# Complexation of Th(IV) and Eu(III) by α-isosaccharinic acid under alkaline conditions

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**Summary.** The complexation of Th(IV) and Eu(III) by α-isosaccharinic acid (ISA) has been studied in the pH range from 10.7 to 13.3 by batch sorption experiments, and the influence of Ca on the complexation was investigated. Sixteen data sets – each determined at variable ISA concentrations – are used to determine the stoichiometry of the complexation reactions and the stability constants. Based on best-fit analysis of the sorption data, it is postulated that 1:1 Th:ISA complexes are formed in the absence of Ca according to the complexation reaction: $Th + ISA \leftrightarrows (ThISA)_{-4H} + 4H$ with $\log K = -10.1$ at $I = 0.3$ M. In the presence of Ca, the sorption data can be interpreted best by a mixed-metal complex, according to the complexation reaction: $Th + 2ISA + Ca \leftrightarrows (Th(ISA)_2Ca)_{-4H} + 4H$ with $\log K^{Ca} = -3.6$ at $I = 0.3$ M. There are no indications that Ca participates in complexes of ISA with Eu. The sorption data suggest that 1:1 Eu:ISA complexes are dominant in the pH range from 10.7 to 13.3 according to the complexation reaction: $Eu + ISA \leftrightarrows (EuISA)_{-4H} + 4H$ with $\log K = -30.6$ at $I = 0.3$ M. It is important to note that the stoichiometric numbers and stability constants proposed here are not independent of the hydrolysis reactions of the two metal cations. Thus, the same hydrolysis data as used here have to be applied in speciation calculations with the ISA complexation data for Eu(III) and Th(IV).

## 1. Introduction

The importance of α-isosaccharinic acid (ISA) as a key ligand formed from cellulose-containing waste conditioned in a cementitious environment, is widely accepted [1–5]. In these publications it has been shown that, among the various degradation products formed during the (abiotic) alkaline degradation of cellulose, ISA is the most important product, both concerning the amount formed and the complexing strength. However, with regard to a stoichiometric description of the complexation reactions between radionuclides and ISA, only little is known. To this end, only apparent stability constants are given in the literature for the interaction

between a few safety-relevant nuclides and ISA [5–7]. Apparent stability constants (sometimes also known as conditional stability constants) reduce the stoichiometric relation between the metal and the ligand and additional reactants to a simple metal-ligand interaction. Side reactions, such as the hydrolysis of the metal ion or the protonation of the ligand, do not have to be known. These constants are easier to determine than the corresponding thermodynamic constants; their use, however, is restricted to the conditions at which they were evaluated. Equilibrium constants for systems that include formation of protons upon complexation of the metal ion are available only for the interaction between Np(IV) and ISA [8]. The pH of these experiments was restricted to a range between 2 and 8. Thus, it is not *a priori* clear, whether these results can be applied to the pH range of interest in the present work.

The influence of Ca on the formation of complexes between Th(IV) and ISA at pH 12.8 and 13.3 has recently been shown [6]. Through high performance ion exchange chromatography (HPIEC) and batch sorption experiments, these authors demonstrated that

(i) in the absence of Ca, 1:1 Th:ISA complexes are formed and
(ii) in the presence of Ca, 1:2:2 Th:ISA:Ca complexes are formed.

It is the aim of the present work to determine the thermodynamic equilibrium constants involved in complex formation between Th(IV) and ISA and the stoichiometric contributions of protons and $Ca^{2+}$ ions involved. For this purpose, batch sorption experiments are carried out, in which pH and concentration of $Ca^{2+}$ are varied. Such experiments can elucidate the stoichiometry of the reactions, i.e. they allow the number of protons and $Ca^{2+}$ ions involved in the complexation reactions to be calculated. In parallel, the complexation of Eu(III) by ISA is also studied. Note that both Eu(III) and Th(IV) are broadly used as redox-insensitive analogues for safety-relevant tri- and tetravalent radionuclides, such as Pu which exhibit a more complicated redox chemistry [9].

## 2. Experimental

All experiments were performed at $23 \pm 2\,°C$ in a glovebox under $N_2$ atmosphere ($O_2$, $CO_2 < 1$ ppm). Doubly-demineralised water, additionally conditioned by ultrafiltra-

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tion with a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used. ISA was supplied as ISA lactone, which was prepared according to a modification [10] of a procedure described by Whistler and BeMiller [11]. ISA lactone hydrolyses in the presence of NaOH to form the open chain form of ISA. A stoichiometric amount of NaOH was therefore added to alkaline solutions of ISA lactone in order to prevent changes in pH. Carrier free Th-234 was prepared by extraction from uranyl nitrate using the method of Dyrssen [12]. Eu-152 was purchased from Amersham Pharmacia Biotech (Dübendorf, Switzerland). Both radionuclides were kept in slightly acidic stock solutions.

pH (activity scale) was measured using a glass electrode (ORION, ROSS Combination pH Electrode). The electrode was calibrated with solutions containing different concentrations of NaOH and suitable amounts of $NaClO_4$ to keep the ionic strength at $\sim 0.3$ M. The proton activity of the calibration solutions was calculated from their hydroxide concentration using activity coefficients obtained by the Davies equation.

The experiments were performed in 40 ml polyallomer centrifuge tubes. Each data point – at given pH, Ca and ISA concentration – was measured in triplicate. Depending on pH and type of radionuclide used, different solid phases were used to obtain optimum working conditions. The sorption of Th(IV) at pH 10.7 was studied on 50–60 mg of feldspar (orthoclase $KAlSi_3O_8$, Fronland, Norway, 63 $\mu$m), at pH 12.0 directly on the polyallomer centrifuge tube, and at pH 13.3 on 100 mg of BioRad 50W-X2 resin. To study the sorption of Eu(III) at the three pH values, 10–15 mg of feldspar (orthoclase $KAlSi_3O_8$, Fronland, Norway, 63 $\mu$m) was used.

For the experiments performed in the absence of Ca, 15 ml aliquots of stock solutions were added to the solid phase. The stock solutions contained ISA at concentrations between $10^{-8}$ and $10^{-2}$ M or no ISA. The pH and ionic strength of the stock solutions were adjusted to the desired values using 1 M NaOH and 1 M $NaClO_4$, respectively ($I = 0.3$ M). Finally, the stock solutions were spiked with Th-234 to give an activity of 200 Bq/ml and a total Th concentration of $1.2$–$1.6 \times 10^{-13}$ M. For the experiments with Eu(III), the stock solutions were spiked with Eu-152 to give an activity of 500 Bq/ml. The total Eu concentration was $5 \times 10^{-10}$ M.

The preparation of the samples for the experiments performed in the presence of Ca was the same as described above except that Ca was added before spiking the stock solutions with Th-234 or Eu-152. For the experiments at pH 12.0 and 10.7, Ca was supplied as $Ca(NO_3)_2$ to give total Ca concentrations of 0.7 mM and 10 mM in the case of Th. For the Eu experiments at pH 12.0 and 10.7 the total Ca concentrations were 1.8 mM and 10 mM. For Th experiments performed at pH 13.3, however, the stock solutions were made starting from a 0.3 M NaOH solution saturated with $Ca(OH)_2$ (solubility of $Ca(OH)_2$ at pH 13.3 is $\sim 1.8$ mM Ca). After equilibration with the resin at pH 13.3, the concentration of total Ca in solution, as measured by ICP-OES (ARL 3410 ICP with Minitorch™), was 0.35 mM for the experiments with Th. This decrease was caused by the sorption of Ca on the resin. For the experiments with Eu at pH 13.3,

the concentration of Ca in solution was found to be unchanged in the presence of feldspar.

After equilibrating the suspensions for 3 days (Th) and 4 days (Eu) on an end-over-end shaker, the tubes were centrifuged (48 360 g, 30 min.). The activity of Th-234 in the supernatant was determined by measuring the Cerenkov radiation mainly caused by the daughter isotope Pa-234m. The activity of Eu-152 in the supernatant was measured by $\gamma$-counting. For some experiments, pH was measured after centrifugation and found to remain unchanged with respect to the initial pH of the stock solutions.

Next, the tubes were emptied, rinsed with water to remove all solid material and filled with 15 ml of a 0.2 M $HNO_3$ solution to desorb Th or Eu from the wall of the tubes. After one day of end-over-end shaking, the Th-234 or Eu-152 activities in these acid extracts were analysed.

The distribution of Th or Eu between the solid phase and the solution is given by the distribution coefficient $K_d$ and was calculated as follows:

$$K_d = \left( \frac{A_{input} - A_{wall} - A_{eq}}{A_{eq}} \right) \left( \frac{V}{W} \right) \tag{1}$$

with $A_{input}$ = activity of the radionuclide added to the system (cpm/ml),

$A_{eq}$ = activity of the radionuclide in the equilibrium solution (cpm/ml),

$A_{wall}$ = activity of the radionuclide sorbed on the tube wall (cpm/ml),

$V$ = volume of the suspension (ml),

$W$ = mass of solid (g).

The systems obey the required conditions for applying this batch sorption technique. It was found that the reference sorption isotherm for Th on the resin was linear at pH 13.3. In view of the low Th ($1.2$–$1.6 \times 10^{-13}$ M) and Eu ($5 \times 10^{-10}$ M) concentrations, it is reasonable to assume that the reference sorption isotherm for the other solid phases and pH values is also linear [13, 14] and that the formation of polynuclear complexes can be excluded. At pH 13.3, the resin is known to be chemically stable (manufacturer's specifications and [15]). Test experiments with feldspar at pH 10.7, 12.0 and 13.3, in which the concentration of K, Si and Al in the supernatant was monitored as a function of time, showed changes only near the experimental uncertainty. Therefore, the possible chemical instability of feldspar and changes in surface properties were assumed to be negligible for this work. Further, from the experimental data at high ISA concentrations, it was concluded that the sorption of Th and Eu on the solid phases was reversible. Finally, test experiments showed the absence of ISA sorption on the resin and feldspar at pH 13.3. It was assumed that neither ISA, nor complexed species sorbed on the polyallomer tube or on feldspar at pH 10.7 and 12.0.

## 3. Results and discussion

The distribution of Th and Eu between the sorbing and the solution phase, given by the $K_d$ values, was determined for Th(IV) and Eu(III) at different pH and Ca concentrations. For each combination of pH and Ca, the ISA concentration was varied between 0 and $10^{-2}$ M. A typical dataset is
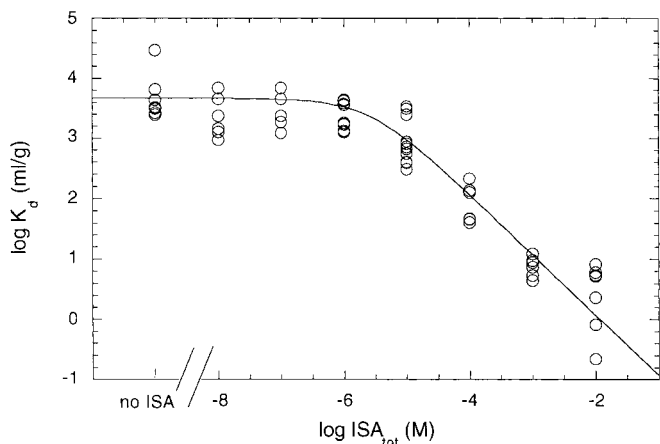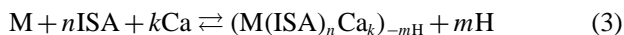
**Fig. 1.** Influence of ISA on the sorption of Th on an ion exchange resin at pH 13.3 in the absence of Ca. The experimental data are fitted to Eq. (6) with $n = 1$.

graphically displayed in Fig. 1[1]. A model previously proposed [17] was used to fit the data. Because of the limited information on the complexation of Eu with ISA at alkaline pH in the literature [5], it is assumed, as a first step, that the formation of Eu-ISA complexes is analogous to the Th-ISA complexes. The model comprises two complexation reactions, i.e.

$$M + n\text{ISA} \rightleftarrows (M(\text{ISA})_n)_{-m\text{H}} + m\text{H} \qquad (2)$$
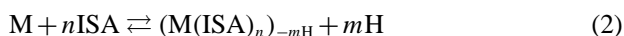
with $n = 1$, in the absence of Ca, and

$$M + n\text{ISA} + k\text{Ca} \rightleftarrows (M(\text{ISA})_n\text{Ca}_k)_{-m\text{H}} + m\text{H} \qquad (3)$$

with $n = 2$, in the presence of Ca. M denotes $Eu^{3+}$ or $Th^{4+}$, respectively, and ISA denotes the α-isosaccharinate ion, i.e. with a deprotonated carboxylic group. Charges are omitted for simplicity. The reasons for including protons in reactions (Eqs. (2) and (3)) are the hydrolysis of Th(IV), Eu(III) and Ca, and the observation that the co-ordination of polyhydroxy ligands with charged cations at alkaline pH is accompanied by deprotonation of the coordinating hydroxo groups [17–22].

The thermodynamic complexation constants ($K$ and $K^{Ca}$) associated to Eqs. (2) and (3) can be written as (note that the nomenclature for equilibrium constants has been slightly modified compared to [6]):

$$K = \frac{[(M(\text{ISA})_n)_{-m\text{H}}] \cdot [\text{H}]^m}{[M] \cdot [\text{ISA}]^n} \qquad (4)$$

and

$$K^{Ca} = \frac{[(M(\text{ISA})_n\text{Ca}_k)_{-m\text{H}}] \cdot [\text{H}]^m}{[M] \cdot [\text{ISA}]^n \cdot [\text{Ca}]^k} . \qquad (5)$$

Brackets denote molar concentrations of the species. For the experimental conditions applied here, the concentration of free ISA in Eqs. (4) and (5) can be approximated by the total ISA concentration, $[\text{ISA}]_{\text{tot}}$, because

(i) the total concentrations of Th and Eu in the experiments are much smaller than the total concentration of ISA,

(ii) the concentration of CaISA-species is negligible with respect to the total ISA concentration (as shown by speciation calculations using the stability constants of [17]) and

(iii) the deprotonation of the hydroxy groups is estimated to occur only at very high pH ($pK_a \approx 13\text{–}15$ [23]).

The dependence of $K_d$ on the ISA concentration, as expressed by apparent stability constants, can be described by [6, 24]

$$\log K_d = \log K_d^0 - \log\left(1 + \frac{\beta}{A}([\text{ISA}]_{\text{tot}})^n\right) \qquad (6)$$

for the complexation reaction in the absence of Ca, and by

$$\log K_d = \log K_d^0 - \log\left(1 + \frac{\beta^{Ca}}{A}([\text{ISA}]_{\text{tot}})^n\right) \qquad (7)$$

for the complexation reaction in the presence of Ca. $\beta$ and $\beta^{Ca}$, the apparent stability constants, are defined as:

$$\beta = \frac{K}{[\text{H}]^m} \qquad (8)$$

and

$$\beta^{Ca} = \frac{K^{Ca} \cdot [\text{Ca}]^k}{[\text{H}]^m} . \qquad (9)$$

$K_d^0$ in Eqs. (6) and (7) is the distribution coefficient measured in the absence of ISA and $n$ is the number of ISA ligands coordinated to one metal ion. $A$ is the side reaction coefficient for the hydrolysis of Th and Eu and can in both cases be approximated by Eq. (10), because tetrahydroxo complexes are the dominant inorganic Th(IV) and Eu(III) species [25]:

$$A \cong 1 + \beta_4^{OH} \cdot [\text{OH}]^4 . \qquad (10)$$

### 3.1 First step: Determination of the number of ISA molecules involved in the complexes

When plotting $\log K_d$ against $\log [\text{ISA}]_{\text{tot}}$ and fitting the experimental results by Eqs. (6) or (7), the intercept of the fitting curve with the $Y$-axis equals $\log K_d^0$. The number of ligands, $n$, participating in the ISA complexes is derived from the slope of the fitting curve in the region where $\log K_d$ is dependent on the ISA concentration. $\beta/A$ and $\beta^{Ca}/A$ are also adjustable parameters, but will be definitively fixed only in the next step. The optimum values found for the three parameters are shown in Table 1.

When comparing the experiments with Th in the absence and the presence of Ca, it becomes obvious that the main difference between both systems is expressed by $n$. For the experiments performed in the absence of Ca, $n$ is close to one, whereas for the Th experiments with Ca $n$ is larger than 1 throughout. In view of the low total Th concentration ($\sim 2 \times 10^{-13}$ M) used in the experiments, the formation of polynuclear complexes is precluded. This means that from a chemical point of view, $n$ must be an integer. For the Th experiments in the absence of Ca, it is therefore postulated that $n$ equals one. As is shown by the fitting curve in Fig. 1,

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[1] Figs. of all the experimental results are given in [16].

**Table 1.** The fitted values of the adjustable parameters $n$, log $K_d^0$, $\beta/A$ and $\beta^{Ca}/A$ in Eqs. (6) or (7), respectively with their standard deviations. No weight was given by the fitting procedure to the experimental data.

| Experiment with Th | $n$ | log $K_d^0$ | $\beta/A$ |
|---|---|---|---|
| pH 13.3, no Ca | $0.9 \pm 0.1$ | $3.7 \pm 0.1$ | $(1.7 \pm 0.9) \times 10^5$ |
| pH 12.0, no Ca | $1.1 \pm 0.1$ | $1.7 \pm 0.1$ | $(6.1 \pm 5.4) \times 10^5$ |
| pH 10.7, no Ca | $0.8 \pm 0.1$ | $4.5 \pm 0.1$ | $(7.1 \pm 3.3) \times 10^3$ |

| Experiment with Th | $n$ | log $K_d^0$ | $\beta^{Ca}/A$ |
|---|---|---|---|
| pH 13.3, 0.35 mM Ca | $2.9 \pm 0.3$ | $4.2 \pm 0.1$ | $(2.1 \pm 4.5) \times 10^{10}$ |
| pH 12.0, 0.7 mM Ca | $1.7 \pm 0.1$ | $1.8 \pm 0.1$ | $(6.2 \pm 7.0) \times 10^7$ |
| pH 12.0, 10 mM Ca | $1.5 \pm 0.1$ | $2.5 \pm 0.1$ | $(2.9 \pm 3.2) \times 10^7$ |
| pH 10.7, 0.7 mM Ca | $1.4 \pm 0.1$ | $4.2 \pm 0.1$ | $(2.2 \pm 1.6) \times 10^5$ |
| pH 10.7, 10 mM Ca | $1.5 \pm 0.1$ | $5.1 \pm 0.1$ | $(4.4 \pm 2.1) \times 10^6$ |

| Experiment with Eu | $n$ | log $K_d^0$ | $\beta/A$ |
|---|---|---|---|
| pH 13.3, no Ca | $0.9 \pm 0.1$ | $4.2 \pm 0.1$ | $(6.9 \pm 1.9) \times 10^3$ |
| pH 12.0, no Ca | $0.8 \pm 0.1$ | $5.1 \pm 0.1$ | $(2.7 \pm 1.3) \times 10^4$ |
| pH 10.7, no Ca | $0.6 \pm 0.1$ | $4.6 \pm 0.1$ | $(8.9 \pm 3.5) \times 10^2$ |

| Experiment with Eu | $n$ | log $K_d^0$ | $\beta^{Ca}/A$ |
|---|---|---|---|
| pH 13.3, 1.8 mM Ca | $1.2 \pm 0.2$ | $5.3 \pm 0.1$ | $(7.2 \pm 8.9) \times 10^4$ |
| pH 12.0, 1.8 mM Ca | $1.1 \pm 0.1$ | $5.4 \pm 0.1$ | $(1.5 \pm 0.9) \times 10^5$ |
| pH 12.0, 10 mM Ca | $1.3 \pm 0.1$ | $5.4 \pm 0.1$ | $(4.8 \pm 2.5) \times 10^5$ |
| pH 10.7, 1.8 mM Ca | $1.2 \pm 0.2$ | $5.0 \pm 0.1$ | $(1.5 \pm 1.7) \times 10^5$ |
| pH 10.7, 10 mM Ca | $1.3 \pm 0.1$ | $5.1 \pm 0.1$ | $(4.0 \pm 2.3) \times 10^5$ |

a slope of one describes well the experiments carried out in the absence of Ca. Therefore, it was postulated that in the pH range from 10.7 to 13.3 and in the absence of Ca, 1:1 Th:ISA complexes are dominant.

Based on the results of Table 1, it is not clear what value has to be assigned to n in those Th experiments, in which Ca is present. The optimised fit parameters suggest that a value of 2 or 3 (pH 13.3) may be suitable. For the purpose of comparison, the experimental data points at pH 13.3 (0.35 mM Ca) are fitted to Eq. (7) with $n = 2$ and $n = 3$ in Fig. 2. Both fitted curves represent the data equally well. In Figs. 3 and 4, the experimental data points at pH 12.0 (0.7 mM Ca) and pH 10.7 (10 mM Ca) are fitted to Eq. (7) with $n = 1$ and $n = 2$. These figures clearly show that the data points are better described by a curve with $n = 2$. Fig. 3 is representative for the experiment at pH 12.0 and 10 mM Ca, and Fig. 4 is representative for the experiment at pH 10.7
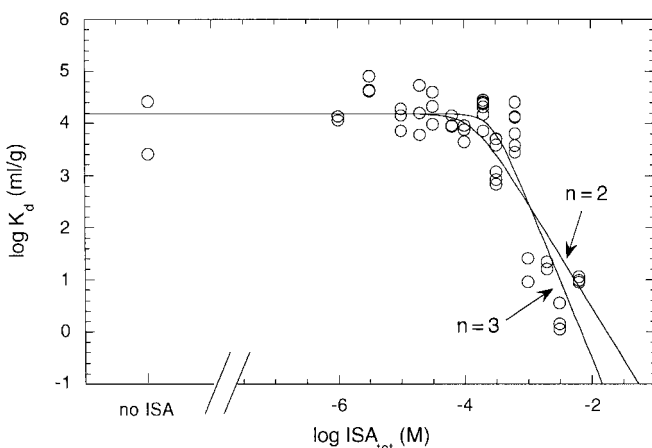


**Fig. 3.** Influence of ISA on the sorption of Th on a polyallomer tube wall at pH 12.0 in the presence of 0.7 mM Ca. The experimental data are fitted to Eq. (7) with $n = 1$ and $n = 2$.



**Fig. 2.** Influence of ISA on the sorption of Th on an ion exchange resin at pH 13.3 in the presence of 0.35 mM Ca. The experimental data are fitted to Eq. (7) with $n = 2$ and $n = 3$.
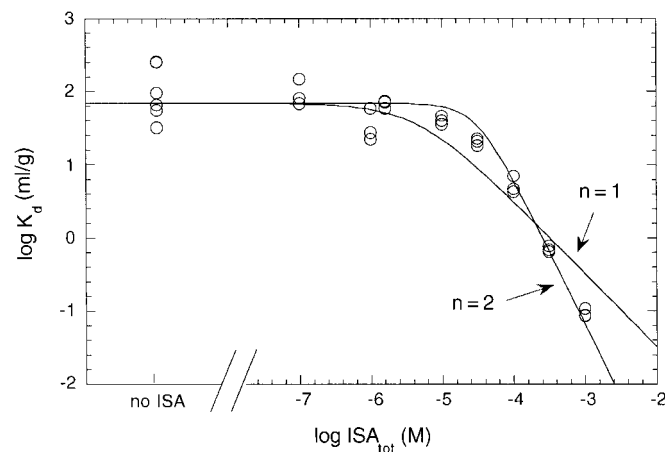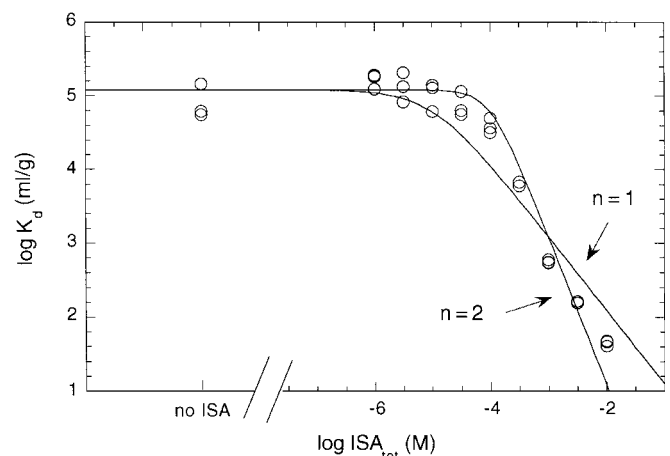


**Fig. 4.** Influence of ISA on the sorption of Th on feldspar at pH 10.7 in the presence of 10 mM Ca. The experimental data are fitted to Eq. (7) with $n = 1$ and $n = 2$.
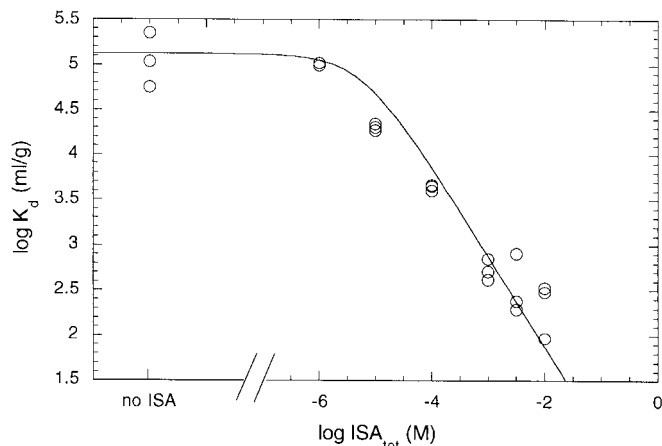
**Fig. 5.** Influence of ISA on the sorption of Eu on feldspar at pH 12.0 in the absence of Ca. The experimental data are fitted to Eq. (6) with $n = 1$.
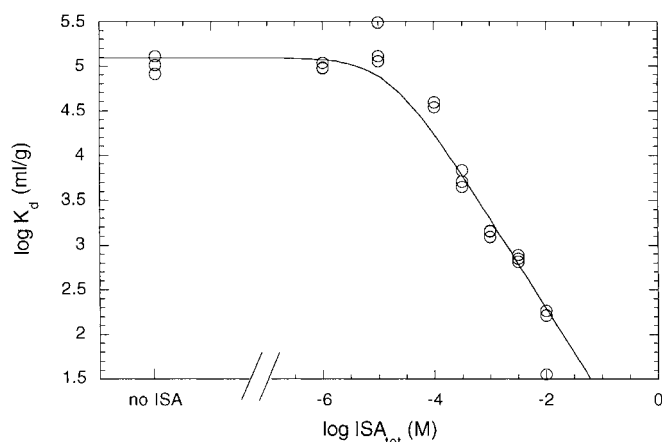


**Fig. 6.** Influence of ISA on the sorption of Eu on feldspar at pH 10.7 in the presence of 10 mM Ca. The experimental data are fitted to Eq. (6) with $n = 1$.

and 0.7 mM Ca. For the sake of simplification, it is postulated that across the whole pH range tested, 1:2:$k$ Th:ISA:Ca complexes are dominant in the presence of Ca. This is also in agreement with earlier studies on the complexation of Th by ISA at pH 13.3, which indicated that two ISA ligands are coordinated with one Th ion, i.e. $n = 2$ [6, 7, 24, 26].

Unlike experiments performed with Th, no effect of Ca on $n$ is noticed in the experiments with Eu, where the value of $n$ is close to one. Therefore, it is postulated that in the pH range from 10.7 to 13.3, 1:1 Eu:ISA complexes dominate, irrespective of the presence or absence of Ca. In Figs. 5 and 6, the experimental data points at pH 12.0 (no Ca) and pH 10.7 (10 mM Ca) are shown. The experimental results, which can be regarded as representative for all the other experiments with Eu[2], are described very well by using $n = 1$ (cf. Eq. (5)).

All postulated models describe the experimental data with a minimum number of species. The introduction of additional species would undoubtedly give better fits to the experimental data. However, without more information on the complexes there is no benefit from such an exercise.

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[2] Figs. of all the experimental results are given in [16].

## 3.2 Second step: Determination of $\beta$ and $\beta^{Ca}$

With fixed values for $n - n$ being an integer now − and log $K_d^0$, the fitting of the data to Eqs. (6) and (7) is now repeated, and values for the remaining adjustable parameters $\beta/A$ and $\beta^{Ca}/A$ are obtained. To take into account the uncertainty of the experimental data points, the following procedure was applied. For each data point, an uncertainty, $u(K_d)$, was calculated, taking into account the uncertainties of weighting, pipetting and radiochemical measurements. Next, for each ISA concentration, the mean value of $K_d$ from the triplicate measurements and its uncertainty were determined. This uncertainty of the mean of $K_d$ takes into account the spread of the three data points around the mean as well as the uncertainties individually calculated for the single data points ($u(K_d)$). For this purpose, the formula used in the compilation of the NEA Thermochemical Data Base [27] for two independent data at variance was slightly modified for the situation with more than two data. The uncertainty $u_{\overline{X}}$ assigned to the mean $\overline{X}$ covers the range of expectation of all the data $X_1, X_2, ...$ as shown in Eq. (11):

$$u_{\overline{X}} = \left| X_i^{max} - \overline{X} \right| u_i^{max}, \qquad (11)$$

where $i = 1, 2, ..., n$ with $n$ the number of data points, $X_i^{max}$ the maximum difference between a data point and the mean $\overline{X}$, and $u_i^{max}$ the largest calculated uncertainty $u(K_d)$ of the data set.

The results of fitting the mean values of $K_d$ with their uncertainties to the Eqs. (6) and (7) using the Chi-square minimisation method with instrumental weights, are shown in Table 2. As can be expected, the values for $\beta/A$ and

**Table 2.** The fitted values of the adjustable parameters $\beta/A$ or $\beta^{Ca}/A$, obtained when fixing $n$ and $K_d^0$ in Eqs. (6) or (7). The uncertainty of the experimental data of $K_d$ was taken into account by giving a weight of $1/u_{\overline{X}}^2$ (Eq. (11)) to each of mean $K_d$ value.

| Experiment with Th | $n$ | log $K_d^0$ | $\beta/A$ |
|---|---|---|---|
| pH 13.3, no Ca | 1 | 3.7 | $(6.1 \pm 0.5) \times 10^5$ |
| pH 12.0, no Ca | 1 | 1.7 | $(2.1 \pm 0.1) \times 10^5$ |
| pH 10.7, no Ca | 1 | 4.5 | $(1.3 \pm 0.3) \times 10^5$ |

| Experiment with Th | $n$ | log $K_d^0$ | $\beta^{Ca}/A$ |
|---|---|---|---|
| pH 13.3, 0.35 mM Ca | 2 | 4.2 | $(3.7 \pm 0.8) \times 10^8$ |
| pH 12.0, 0.7 mM Ca | 2 | 1.8 | $(2.5 \pm 0.4) \times 10^9$ |
| pH 12.0, 10 mM Ca | 2 | 2.5 | $(1.0 \pm 0.2) \times 10^{10}$ |
| pH 10.7, 0.7 mM Ca | 2 | 4.2 | $(1.1 \pm 0.2) \times 10^8$ |
| pH 10.7, 10 mM Ca | 2 | 5.1 | $(1.1 \pm 0.1) \times 10^8$ |

| Experiment with Eu | $n$ | log $K_d^0$ | $\beta/A$ |
|---|---|---|---|
| pH 13.3, no Ca | 1 | 4.2 | $(3.4 \pm 0.4) \times 10^4$ |
| pH 12.0, no Ca | 1 | 5.1 | $(3.6 \pm 0.5) \times 10^5$ |
| pH 10.7, no Ca | 1 | 4.6 | $(2.1 \pm 1.2) \times 10^3$ |

| Experiment with Eu | $n$ | log $K_d^0$ | $\beta^{Ca}/A$ |
|---|---|---|---|
| pH 13.3, 1.8 mM Ca | 1 | 5.3 | $(5.1 \pm 4.0) \times 10^3$ |
| pH 12.0, 1.8 mM Ca | 1 | 5.4 | $(1.8 \pm 4.1) \times 10^4$ |
| pH 12.0, 10 mM Ca | 1 | 5.4 | $(7.3 \pm 3.7) \times 10^4$ |
| pH 10.7, 1.8 mM Ca | 1 | 5.0 | $(0.9 \pm 1.5) \times 10^4$ |
| pH 10.7, 10 mM Ca | 1 | 5.1 | $(0.5 \pm 2.7) \times 10^5$ |

$\beta^{Ca}/A$ in Table 2 differ significantly from those in Table 1. In this context it is important to note that – for any application of the data – it is necessary to use a consistent set of data, i.e. either taken from Table 1 or from Table 2. The values of $\beta/A$ and $\beta^{Ca}/A$ in Table 2 are finally the basis for evaluating the thermodynamic equilibrium constants and the reaction stoichiometry of Eqs. (2) and (3).

### 3.3 Third step: Reaction stoichiometry and the stability constants $K$ and $K^{Ca}$

The complexation constant $K$ and the number of protons involved in the complexation reaction Eq. (2) were determined for the Th systems without Ca, and for the Eu systems with and without Ca. Based on Eq. (8), values for $\log K$ and $m$ result from the relationship:

$$\log \beta = \log K - m \cdot \log [H] . \tag{12}$$

For this purpose, the logarithms of $\beta$ were plotted versus the logarithms of the experimental proton concentration, as shown in Fig. 7 for the Th systems without Ca and in Fig. 8 for the Eu systems with and without Ca. The values for
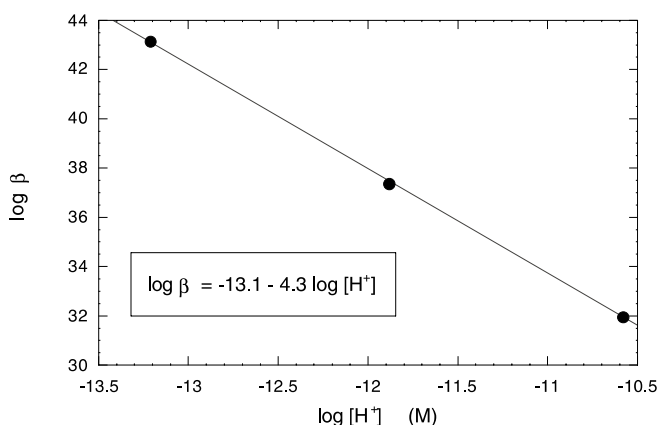


**Fig. 7.** Determination of the number of protons involved in the complexation reaction between Th(IV) and ISA and of the stability constant $K$ in the absence of Ca by plotting $\log \beta$ (cf. Table 2) as a function of the experimental pH (uncertainties of $\log \beta$ were not taken into account).
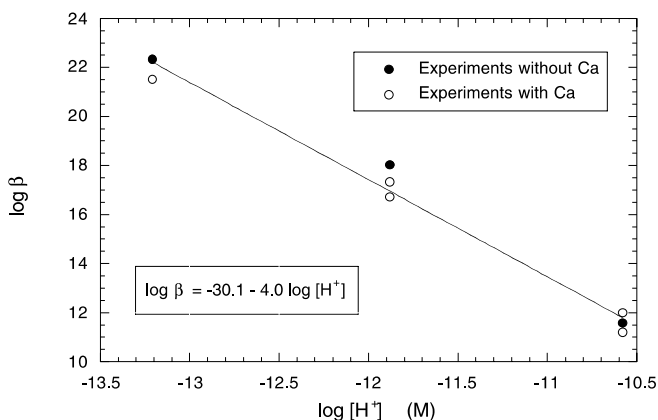


**Fig. 8.** Determination of the number of protons involved in the complexation reaction between Eu(III) and ISA and of the stability constant $K$ by plotting the $\log \beta$ as a function of the experimental pH (uncertainties of $\log \beta$ were not taken into account).

**Table 3.** Stoichiometry coefficients and stability constants ($I = 0.3$ M) for the complexation of Th(IV) and Eu(III) by ISA. The corresponding equilibrium reactions are defined by Eqs. (2) and (3).

|  | Th(IV) | Eu(III) |
|---|---|---|
| Complex formation without Ca |  |  |
| $m$ | 4 | 4 |
| $\log K$ | $-10.1 \pm 0.2$ | $-30.6 \pm 0.2$ |
| Complex formation with Ca |  |  |
| $k$ | 1 | – |
| $m$ | 4 | – |
| $\log K^{Ca}$ | $-3.6 \pm 0.2$ | – |

$A$ were calculated according to the Eq. (10), with $\log \beta_4^{OH} = 39.44$ at $I = 0.3$ M for Th(IV) [28] and $\log \beta_4^{OH} = 19.89$ at $I.S. = 0.3$ M for Eu(III) [25]. The activity coefficients were calculated using the Davies equation, as given in [17]. The results of the fitting procedure are $m = 4.3 \pm 0.1$ and $\log K = -13.1 \pm 0.7$ for the Th systems without Ca, and $m = -3.96 \pm 0.21$ and $\log K = -30.1 \pm 2.5$ for the Eu systems. Because of the absence of polynuclear Th species $m$ must be integer. Therefore, $m$ was fixed at four and this resulted in $\log K = -10.1 \pm 0.2$ and $\log K = -30.6 \pm 0.2$ for the Th systems without Ca and the Eu systems, respectively (cf. Table 3). Fig. 8 again shows that no difference in Eu sorption can be observed between systems with and without Ca.

Note that the combination of Eqs. (8) and (10) leads to the following relationship:

$$\frac{\beta}{A} = \frac{K}{[H]^m \cdot \left(1 + \beta_4^{OH} \cdot \frac{K_w^4}{[H]^4}\right)} \cong \frac{K \cdot [H]^4}{[H]^m \cdot \beta_4^{OH} \cdot K_w^4} . \tag{13}$$

$K_w$ is the dissociation product of water. The approximation given in Eq. (13) is valid for the pH range covered by the experiments. For $m = 4$, the adjustable parameter $\beta/A$ in Eq. (13) is independent of pH, which is in agreement with the values of $\beta/A$ in Table 2. However, the existence of Eu(OH)$_4^-$ species is not fully corroborated in the literature [25]. On the assumption that Eu(OH)$_3^0$ species dominate at alkaline pH instead of Eu(OH)$_4^-$, $\beta/A$ is pH independent for $m = 3$. This would mean that only three protons are involved in the complexation reaction (Eq. (2)). Consequently, the involvement of four protons is only valid if Eu(OH)$_4^-$ species are the dominant hydrolysis species at alkaline pH. The stability constant $K$ can only be used for further calculations when taking the hydrolysis constant of Eu(OH)$_4^-$ into account. When using Eu(OH)$_3^0$ as the dominant species, other values for $A$ and, consequently, for $\beta$ and $K$ result.

The five Th experiments performed in the presence of Ca were used to determine the complexation constant $K^{Ca}$ and the number of protons and Ca ions involved in the complexation reaction Eq. (3). In accordance with Eq. (9), the logarithms of $\beta^{Ca}$ were plotted against the logarithms of the proton and the free Ca concentrations of the experiments.

$$\log \beta^{Ca} = k \cdot \log [Ca] - m \cdot \log [H] + \log K^{Ca} . \tag{14}$$

The concentration of free Ca, [Ca], is a function of the total Ca in solution, $[\text{Ca}]_{\text{tot}}^{\text{sol}}$, the concentration of complexed Ca, $[\text{Ca}]_{\text{org}}$, and the CaOH$^+$ concentration:

$$[\text{Ca}] = [\text{Ca}]_{\text{tot}}^{\text{sol}} - k[\text{Ca}]_{\text{org}} - [\text{CaOH}]. \tag{15}$$

Complexed Ca species are Th-ISA-Ca complexes and ISA-Ca complexes. Because the concentration of Th in the experiments is much smaller than the total concentration of Ca, the amount of Th-ISA-Ca species is negligible compared to the total Ca concentration. Speciation calculations based on the stability constants for CaISA$^+$ and CaISA$^0$ [17] show that the concentrations of CaISA$^+$ and CaISA$^0$ are also negligible compared to the total Ca concentration. The concentration of CaOH$^+$ is, depending on pH, not negligible in all cases. At pH 10.7 the major species is Ca$^{2+}$ and the total Ca concentration can be approximated by the free Ca concentration. However, at pH 13.3 and 12.0 the fraction of CaOH$^+$ equals approximately 58% and 8% of the total Ca concentration, respectively (log $K_{\text{CaOH}} = -12.78$ [29]).

By fitting the $\beta^{\text{Ca}}$ values of Table 2 to Eq. (14) the following optimum parameters are obtained: $k = 1.2 \pm 0.4$, $m = 4.4 \pm 0.3$ and log $K^{\text{Ca}} = -8.1 \pm 2.9$, respectively. These results show that approximately four protons and approximately one Ca ion are involved in the complexation reaction. The latter result contrasts with the HPIEC study [6] that rather gave evidence for two Ca ions participating in the complex. The large uncertainty of log $K^{\text{Ca}}$ (i.e. $\pm 2.9$) is not a good measure for the deviation of the experimental points from the plane, however, it shows the sensitivity of log $K^{\text{Ca}}$ for small changes in $k$ and $m$. Because log $K^{\text{Ca}}$ is actually the intercept on the $Z$-axis at $[\text{H}^+] = 1$ M and $[\text{Ca}^{2+}] = 1$ M, small changes in the angle of the plane cause a large change of the log $K^{\text{Ca}}$ value. With $k$ and $m$ being integer, the species postulated are 1:2:1 Th:ISA:Ca complexes with four protons involved in the complexation reaction. The

fitting of the plane function is repeated with fixed values for $k$ and $m$. The corresponding stability constant for this model is log $K^{\text{Ca}} = -3.6 \pm 0.2$ (cf. Table 3). The plane fitted to Eq. (14) using integer parameters $m$ and $k$ is shown in Fig. 9 and describes the experimental results very well. Note that the decreased uncertainty of log $K^{\text{Ca}}$ ($\pm 0.2$ instead of $\pm 2.9$) is simply a result of the reduced number of degrees of freedom in the fitting exercise and does not imply any improvement of the reliability of the stability constant obtained.

## 3.4 Appraisal of the model proposed and the parameters involved

The relatively large scatter in the experimental data and the inherent uncertainties associated with their interpretation in terms of stoichiometric numbers shows that the parameters determined here ($K$, $K^{\text{Ca}}$, $m$, $k$, $n$) have to be appraised rather as fit parameters than a comprehensive chemical description of the species that are formed in reality. However, it is most important to note that any application of the results given here may lead to useful predictions of equilibrium concentrations, as long as these data are applied within the chemical parameter space, at which they were determined (viz. range of pH, range of Ca concentrations).

One possibility of assessing the results presented here would be a comparison to stability constants of structurally related complexes. However, no such data can be found in the literature. The only possible link can be established through the stability of Np(IV)-ISA complexes [8] measured at pH between 2 and 8. From a comparison of stability constants of a series of carboxylic and aminocarboxylic acids (IUPAC database [30]) for Np(IV) and Th(IV) it can be expected that the stability constants for ISA complexes of these two actinide ions are of similar order of magnitude. In the following it is tested whether the stability of Np(IV) complexes with ISA can be used to explain the sorption reduction factors observed in the present Th experiments at alkaline pH. For this comparison only systems lacking in Ca can be considered, since Ca was not present in the experiments with Np(IV). For this purpose the stability constants [8] for the formation of Np(OH)$_3$ISA (log $K_1$ 43.2 at $I = 0$ M) and Np(OH)$_2$(ISA)$_2$ (log $K_2$ 36.9 at $I = 0$ M) are recalculated at $I = 0.3$ M by using the Davies equation [17] and then transformed to conditional stability constants ($\beta_1$ and $\beta_2$) valid for the pH values of interest by multiplication with the suitable concentration of hydroxide ions at the power of their stoichiometric coefficients. Using these conditional stability constants sorption reduction factors ($F_{\text{red}}$) are calculated [5]:

$$F_{\text{red}} = \frac{K_{\text{d}}^0}{K_{\text{d}}} = 1 + \frac{\sum_n \beta_n \cdot [\text{L}]^n}{A}. \tag{16}$$
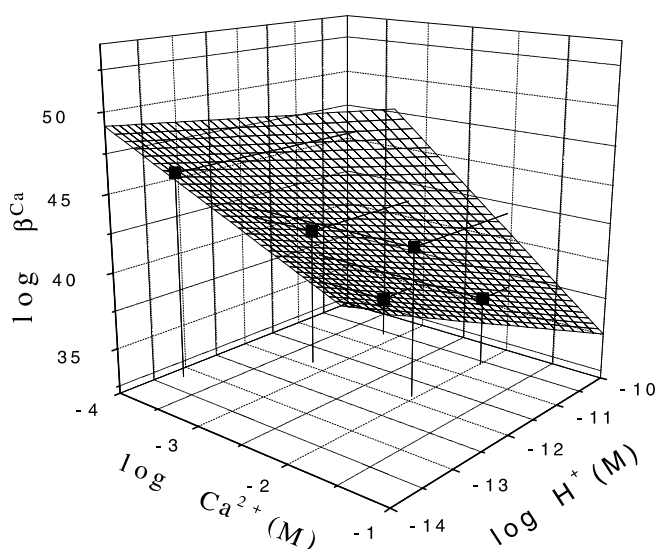


**Fig. 9.** Determination of the number of protons and Ca$^{2+}$ ions involved in the complexation reaction between Th(IV) and ISA and of the stability constant $K^{\text{Ca}}$ by fitting the five experiments with Th performed in the presence of Ca by Eq. (14) (uncertainties of log $\beta^{\text{Ca}}$ were not taken into account). The plane represents the best-fit for integer parameters as given in Table 3.

The comparison between the values calculated using the Np(IV) data [8] and the results of the Th experiments is shown in Table 4 for $10^{-2}$ M ISA. A fair agreement is obtained at pH 10.7, however, with increasing pH, the agreement deteriorates. A possible explanation for this trend can be found in the assumption that, also in the case of Np(IV), complexes with more than three hydroxide ions can be found

**Table 4.** Comparison of the effect of $10^{-2}$ M ISA on the sorption of Th(IV) based on Np(IV) complexation data [8] and Th(IV) complexation data (cf. Table 2).

| | Conditional stability constants | | | Sorption reduction factors | |
| | Np(IV) data | | Th(IV) data | Np(IV) data | Th(IV) data |
| pH | $\beta_1/A$ | $\beta_2/A$ | $\beta/A$ | $F_{red}$ | $F_{red}$ |
|---|---|---|---|---|---|
| 10.7 | $1.7 \times 10^4$ | $1.3 \times 10^1$ | $1.3 \times 10^5$ | $1.7 \times 10^2$ | $1.3 \times 10^3$ |
| 12.0 | $8.7 \times 10^2$ | $3.2 \times 10^{-2}$ | $2.1 \times 10^5$ | $8.7 \times 10^0$ | $2.1 \times 10^3$ |
| 13.3 | $4.4 \times 10^1$ | $8.0 \times 10^{-5}$ | $6.1 \times 10^5$ | $4.4 \times 10^{-1}$ | $6.1 \times 10^3$ |

at high pH and that these complexes will be dominating in this particular pH range. Therefore it can be assumed that the set of Np(IV) data used is not sufficient to explain the observed sorption reduction factors for Th(IV), i.e. the sorption reduction factors are rather underestimated. Thus, as a positive conclusion from this comparison, it can be stated that the sorption reduction factors based on the Np(IV) data are actually smaller than the experimental ones, which makes sense with respect to chemical reasoning.

In another attempt to assess the question, whether the model proposed is reasonable from a chemical point of view, the values of $\log K$ and $\log K^{Ca}$ for the Th(IV) complexes are compared. Combination of Eq. (2) ($n = 1$, $m = 4$) and Eq. (3) ($n = 2$, $k = 1$, $m = 4$) leads to

$$(ThISA)_{-4H} + ISA + Ca \rightleftarrows (Th(ISA)_2Ca)_{-4H} \qquad (17)$$
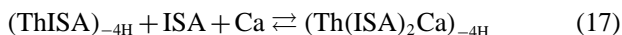
with an equilibrium constant $\log K = 6.5$ (difference of the values given in Table 3). In view of the fact that the interaction between Ca and ISA is fairly weak [17] and that the binding of the second ISA molecule occurs formally via the carboxylate group, this value seems to be on one hand quite large. On the other hand, it can be hypothesised that the binding of the two ISA molecules by Th(IV) may offer a favourable arrangement of ligand sites to Ca, since not all of the ligand sites of ISA can be absorbed by the Th(IV) center. Such entropic effects make it difficult to estimate a reasonable value for the equilibrium constant involved in Eq. (17), and therefore the value calculated cannot be regarded as a direct argument against the model proposed. Note that the stabilisation of Ca–carboxylate interactions by concomitant formation of chelates with other metal ions has been described several times in the literature, e.g. [31, 32].

Summarising all these considerations two conclusions may be drawn:

(i) There is no independent proof that the model proposed represents the real chemical structures.
(ii) No argument has been found that conflicts with the model proposed on the level of "chemical reasoning".

## 4. Conclusions

This work is the first detailed study on the complexation of radionuclides by ISA under alkaline conditions (pH 10.7–13.3). Models are postulated that describe the experimental results for the complexation of Th(IV) by ISA and the complexation of Eu(III) by ISA including effects of pH and Ca concentration. These models and their corresponding stability constants, however, should only be applied to the experimental range of pH and Ca concentration, i.e.

pH between 10.7 and 13.3 and Ca between 0 and 10 mM. It is an inherent drawback of the batch sorption technique applied that the stoichiometric numbers and stability constants proposed here are not independent of the hydrolysis reactions of the two metal cations. Thus, the same hydrolysis data as used here have to be applied in speciation calculations with the ISA complexation data for Eu(III) and Th(IV). In the case that other hydrolysis data, such as those very recently published for Th(IV) [33], are used, the stability of the Th complexes with ISA would have to be recalculated on the basis of the new hydrolysis data.

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