selected in our recent review [47]) and Pu(IV) (from the solvent extraction study of Metivier and Guillaumont [43]).

**Table 6.** Formation constants for mononuclear An(IV) hydrolysis species at 25 °C: experimental data[a], estimated[b] and selected values.

| | $\log \beta^\circ_{11}$ | $\log \beta^\circ_{12}$ | $\log \beta^\circ_{13}$ | $\log \beta^\circ_{14}$ |
|---|---|---|---|---|
| Thorium(IV) | | | | |
| Baes *et al.* [21] | $11.0 \pm 0.2$ | $22.2 \pm 0.2$ | | |
| Grenthe, Lagerman [23] | $10.9 \pm 0.3$ | | $32.7 \pm 0.4$ | $42.4 \pm 0.4$ |
| Nakashima, Zimmer [27] | $11.8 \pm 0.2$ | | | |
| Brown *et al.* [20] | $11.7 \pm 0.1$ | | | |
| Ekberg *et al.* [24] | $11.9 \pm 0.2$ | $21.4 \pm 0.2$ | 30.6 | $39.0 \pm 0.5$ |
| Estimation (A) | 13.4 | 26.5 | 36.7 | 43.9 |
| Estimation (B) | 11.9 | 22.9 | 31.4 | 37.0 |
| Selected | $11.8 \pm 0.2$ | $22.0 \pm 0.6$ | $31.0 \pm 1$ | $(39.0 \pm 0.5)$<br>$38.5 \pm 1.0$[c] |
| Uranium(IV) | | | | |
| NEA [7] | $13.46 \pm 0.1$ | | | |
| IAEA [32] | $13.66 \pm 0.2$ | | | |
| Estimation (A) | 13.9 | 27.5 | 38.2 | 45.7 |
| Estimation (B) | 13.6 (fixed) | 26.3 | 36.4 | 43.6 |
| Selected | $13.6 \pm 0.2$ | $26.9 \pm 1$ | $37.3 \pm 1$ | $(44.7 \pm 1)$<br>$46.0 \pm 1.4$[c] |
| Neptunium(IV) | | | | |
| Duplessis, Guillaumont [44] | $14.55 \pm 0.2$ | $28.35 \pm 0.3$ | | |
| Estimation (A) | 14.2 | 28.0 | 39.0 | 46.6 |
| Estimation (B) | 14.6 | 28.3 | 39.4 | 47.5 |
| Selected | $14.5 \pm 0.2$ | $28.3 \pm 0.3$ | $39.2 \pm 1$ | $(47.1 \pm 1)$<br>$47.7 \pm 1.1$[c] |
| Plutonium(IV) | | | | |
| Metivier, Guillaumont [43] | $14.6 \pm 0.2$ | $28.6 \pm 0.3$ | $39.7 \pm 0.4$ | $47.5 \pm 0.5$ |
| Estimation (A) | 14.5 | 28.5 | 39.7 | 47.5 |
| Estimation (B) | 14.6 | 28.3 | 39.4 | 47.5 |
| Selected | $14.6 \pm 0.2$ | $28.6 \pm 0.3$ | $39.7 \pm 0.4$ | $(47.5 \pm 0.5)$<br>$48.1 \pm 0.9$[c] |

a: Constants at $I = 0$ are calculated with the ion interaction SIT coefficients in Table 1.
b: Estimation (A) is based on the correlation $\log \beta^\circ \propto (z_{An}/d_{An\text{-}OH})$. Estimation (B) is based on the electrostatic approach of Neck and Kim [16].
c: Calculated from solubility data for $AnO_2 \cdot xH_2O$(am) in neutral to alkaline solutions (c.f. sections 3.1−3.4).

The angle $\Theta_{L\text{-}M\text{-}L'}$ is given by the assumption of complex symmetries with minimum ligand repulsion for the complexes $ML_2$ (linear), $ML_3$ (trigonal planar), $ML_4$ (tetrahedral), $ML_5$ (trigonal bipyramidal) and $ML_6$ (octahedral). The electrostatic shielding between the ligands L and L′, due to the metal ion and hydration water molecules between them, is described semi-empirically by a virial equation:

$$\varepsilon_{L\text{-}L'} = C^{(0)}_{L\text{-}M\text{-}L'} + C^{(1)}_{L\text{-}M\text{-}L'}(\Theta_{L\text{-}M\text{-}L'}/180°) + \ldots + C^{(20)}_{L\text{-}M\text{-}L'}(\Theta_{L\text{-}M\text{-}L'}/180°)^{20} \quad (10)$$

The shielding coefficients $C^{(n)}_{L\text{-}M\text{-}L'}$ are specific for different ligands but independent of the actinide ion. The shielding coefficients for $OH^-$ ligands ($C^{(0)}_{L\text{-}M\text{-}L'} = -23$, $C^{(1)}_{L\text{-}M\text{-}L'} = 94$, and $C^{(20)}_{L\text{-}M\text{-}L'} = -15$) are derived from the known hydrolysis constants of Am(III) and Cm(III) [47] and Pu(IV) [43] as shown in Fig. 2.

In Table 6, the formation constants $\log \beta^\circ_{1n}$ of mononuclear An(IV) hydroxide complexes, both experimental data and estimated values, are summarized for the purpose of comparison. If the selected constant is based on the estimations, the uncertainty is assumed to be ± 1 logarithmic unit. The hydrolysis constants of Pu(IV) are used as input data in both estimation methods and accordingly the estimations for Pu(IV) are close to the experimental values. The estimations (A) and (B) for the unknown constants $\log \beta^\circ_{13}$ and $\log \beta^\circ_{14}$ of Np(IV) are also in reasonable agreement with each other. In the case of U(IV) the discrepancies between the two estimation methods are larger and thus the mean values are selected for the unknown constants $\log \beta^\circ_{12}$ and $\log \beta^\circ_{13}$. The mononuclear Th(IV) hydrolysis constants proposed in the literature differ largely, and the constants interpolated with estimation method (A) are considerably overestimated. Therefore the ligand repulsion approach (estimation method (B)) is applied for their critical examination (Fig. 3). The application of Eqs. (7)−(10) with either $\log \beta^\circ_{11} = 11.9$ (solid line in Fig. 3) or 11.0 (dashed line) indicates that the higher $\log \beta^\circ_{11}$ values in the range 11.7 to 11.9 [20, 24, 27] and the lower $\log \beta^\circ_{13}$ and $\log \beta^\circ_{14}$ values of Ekberg *et al.* [24] should be preferred. The constants proposed by Grenthe and Lagerman [23] suggest a linear increase of $\log \beta^\circ_{1n}$ with the number of hydroxide ligands. This is in contradiction to the observations made for the hydroxide complexes of other actinide ions and also for actinide complexes with other inorganic ligands [16]. As the extrapolation to $\log \beta^\circ_{14}$ implies large uncertainties, the constants $\log \beta^\circ_{14}$ are evaluated in sections 3.1−3.4 from the solubilities of $AnO_2 \cdot xH_2O$(am) in neutral and alkaline solutions, where the neutral complexes $An(OH)_4$(aq) are the predominant aqueous species.

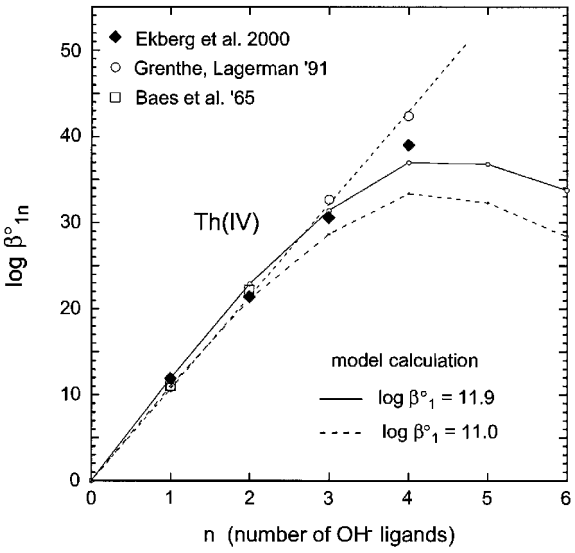


**Fig. 3.** Application of the electrostatic ligand repulsion approach of Neck and Kim [16] to the hydroxide complexes of Th(IV). The constants log $\beta^\circ_{1n}$ are calculated according to Eq. (7) for log $\beta^\circ_{11}$ = 11.9 (solid line) and alternatively with log $\beta^\circ_{11}$ = 11.0 (dashed line).

## 3. Solubility of An(IV) hydroxides and oxides

The chemical form of freshly precipitated or aged An(IV) solid phases is not clear. In the literature, they are called either amorphous hydroxides $An(OH)_4(am)$ or amorphous, partly microcrystalline hydrous oxides $AnO_2 \cdot xH_2O(am)$. Possibly they do not have a unique composition but consist of a hydrated oxyhydroxide $AnO_{(2-n)}(OH)_{2n}(am)$ with $0 < n < 2$, where n decreases with aging or temperature. The preparation of water-free crystalline dioxide $AnO_2(cr)$ requires heating above 700 °C [3, 6, 29].

The conditional solubility products $K'_{sp}$ and $K^\circ_{sp}$ (at infinite dilution) of amorphous An(IV) precipitates, $An(OH)_4(am)$ or $AnO_2 \cdot xH_2O(am)$, and crystalline dioxides $AnO_2(cr)$ refer to the dissolution equilibria

$$An(OH)_4(s) \leftrightarrow An^{4+} + 4\,OH^-$$

and

$$AnO_2 \cdot xH_2O(s) + (2 - x)\,H_2O \leftrightarrow An^{4+} + 4\,OH^-$$

with

$$K'_{sp} = [An^{4+}][OH^-]^4 \quad (11)$$

and

$$K^\circ_{sp} = K'_{xy}\,(\gamma_{An})(\gamma_{OH})^4 \quad \text{(for } An(OH)_4(am)) \quad (12)$$

$$K^\circ_{sp} = K'_{xy}\,(\gamma_{An})(\gamma_{OH})^4\,(a_w)^{(x-2)} \quad \text{(for } AnO_2 \cdot xH_2O(s)) \,. \quad (13)$$

If there are no complexes with other inorganic ligands or colloidal species present in solution, the total An(IV) equilibrium concentration is given by

$$[An]_{tot} = [An^{4+}] + \Sigma\, x\,[An_x(OH)_y^{4x-y}] = K'_{sp}\,[OH^-]^{-4} + \Sigma\, x\,(K'_{sp}\,[OH^-]^{-4})^x\,\beta'_{xy}\,[OH^-]^y). \quad (14)$$

In neutral and alkaline solutions, which are of interest for natural goundwater systems, salt or cement brines, $An(OH)_4(aq)$ is the predominant aqueous species. The dissolution equilibrium can hence be written as

$$AnO_2 \cdot xH_2O(s) + (2 - x)\,H_2O \leftrightarrow An(OH)_4(aq)$$

and the pH-independent solubility in this range ($\log [An(IV)]_{tot} \approx \log [An(OH)_4(aq)]$) is given by the solubility constant

$$\log K'_{s(14)} = \log [An(OH)_4(aq)] = \log K'_{sp} + \log \beta'_{14} \,. \quad (15)$$

In neutral and alkaline solution of low ionic strength the solubility is independent of the medium and ionic strength ($\log K'_{s(14)} \approx \log K^\circ_{s(14)}$), because the water activity and the activity coefficients of $An(OH)_4(aq)$ are approximately equal to 1.

Solubility data determined with crystalline $AnO_2(cr)$ as an initial solid phase imply a certain ambiguity, because radiolytic amorphization and hydration on the surface cannot be ruled out [3]. In the following sections the experimental solubility data measured with crystalline An(IV) dioxides are compared with the solubility products for $AnO_2(cr)$ calculated from known thermochemical data for $AnO_2(cr)$ and $An^{4+}(aq)$ according to

$$-RT \ln K^\circ_{sp} = \Delta_r G^\circ_m = \Delta_f G^\circ_m(An^{4+}(aq)) + 4\,\Delta_f G^\circ_m(OH^-(aq)) - \Delta_f G^\circ_m(AnO_2(cr)) - 2\,\Delta_f G^\circ_m(H_2O(l)) \,. \quad (16)$$

Table 7 shows the solubility products for $ThO_2(cr)$, $UO_2(cr)$, $NpO_2(cr)$ and $PuO_2(cr)$ calculated by Rai *et al.* [50] with critically evaluated standard data $\Delta_f H^\circ_m(AnO_2(cr))$ and $S^\circ_m(AnO_2(cr))$ [51], $S^\circ_m(An(cr))$ [52], $\Delta_f G^\circ_m(An^{4+}(aq))$ [53], and $S^\circ_m(O_2(g))$, $\Delta_f G^\circ_m(OH^-(aq))$, $\Delta_f G^\circ_m(H_2O(l))$ [54]. Slightly different values for $\Delta_f G^\circ_m(AnO_2(cr))$ and log $K^\circ_{sp}$ are calculated by Kim and Kanellakopulos [3] for $PuO_2(cr)$ and from the data selected in the NEA review on uranium [7] for $UO_2(cr)$.

**Table 7.** Solubility products for crystalline An(IV) dioxides at 25 °C, calculated from thermochemical data.

| An(IV) | log $K^\circ_{sp}(AnO_2(cr))$ | |
|---|---|---|
| Th(IV) | $-54.2 \pm 1.3$ [50] | |
| U(IV) | $-60.6 \pm 0.5$ [50], | $-60.86 \pm 0.36$ [7] |
| Np(IV) | $-63.7 \pm 1.8$ [50] | |
| Pu(IV) | $-64.1 \pm 0.7$ [50], | $-63.8 \pm 1.0$ [3] |
| Am(IV) | $-65.4 \pm 1.7$ [18] | |

### 3.1 Solubility of Th(IV)

The solubility of amorphous Th(IV) precipitates, considered as either amorphous $Th(OH)_4(am)$ [28, 29]) or $ThO_2 \cdot xH_2O(am)$ ([8−10] has been investigated by Nabivanets and Kudritskaya [28] at 17 °C in 0.1 M $NaClO_4$, by Moon [29] at 18 °C in 0.5 M $NaClO_4$, and by Rai *et al.* [8−10] at room temperature in 0.1 M $NaClO_4$, 0.6 M NaCl, 0.6 M KCl, and concentrated NaCl and $MgCl_2$ solutions. In these studies, the amorphous precipitates are not treated at higher temperature but only washed with water. Moon [29] also determined solubility data in 0.1 M $NaClO_4$ with crystalline $ThO_2(cr)$ prepared at 700 °C. At low pH, the solu-

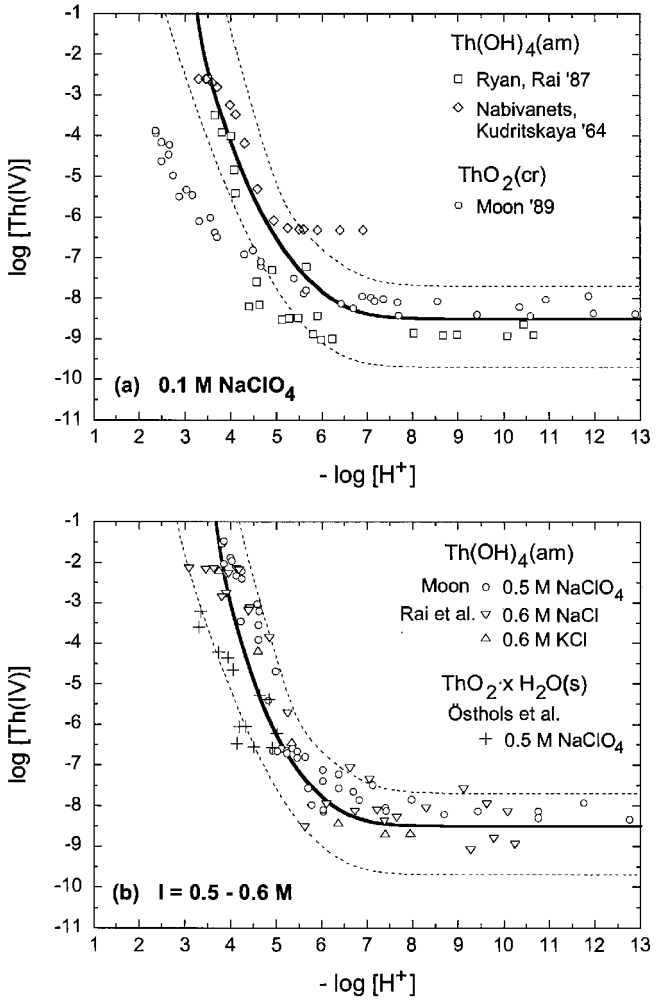


**Fig. 4.** Solubility of Th(IV) at 17−25 °C as a function of the $H^+$ concentration **(a)** in 0.1 M $NaClO_4$ (above) and **(b)** at I = 0.5−0.6 mol/l (below). The experimental data are from Refs. [8, 9, 28−30]. The solid curves are calculated with log $K^\circ_{sp} = -47.0$ for amorphous Th(IV) hydroxide or hydrous oxide, the selected hydrolysis constants for mononuclear species and log $K'_{4,12}$ and log $K^\circ_{6,15}$ from Brown *et al.* [20]. The upper and lower limits (dotted lines) are calculated with log $K^\circ_{sp} = -46.2$ and −48.2, respectively.

bility data for $ThO_2$(cr) are essentially lower than those for $Th(OH)_4$(am), but at pH > 5 equal thorium concentrations are observed. Similar observations are reported by Östhols *et al.* [30] for the solubility of microcrystalline $ThO_2 \cdot xH_2O$(s) at 25 °C in 0.5 M $NaClO_4$. In this study the precipitate is dried at room temperature for one week in a vacuum desiccator. X-ray powder diffraction indicates a low degree of crystallinity and the water content is determined to be $x \approx 2.5$. The solubility data measured at 17−25 °C and I = 0.1 M ($NaClO_4$) or I = 0.5−0.6 M ($NaClO_4$, NaCl and KCl) are shown in Fig. 4a and b, respectively.

The pH-independent solubilities measured by Moon and Rai *et al.* in neutral and alkaline solutions (log [Th] = $-8.2 \pm 0.3$ in 0.1 and 0.5 M $NaClO_4$ [29], $-8.8 \pm 0.2$ in 0.1 M $NaClO_4$ [8] and $-8.5 \pm 0.6$ in 0.6 M NaCl and KCl [9]), are in fair agreement. The significantly higher solubilities reported by Nabivanets and Kudritskaya [28] (log [Th] = − 6.3 at pH = 5.5−7 in 0.1 M $NaClO_4$, 17 °C) may be ascribed to insufficient phase separation by centrifugation. These authors do not mention filtration, whereas in the other studies, the thorium concentration was determined after ultrafiltration at a filter pore size of 2 nm [8, 9, 29] to exclude colloidal particles.

The following comparison shows the problem connected with the evaluation of thermodynamic constants from the experimental solubility data. As shown in Fig. 4b the solubilities of Th(IV) hydroxide or hydrous oxide determined by Moon [29] and Felmy, Rai and Mason [9] at I = 0.5 or 0.6 M are in reasonable agreement. Despite of this, the proposed solubility products differ by many orders of magnitude (cf. Table 8). Rai *et al.* [9, 10] interprete the decrease of the thorium concentration with a slope of −4 by assuming the non-hydrolyzed $Th^{4+}$(aq) to be the prevailing aqueous species and neglected all hydrolysis species except $Th(OH)_4$(aq). This interpretation is not consistent with the results of potentiometric titration and solvent extraction studies [20−24, 27], which clearly demonstrate that thorium is strongly hydrolyzed under these conditions with polynuclear species being predominant. Moon [29] evaluated the mononuclear hydrolysis constants from the solubility data obtained with $ThO_2$(cr) in 0.1 M $NaClO_4$. Assuming the crystalline dioxide to be the solubility limiting solid phase over the whole pH range, the evaluated mononuclear hydrolysis constants are several orders of magnitude too large, as compared to those from other experimental methods [20−24, 27]. Since the solubilities in the neutral and alkaline range are practically the same for $Th(OH)_4$(am) in 0.5 M $NaClO_4$ and $ThO_2$(cr) in 0.1 M $NaClO_4$, Moon concludes that the solubility products must be similar as well. Using only slightly different constants log $K'_{sp}$ and log $\beta'_{1y}$ in 0.5 M $NaClO_4$ the higher solubilities of $Th(OH)_4$(am) at pH < 5 are then described simply by fitting an additional formation constants for the dimeric species $Th_2(OH)_4^{4+}$. This interpretation disregards that the hydrolysis equilibria in solution are independent of the solid phase.

In the present review an attempt is made to evaluate a set of thermodynamic constants, which is consistent with both, hydrolysis constants from potentiometric titration and solvent extraction studies and solubilities of amorphous Th(IV) precipitates. For this purpose, the hydrolysis constants log $K'_{4,12}$ and log $K'_{6,15}$ derived by Brown *et al.* [20] (c.f. Table 2) from potentiometric titrations at pH = 3−4 in 0.1 $KNO_3$ are used in combination with the selected constants for the mononuclear hydrolysis species. From the solubility data of amorphous Th(IV) hydroxide or hydrous oxide in the same pH range and at the same ionic strength (0.1 M $NaClO_4$) the following solubility products are calculated:

Exp. data of Ryan and Rai [8]:
log $K'_{sp} = -45.2$ (log $K^\circ_{sp} = -47.3$)

Exp. data of Nabivanets and Kudritskaya [28]:
log $K'_{sp} = -44.7$ (log $K^\circ_{sp} = -46.8$) .

In Table 2, the hydrolysis constants log $K'_{4,12}$ and log $K'_{6,15}$ of Brown *et al.* [20] are combined with literature data in 1 and 3 M $NaClO_4$ to evaluate the constants at I = 0 and the SIT parameters $\Delta\varepsilon$. These parameterizations imply unknown uncertainties, because the literature data refer to different hydrolysis schemes. Nevertheless, they allow the estimation of log $K'_{4,12}$ and log $K'_{6,15}$ in 0.5 M $NaClO_4$ and

**Table 8.** Different sets of thermodynamic constants (I = 0) for modelling the solubility of amorphous $ThO_2 \cdot xH_2O$(s) at 25°C

| | Rai *et al.* [8, 9] | Moon [29][a] | Östhols *et al.* [30][c] | present study |
|---|---|---|---|---|
| $\log K^\circ_{sp}$ | −45.5 | −52.9/−53.6 | −48.7 | −47.0 ± 0.8 |
| $\log \beta^\circ_{11}$ | − | 13.3/13.8 | 10.9 | 11.8 ± 0.2 |
| $\log \beta^\circ_{12}$ | − | 23.9/24.5 | − | 22.0 ± 0.6 |
| $\log \beta^\circ_{13}$ | − | 36.3/37.2 | 32.9 | 31.0 ± 1.0 |
| $\log \beta^\circ_{14}$ | 36.7 | 44.7/45.4 | 42.1 | 38.5 ± 1.0 |
| $\log \beta'_{2,4}$ | | − /59.1[b] | | |
| $\log \beta^\circ_{4,12}$ | | | | 141.3[d] |
| $\log \beta^\circ_{6,15}$ | | | | 176.0[d] |

a: The conditional constants reported by Moon [29] for 0.1 M/0.5 M $NaClO_4$ are converted to I = 0 with the SIT coefficients in Table 1.
b: In 0.5 M $NaClO_4$.
c: The authors applied the hydrolysis constants from Grenthe and Lagerman [23] in 3 M $NaClO_4$ and their ionic strength corrections are based on SIT coefficients similar to those in Table 1.
d: The constants (extrapolated to I = 0 with the SIT, cf. Table 2) are based on experimental data in 0.1 M $KNO_3$ [20], 1 M $NaClO_4$ [21], and 3 M $NaClO_4$ [23].

hence the evaluation of the solubility products in 0.5 M $NaClO_4$ from the data at pH < 5:

Exp. data of Moon [29]:
$\log K'_{sp} = -43.5$ ($\log K^\circ_{sp} = -46.6$)

Exp. data of Östhols *et al.* [30]:
$\log K'_{sp} = -45.1$ ($\log K^\circ_{sp} = -48.2$) .

The solubility measured by Östhols *et al.* [30] for microcrystalline $ThO_2 \cdot xH_2O$(s) represents a lower limit for an amorphous precipitate. At this concentration level, polynuclear species are negligible. An absolute upper limit is obtained with $\log K^\circ_{sp} = -46.2$ (cf. dotted lines in Fig. 4b). According to these calculations, the solubility product of amorphous Th(IV) hydroxide or hydrous oxide is considered to be

$$\log K^\circ_{sp} = -47.0 \pm 0.8 \ .$$

In contrast to the large discrepancies between the solubility products reported by the different authors [8, 9, 29, 30] (cf. Table 8), the corresponding $\log K^\circ_{sp}$ values are in reasonable agreement if evaluated with the present set of hydrolysis constants including the literature data for $Th_4(OH)_{12}^{4+}$ and $Th_6(OH)_{15}^{9+}$. The polynuclear species $Th_2(OH)_2^{6+}$ and $Th_4(OH)_8^{8+}$ proposed in the literature [21−24] are found to be less suitable for modelling the experimental solubility data discussed above. As the solubilities in the pH range 3.5 to 4.5 decrease with a slope of about −4, they are much better fitted with a model that includes a hydroxide complex of charge +4. In this context, it should be emphasized that the high thorium concentrations in this pH range might also include a considerable amount of small colloids.

According to the solubilities in neutral to alkaline solutions ($\log [Th(OH)_4(aq)] = -8.5 \pm 0.6$ [8, 9, 29]) the solubility constant $\log K^\circ_{s(14)}$ and the formation constant of $Th(OH)_4$(aq) are calculated as

$$\log K^\circ_{s(14)} = -8.5 \pm 0.6$$

and

$$\log \beta^\circ_{14} = 38.5 \pm 1.0 \ .$$

The latter value is consistent with $\log \beta^\circ_{14} = 39.0 \pm 0.5$ from Ekberg *et al.* [24]. The constant solubility up to pH 13 (cf. Fig. 4) sets an upper limit for the formation of the anionic complex $Th(OH)_5^-$ ($\log \beta^\circ_{15} < 39.5$).

## Solubility of crystalline $ThO_2$(cr)

The solubility data determined by Moon [29] in 0.1 M $NaClO_4$ with $ThO_2$(cr) are shown in Fig. 5. At low pH they are comparable with the results of Baes *et al.* [21] at 95 °C in 1 M $NaClO_4$. The latter data are measured after addition of crystalline $ThO_2$(cr) to oversaturated acidic Th(IV) solutions. In a most recent paper Bundschuh *et al.* [31] report the solubility of colloidal $ThO_2$(cr) particles at I = 0.5 M (HCl/NaCl) and 25 °C. In this study coulometric pH titration is combined with laser-induced breakdown detection

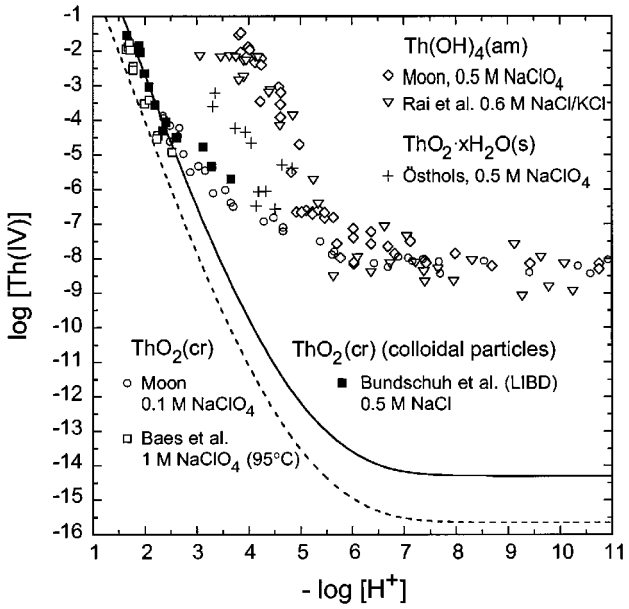


**Fig. 5.** Experimental and calculated solubility of $ThO_2$(cr) in comparison with Th(IV) hydroxide or hydrous oxide. The experimental data for $ThO_2$(cr) are from Moon [29] (0.1 M $NaClO_4$, 18 °C), Baes *et al.* [21]( 1 M $NaClO_4$, 95 °C) and from the LIBD study of Bundschuh *et al.* [31] (0.5 M NaCl, 25 °C). The solid line is calculated for I = 0.5 M with the selected hydrolysis constants and the experimental solubility product for small $ThO_2$(cr) particles (about 20 nm). The dashed line is based on the thermochemical value of $\log K^\circ_{sp}(ThO_2(cr)) = -54.2$ [50].

(LIBD) to determine the initial colloid formation as a function of the $H^+$ concentration in a series of $3 \cdot 10^{-2}$–$9 \cdot 10^{-5}$ M thorium solutions. Considering colloids as small solid particles, their formation indicates that the total thorium concentration reaches or just exceeds the solubility at given pH. The solubility product determined by this method is found to be log $K'_{sp} = -49.54 \pm 0.22$ in 0.5 M NaCl (log $K^\circ_{sp} = -52.8 \pm 0.3$). Because of the small diameter (about 20 nm) of the thorium colloids formed in these pH titration experiments, the equations of Schindler [55] are used to estimate the effect of particle size on the solubility product. Accordingly the solubility product of a bulk $ThO_2$(cr) crystal is expected to be about 1.2 orders of magnitude lower than that of the observed $ThO_2$ colloids. This result is in good agreement with log $K^\circ_{sp}(ThO_2(cr)) = -54.2 \pm 1.3$ [50] as calculated from thermochemical data.

In Fig. 5 the solubility of $ThO_2$(cr) is calculated as a function of the $H^+$ concentration with the hydrolysis constants selected in section 2. The two curves obtained with the experimental solubility product of log $K^\circ_{sp}(ThO_2$(coll)) $= -52.8$ [31] (solid line) and the thermochemical value of log $K^\circ_{sp}(ThO_2(cr)) = -54.2$ [50] (dashed line) can be considered as upper and lower limits, respectively. At pH $< 2.5$, the experimental solubility data for bulk or colloidal $ThO_2$(cr) decrease with a slope of $-4$. This indicates that the experimental data actually refer to the equilibrium between $ThO_2$(cr) and $Th^{4+}$(aq). However, with increasing pH the solubility data measured by Moon [29] with $ThO_2$(cr) deviate more and more from the expected solubility of $ThO_2$(cr) and at pH $> 6$ they become equal to those of $Th(OH)_4$(am). Comparable results are obtained when the LIBD experiment of Bundschuh *et al.* [31] is extended to lower thorium concentrations. Obviously the hydrolysis of the $Th^{4+}$(aq) ion at pH $> 2.5$ leads to increased Th(IV) concentrations, which are not in equilibrium with $ThO_2$(cr). For the pH range, where $An(OH)_4$(aq) is the predominant aqueous species, it must be concluded that the bulk crystalline solid is covered with an amorphous surface layer of $Th(OH)_4$(am).

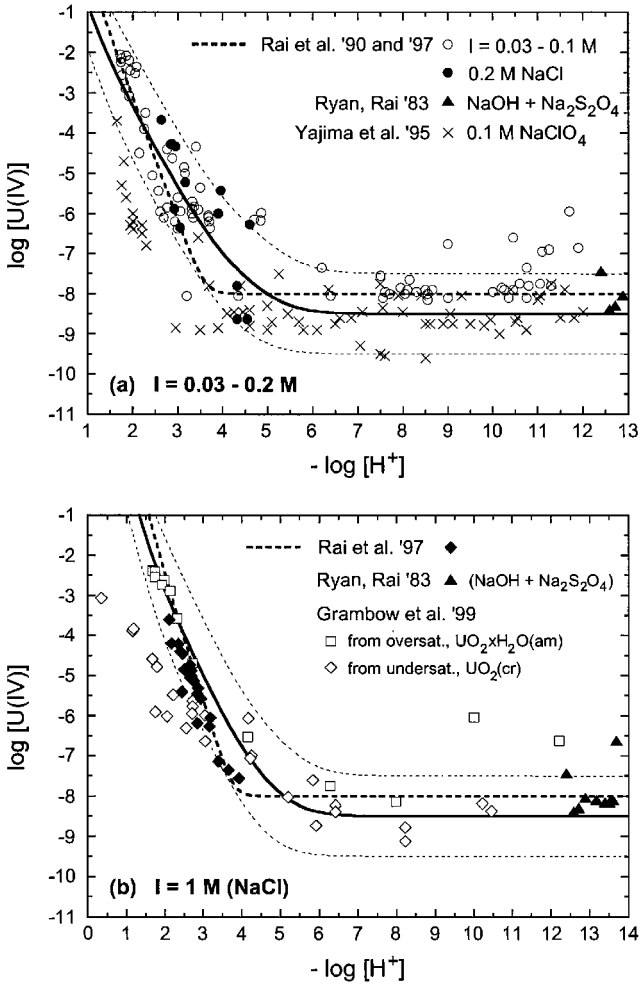


**Fig. 6.** Solubility of $UO_2$(s) as a function of the $H^+$ concentration at 20–25 °C, **(a)** at I = 0.03–0.2 M (above), **(b)** in 1 M NaCl (below). The experimental data are from Refs. [10, 11, 56–58]. The solid lines are calculated for 0.1 and 1 M NaCl, respectively, with log $K^\circ_{sp} = -54.5 \pm 1.0$ and the hydrolysis constants selected in the present paper. The dotted lines show the range of uncertainty. The dashed line is calculated with the model proposed by Rai *et al.* [10, 56].

### 3.2 Solubility of U(IV)

The solubilities reported in the literature for hydrous $UO_2 \cdot xH_2O$(s), amorphous or microcrystalline $UO_2$(s) are extremely scattered. As pointed out in the NEA review [7], they probably do not refer to a unique material, but rather to a range of solids with different thermodynamic stabilities. The experimental data in solutions of I = 0.03–0.2 mol/l and in 1.0 M NaCl are shown in Fig. 6a and b, respectively. Rai *et al.* [10, 56] determined the solubility of freshly precipitated $UO_2 \cdot xH_2O$(am) in NaCl and $MgCl_2$ solutions of various ionic strength. The solid was X-ray amorphous before and after the solubility measurements. Fe powder and $EuCl_2$ were added to prevent U(IV) from oxidation. An earlier study was performed in alkaline $NaOH/Na_2S_2O_4$ solutions containing Zn powder [58]. In comparable studies of Yajima *et al.* [11] (in 0.1 M $NaClO_4$) and Grambow *et al.* [57] (in 1 M NaCl), redox conditions were controlled electrochemically. Yajima *et al.* [11] observed an increase in crystallinity with the time of aging. Their solubilties in the range pH $< 5$ are several orders of magnitude below those observed by Rai *et al.* [10, 56] and Grambow *et al.* [57] for fresh precipitates.

In addition to the uncertainty involved in the solid phase, Rai *et al.* [10, 56] point out the difficulty to maintain properly reducing conditions. Even traces of dissolved oxygen cause at least partly oxidation of U(IV) to U(VI). It is clearly demonstrated that the high solubilities reported by Bruno *et al.* [59] and Gayer and Leider [60] (log [U] = $-4.4 \pm 0.4$ at pH 5–10 in 0.5 M $NaClO_4$ and $-5.3$ to $-4.2$ in alkaline NaOH solutions, respectively) are caused by oxidized U(VI) species. Rai *et al.* [56, 58] estimate the concentration of $U(OH)_4$(aq) in equilibrium with $UO_2 \cdot xH_2O$(am) to be about $10^{-8.0}$ mol/l, and a number of data with greater concentrations in the neutral and alkaline range are ascribed to the presence of U(VI). As discussed by Rai *et al.* [56, 58] there is no experimental verification for the formation of $U(OH)_5^-$ at high pH as claimed in earlier papers [1, 60].

In order to evaluate the solubility product of $UO_2 \cdot xH_2O$(am), the present calculations refer to the solubility data of Rai *et al.* [10, 56] and Grambow *et al.* [57]

**Table 9.** Different sets of thermodynamic constants (I = 0) for modelling the solubility of amorphous $UO_2 \cdot xH_2O$(s) at 25°C.

| | Rai *et al.* [10, 56] | Yajima *et al.* [11] | Present study |
|---|---|---|---|
| $\log K^\circ_{sp}$ | $-53.45$ | $-55.7 \pm 0.3$ | $-54.5 \pm 1.0$ |
| $\log \beta^\circ_{11}$ | 13.5 | – | $13.6 \pm 0.2$ |
| $\log \beta^\circ_{12}$ | – | – | $26.9 \pm 1.0$ |
| $\log \beta^\circ_{13}$ | – | – | $37.3 \pm 1.0$ |
| $\log \beta^\circ_{14}$ | 45.45 | $47.0 \pm 0.5$ | $46.0 \pm 1.4$ |

for fresh, amorphous precipitates in chloride solutions of $I \leq 1$ mol/l (Fig. 6a and b). Based on $\log \beta^\circ_{11} = 13.6 \pm 0.2$ [7, 32] and the estimated values of $\log \beta^\circ_{12} = 26.9 \pm 1$ and $\log \beta^\circ_{13} = 37.3 \pm 1$ (Table 6, section 2). the solubility product is calculated to be:

$$\log K^\circ_{sp} = -54.5 \pm 1.0 \ .$$

The reported solubilities may include polynuclear or colloidal species but there is no information available to quantitatify their presence. On the other hand, the solubility of $UO_2 \cdot xH_2O$(am) in acidic solution is several orders of magnitude below that of $ThO_2 \cdot xH_2O$(am) and hence, the effect of polynucleation can be considerably smaller.

In contrast to the data at low pH, the U(IV) concentrations at pH > 5 show no significant dependence on the initial solid phase, either fresh precipitates in experiments from oversaturation or electrodeposited microcrystalline $UO_2$(s) in undersaturation experiments [57]. Yajima *et al.* [11] evaluated a value of $\log [U(OH)_4(aq)] = -8.7 \pm 0.4$ from both over- and undersaturation experiments, independent of the degree of crystallinity. This is in fair agreement with the value of −8.0 proposed by Rai *et al.* [56]. Accepting the solubility data of these authors [11, 56−58] the following constants are obtained:

$$\log K^\circ_{s(14)} = -8.5 \pm 1.0$$

and

$$\log \beta^\circ_{14} = 46.0 \pm 1.4 \ .$$

The solubility calculated with the selected constants is shown as solid lines in Fig. 6a and b. The dashed lines represent the solubilities predicted by the model of Rai *et al.* [10, 56], which includes only the hydrolysis species $U(OH)^{3+}$ and $U(OH)_4$(aq). Yajima *et al.* [11] even proposed a simpler scheme, neglecting all hydrolysis species except of $U(OH)_4$(aq). These different sets of constants are shown for comparison in Table 9.

Parks and Pohl [61] investigated the solubility of crystalline uraninite in diluted chloride solutions ($I \leq 0.1$ mol/l, pH = 1.0−10.4) at 100−300 °C under a pressure of 500 bar $H_2$. No significant dependence on temperature could be observed (Fig. 7). The data at pH < 2 are comparable with the solubility calculated for $UO_2$(cr) at 25 °C with $\log K^\circ_{sp}(UO_2(cr)) = -60.85$, derived from $\Delta_f G^\circ(UO_2(cr)) = -1031.83 \pm 1.00$ kJ/mol [7], whereas the constant solubilities at pH > 4 ($\log [U(OH)_4(aq)] = -9.5 \pm 0.6$) are close to the data for $UO_2 \cdot xH_2O$(am) at 25°C. The comparison between the experimental solubility data at 100−300 °C and the calculated solubility curves at 25 °C (Fig. 7) supports the conclusion that the solubility data in neutral to alkaline solutions do not refer to $UO_2$(cr), but rather to an amorphous surface layer.

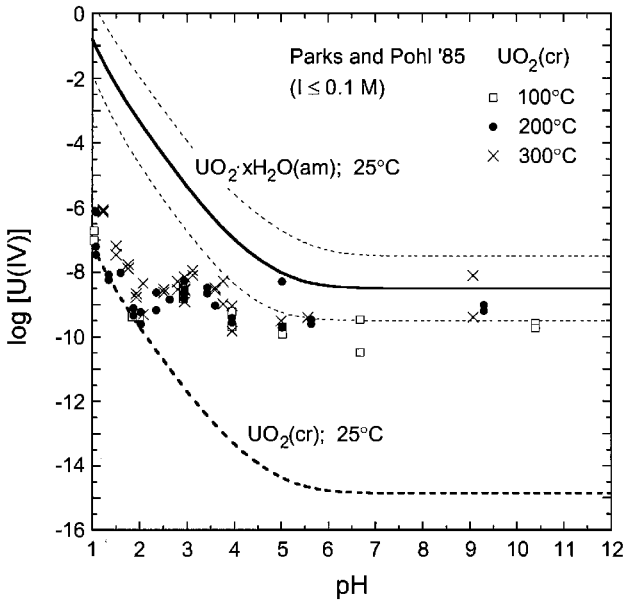


**Fig. 7** Solubility of $UO_2$(cr) at 100, 200 and 300 °C (Parks and Pohl [61]) in comparison with $UO_2 \cdot xH_2O$(am) and $UO_2$(cr) at 25°C. The solubility curves at 25 °C are calculated for I = 0.1 M with the constants selected in the present study and $\log K^\circ_{sp}(UO_2(cr)) = -60.85 \pm 0.3$ [7].

### 3.3 Solubility of Np(IV)

The solubility of Np(IV) hydrous oxide in acidic solutions has been investigated by Rai *et al.* [50] in the presence of $CuCl/CuCl_2$ redox buffer in solutions of low ionic strength (I = 0.02−0.04 mol/l). The oxidation state of the dissolved neptunium, Np(IV) and Np(V), was determined by solvent extraction with TTA. Based on $\log K^\circ_{11} = -1.5$ and neglecting further hydrolysis species, the solubility product was calculated to be $\log K^\circ_{sp} = -54.5 \pm 0.3$. However, accepting the hydrolysis constants from Duplessis and Guillaumont ($\log \beta^\circ_{11} = 14.5 \pm 0.2$, $\log \beta^\circ_{12} = 28.3 \pm 0.3$ [44]) selected in section 2, the following solubility product is calculated from the experimental data of Rai *et al.* [50]:

$$\log K^\circ_{sp} = -56.7 \pm 0.4 \ .$$

Rai *et al.* [50] disregarded a couple of their experimental data, because the dissolved Np(IV) was only about 5% of the total Np concentration, but within the range of uncertainty, these data agree also with the present calculation (solid line in Fig. 8).

The solubility at pH > 6 was determined by Rai *et al.* [62] in NaOH solutions containing reducing agents ($Na_2S_2O_4$, Fe or Zn) and by Eriksen *et al.* [63] in 0.5 M $NaClO_4$ containing $Na_2S_2O_4$. The observed neptunium concentrations were at or below the detection limit ($\log [Np] \leq -8.3 \pm 0.3$). Similar results, with log [Np] in the range −8 to −9.5, were reported by Nakayama *et al.* [64] at pH = 6−14 in 0.1 and 1 M $NaClO_4$/NaOH containing $Na_2S_2O_4$, Fe or Cu. As small contributions of oxidized

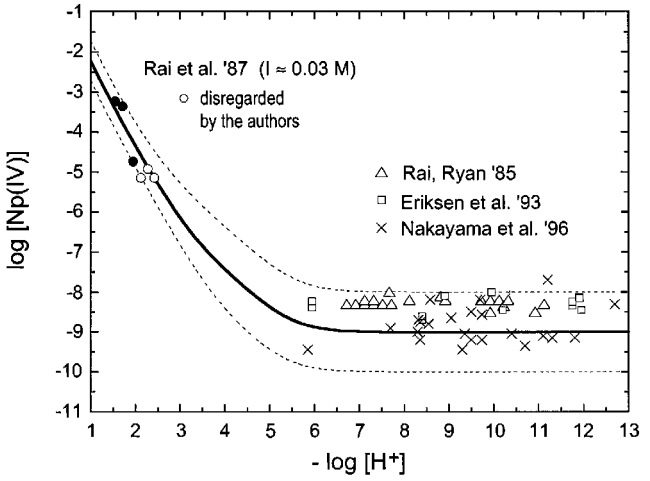


**Fig. 8** Solubility of Np(IV) hydrous oxide as a function of the $H^+$ concentration at 25 °C. Experimental data in acidic solutions of low ionic strength from Ref. [50], in the range pH = 6−13 from Refs. [62−64]. The solid line is calculated for I = 0.03 M, with $\log K^\circ_{sp} = -56.7 \pm 0.5$ and the selected hydrolysis constants. The dotted lines show the range of uncertainty.

Np(V) can increase the total Np concentration, and the oxidation state of Np can hardly be ascertained as Np(IV), when the concentration is at the detection limit, the following constants are selected:

$$\log K^\circ_{s(14)} = -9.0 \pm 1.0$$

and

$$\log \beta^\circ_{14} = 47.7 \pm 1.1 \ .$$

Within the range of uncertainty the formation constant of $Np(OH)_4(aq)$ agrees with the estimations in Table 6, $\log \beta^\circ_{14} = 46.6$(A) and 47.5(B). Therefore the estimated constant of $\log \beta^\circ_{13} = 39.2 \pm 1$ is also considered to be a reasonable approximation. There is no indication for the formation of $Np(OH)_5^-$ at pH = 12−14 [62−64], which sets an upper limit for its formation constant ($\log \beta^\circ_{15} < 48.5$).

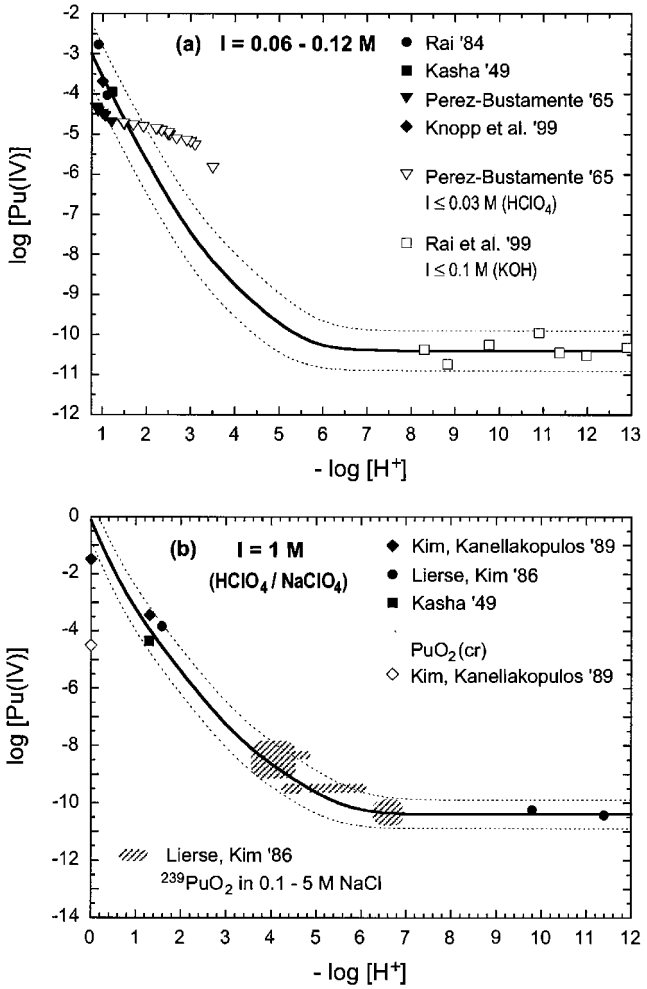


**Fig. 9.** Solubility of Pu(IV) hydrous oxide as a function of the $H^+$ concentration at 20−25 °C, **(a)** at low ionic strength (above), **(b)** in 1 M $HClO_4/NaClO_4$ (below). The experimental data are from Refs. [3, 45, 65−68, 70]. The solid lines are calculated for I = 0.1 and 1.0 M, respectively, with $\log K^\circ_{sp} = -58.5 \pm 0.7$, hydrolysis constants from Metivier and Guillaumont [43], and $\log K^\circ_{s(14)} = -10.4 \pm 0.5$. The dotted lines show the range of uncertainty.

### 3.4 Solubility of Pu(IV)

The solubility of amorphous $Pu(OH)_4$(am) or $PuO_2 \cdot xH_2O$(am), has been investigated in numerous studies [3, 4, 45, 65−72]. However, particularly at pH > 1.5, Pu(IV) is easily oxidized to Pu(V) and disproportionation reactions lead to Pu(III) and Pu(VI) [3, 4, 66, 69, 73]. The solubility product can only be evaluated from well ascertained Pu(IV) concentrations, i.e. from experimental studies where the oxidation state of the aqueous species is controlled by solvent extraction or spectroscopic methods [3, 45, 65−69]. The data of Pérez-Bustamente [70] in $3 \cdot 10^{-4}$−0.03 M $HClO_4$ (Fig. 9a) represent a typical example for the solubility increase due to aqueous species of other oxidation states. Similar data are reported in other papers [4, 67, 71, 72], with aqueous species of different oxidation states being predominant and the fraction of Pu(IV) not known.

Contributions from Pu(IV) colloids is another possible source of error. As demonstrated by Kim and Kanellakopulos [3], colloidal Pu(IV) can be present even at pH = 0−1 and the total Pu concentration below $10^{-3}$ mol/l. However, the reported solubility data are usually measured after filtration in order to minimize this effect. According to the filtration and LIBD experiments of Knopp *et al.* [45], the greatest part of colloidal Pu(IV) is removed by filtration at filter pore sizes of 1 nm. The error in evaluating $\log K_{sp}$ from solubility data, which possibly include a certain amount of colloids, does not exceed the range of other uncertainties (e.g. different crystallinities of solids). In this recent paper [45] it is further demonstrated that the hydrolysis constants of Metivier and Guillaumont [43] (cf. section 2.1, Table 4) correctly predict the pH-dependence of the solubility of Pu(IV) hydroxide or hydrous oxide. Based on these hydrolysis constants, a mean value of $\log K^\circ_{sp} = -58.7 \pm 0.9$ is calculated from the available solubility data at I = 0.06−1 mol/l and pH = 0−12.

A similar value, $\log K^\circ_{sp}(Pu(OH)_4(am)) = -58.3 \pm 0.5$, is determined by Capdevila and Vitorge [69] with an indirect method. In that study, the solubility of $Pu(OH)_4$(am) is investigated in 0.1−3 M $HClO_4/NaClO_4$ under conditions, where $PuO_2^+$, $PuO_2^{2+}$ and $Pu^{3+}$ are the predominant aqueous species. When the disproportionation reaction re-

**Table 10.** Experimental solubility data for Pu(IV) hydroxide/hydrous oxide at 20−25 °C and the solubility products calculated on the basis of the hydrolysis constants of Metivier and Guillaumont [43].

| Authors/Medium | log $[Pu(IV)]_{tot}$ | log $K'_{sp}$ | log $K^\circ_{sp}$ |
|---|---|---|---|
| Kasha '49 [65] | | | |
| 1 M $NaClO_4$/0.05 M $H^+$ | −4.34 | −55.9 ± 0.3 | −58.9 ± 0.3 |
| 0.06 M HCl | −3.95 | −56.6 ± 0.3 | −58.4 ± 0.3 |
| Pérez-Bustamente '65 [70] | | | |
| 0.06−0.12 M $HClO_4$ | −4.72 to −4.35 | −57.4 ± 0.4 | −59.4 ± 0.4 |
| 0.25−0.29 M $HClO_4$ | −3.96 ± 0.03 | −57.3 ± 0.3 | −59.9 ± 0.3 |
| Rai '84 [66] | | | |
| I = 0.112 M, pH = 1.00[a] | −2.77 | −55.8 ± 0.3 | −58.0 ± 0.3 |
| I = 0.064 M, pH = 1.20[a] | −4.03 | −56.9 ± 0.3 | −58.7 ± 0.3 |
| Lierse and Kim '86 [67] | | | |
| 1 M $NaClO_4$, $pH_{exp}$ = 1.38[b] | −3.83 | −54.8 ± 0.3 | −57.8 ± 0.3 |
| 1 M $NaClO_4$, $pH_{exp}$ = 9−12 | −10.4 ± 0.2 | −54.9 ± 0.6 | −57.9 ± 0.6 |
| Kim and Kanellakopulos '89 [3] | | | |
| 1 M $HClO_4$ | −1.48 | −56.9 ± 0.2 | −59.9 ± 0.3 |
| 1 M $NaClO_4$, $pH_{exp}$ = 1.09[b] | −3.44 | −55.0 ± 0.3 | −58.0 ± 0.3 |
| Knopp *et al.* '99 [45] | | | |
| 0.1 M $HClO_4$ | −3.7[c] | −56.5 ± 0.3 | −58.6 ± 0.3 |
| Rai *et al.* '99 [68] | | | |
| ≤0.1 M KOH, pH = 8−13 | −10.4 ± 0.5 | | −57.9 ± 0.7 |
| Capdevila and Vitorge '98 [69] | | | |
| 0.1 M $HClO_4$ | − | −55.9 ± 0.3[d] | −58.0 ± 0.3 |
| 0.1 M $HClO_4$/0.4 M $NaClO_4$ | − | −55.7 ± 0.3[d] | −58.7 ± 0.3 |
| 0.1 M $HClO_4$/0.9 M $NaClO_4$ | − | −55.0 ± 0.3[d] | −58.0 ± 0.3 |
| 0.1 M $HClO_4$/1.9 M $NaClO_4$ | − | −56.0 ± 0.3[d] | −58.4 ± 0.3 |
| 0.1 M $HClO_4$/2.9 M $NaClO_4$ | − | −56.7 ± 0.3[d] | −58.1 ± 0.3 |

a: The $H^+$ concentration is derived from pH = − log $[H^+]$ − log $\gamma_{H^+}$ by calculating the activity coefficients $\gamma_{H^+}$ with the SIT equation.
b: The $H^+$ concentration is calculated with the relation: log $[H^+]$ = − $pH_{exp}$ − 0.23 [74] for pH measuremeants with Ross electrodes (3 M NaCl junction) in 1 M $NaClO_4$
c: Pu(IV) concentration in equilibrium with colloidal $Pu(OH)_4$(am) particles.
d: Determined by an indirect method, independent of Pu(IV) hydrolysis reactions (see text).

aches the equilibrium state, the $Pu^{4+}$ concentration can be calculated from the known redox potentials $E(Pu^{4+}/Pu^{3+})$ and $E(PuO_2^{2+}/PuO_2^{+})$ and the spectroscopically determined concentrations of $PuO_2^{+}$, $PuO_2^{2+}$, and $Pu^{3+}$. The agreement between the solubiliy products evaluated in these papers [45, 69] is noteworthy, because they are based on completely different methods. The calculation of Knopp *et al.* [45] depends directly on Pu(IV) solubilities and the selected Pu(IV) hydrolysis constants, whereas the indirect determination of Capdevila and Vitorge [69], which relies on redox equilibria, is independent of Pu(IV) hydrolysis reactions. The SIT coefficients for the extrapolation to I = 0 [45, 69] are also used in the present work. The average from all experimental data listed in Table 10 is considered to represent a best value for the solubility product of amorphous Pu(IV) hydroxide or hydrous oxide:

$$\log K^\circ_{sp} = -58.5 \pm 0.7 \ .$$

Combining this solubility product with $\log \beta^\circ_{14} = 47.5 \pm 0.5$ from the solvent extraction study of Metivier and Guillaumont [43], the solubility in neutral to alkaline solutions is calculated to be log $[Pu(OH)_4(aq)] = -11.0 \pm 0.9$. Within the uncertainty range this value covers the experimental data of Lierse and Kim [67] and Rai *et al.* [68] (log $[Pu(IV)] = -10.4 \pm 0.5$ at pH > 7). *Vice versa*, these solubility data are best fitted with somewhat different constants:

$$\log K^\circ_{s(14)} = -10.4 \pm 0.5$$

and

$$\log \beta^\circ_{14} = 48.1 \pm 0.9 \ .$$

In Fig. 9a and b the solubility of Pu(IV) is calculated with the hydrolysis constants $\log \beta^\circ_{11}$, $\log \beta^\circ_{12}$, $\log \beta^\circ_{13}$ from Metivier and Guillaumont [43], $\log K^\circ_{sp} = -58.5 \pm 0.7$ and $\log K^\circ_{s(14)} = -10.4 \pm 0.5$ and compared with the experimental solubilities in diluted solutions of I ≤ 0.1 mol/l and in 1 M $HClO_4$/$NaClO_4$. Within the range of uncertainty, the calculated solubility covers also some data reported by Lierse and Kim [67] for $^{239}PuO_2$(s) in 0.1−5 M NaCl in the range pH = 3−7. There is no indication for the formation of $Pu(OH)_5^-$ up to pH 13, which corresponds to an upper limit of $\log \beta^\circ_{14} < 49$.

Kim and Kanellakopulos [3] investigated the solubility of crystalline $PuO_2$(cr) sintered at 900 °C (Fig. 9b). From the Pu(IV) concentration measured at 20 °C after equilibration for 3 years in 1 M $HClO_4$ (log $[Pu(IV)] = -4.5 \pm 0.2$) a solubility product of $\log K^\circ_{sp} = -62.9 \pm 0.4$ is calculated. This value differs about an order of magnitude from those calculated for $PuO_2$(cr) from thermochemical data ($\log K^\circ_{sp}(PuO_2(cr)) = -63.8 \pm 1.0$ [3] and $-64.1 \pm 0.7$ [50]).

**Table 11.** Selected thermodynamic data for aqueous An(IV) hydrolysis species and solid An(IV) oxides and hydroxides at I = 0 and 25 °C.

| | Th(IV) | U(IV) | Np(IV) | Pu(IV) |
|---|---|---|---|---|
| log $K^\circ_{sp}$ | | | | |
| $AnO_2$(cr) | $-54.2 \pm 1.3^a$ | $-60.86 \pm 0.36^a$ | $-63.7 \pm 1.8^a$ | $-64.0 \pm 1.2^a$ |
| $An(OH)_4$(am)/ $AnO_2 \cdot xH_2O$(am) | $-47.0 \pm 0.8$ | $-54.5 \pm 1.0$ | $-56.7 \pm 0.5$ | $-58.5 \pm 0.7$ |
| log $K^\circ_{s(14)}$ | $-8.5 \pm 0.6^b$ | $-8.5 \pm 1.0^b$ | $-9.0 \pm 1.0^b$ | $-10.4 \pm 0.5^b$ |
| log $\beta^\circ_{xy}$ | | | | |
| $An(OH)^{3+}$ | $11.8 \pm 0.2^c$ | $13.6 \pm 0.2^d$ | $14.5 \pm 0.2^e$ | $14.6 \pm 0.2^e$ |
| $An(OH)_2^{2+}$ | $22.0 \pm 0.6^c$ | $26.9 \pm 1.0^f$ | $28.3 \pm 0.3^e$ | $28.6 \pm 0.3^e$ |
| $An(OH)_3^{+}$ | $31.0 \pm 1.0^c$ | $37.3 \pm 1.0^f$ | $39.2 \pm 1.0^f$ | $39.7 \pm 0.4^e$ |
| $An(OH)_4$(aq) | $(39.0 \pm 0.5)^c$ | $(44.7 \pm 1.0)^f$ | $(47.1 \pm 1.0)^f$ | $(47.5 \pm 0.5)^e$ |
| | $38.5 \pm 1.0^b$ | $46.0 \pm 1.4^b$ | $47.7 \pm 1.1^b$ | $48.1 \pm 0.9^b$ |
| $An(OH)_5^{-}$ | $<39.5^b$ | $<47^b$ | $<48.5^b$ | $<49^b$ |
| $An_4(OH)_{12}^{4+}$ | $141.3^c$ | | | |
| $An_6(OH)_{15}^{9+}$ | $176.0^c$ | | | |

a: Calculated in Refs. [3, 7, 50] from thermochemical data.
b: From experimental solubility data in neutral to alkaline solutions: $\log K^\circ_{s(14)} = \log [An(OH)_4(aq)] = \log K^\circ_{sp}(AnO_2 \cdot xH_2O(am)) + \log \beta^\circ_{14}$.
c: Selected from potentiometric and solvent extraction studies [20−24, 27] (cf. section 2). The polynuclear Th(IV) species are adopted from the model of Brown *et al.* [20].
d: Taken from the NEA and IAEA reviews [7, 32].
e: From solvent extraction studies of Guillaumont *et al.* [43, 44].
f: Estimated in the present work.

## 4. Conclusions and summary of thermodynamic constants

The hydrolysis constants and solubility products of An(IV) oxides and hydroxides selected in the present review are summarized in Table 11. The formation constants of mononuclear hydrolysis species are taken from the literature, preferentially from the studies at low An(IV) concentrations. The constants $\log \beta^\circ_{12}$ and $\log \beta^\circ_{13}$ for U(IV) and $\log \beta^\circ_{13}$ for Np(IV) are estimated, because no experimental data are available. The constants $\log \beta^\circ_{14}$ and the upper limits for $\log \beta^\circ_{15}$ are derived from solubility data in neutral to alkaline solutions. The high solubility of amorphous Th(IV) precipitates at low pH include considerable contributions of polynuclear species as proposed in potentiometric titration studies or small colloids. The essentially lower solubilities of U(IV), Np(IV), and Pu(IV) can be calculated by taking only mononuclear species into account. The contributions of polynuclear and colloidal species do not exceed 0.5−1.0 orders of magnitude, which is within the uncertainty range of the evaluated solubility products.

The An(IV) concentrations measured in acidic solutions depend strongly on the pretreatment and alteration of the solid phase. Solubility data measured at pH = 0−3 with crystalline $ThO_2$(cr), $UO_2$(cr), and $PuO_2$(cr) are considerably lower than those of the corresponding amorphous precipitates, even after equilibration periods of several months or years. The opposite behaviour has been observed in neutral and alkaline solutions, where $An(OH)_4$(aq) is the predominant aqueous species: the measured solubilities are independent of whether $AnO_2$(cr) or $AnO_2 \cdot xH_2O$(am) is used as the initial solid phase, although the solubility products of the crystalline An(IV) dioxides are about 6−7 orders of magnitude lower than those of the amorphous hydroxides or hydrous oxides. Since the pH-independent solubilities in this range correspond to the sums $(\log K^\circ_{sp}(AnO_2 \cdot xH_2O(am)) + \log \beta^\circ_{14})$, it is assumed that a bulk crystalline dioxide must be covered with an amorphous surface layer. The solubility data measured for $ThO_2$(cr) and $UO_2$(cr) indicate that the crystalline dioxide remains the solubility limiting solid only at very low pH, where $An^{4+}$(aq) is the predominant aqueous species. If the $An^{4+}$ ion undergoes hydrolysis reactions, e.g. at pH > 2.5 in the case of Th(IV), the dissolution of $AnO_2$(cr) seems to become quasi-irreversible. Further investigations are neede to verify this hypothesis and to ascertain the chemical form of the solubility limiting solid in natural systems.

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