Rapid Communication

Evidence for the Existence of Complexes between Th(IV) and α-Isosaccharinic Acid under Alkaline Conditions

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Summary.

The complexation of Th(IV) with α-isosaccharinic acid (ISA) was studied under alkaline conditions (pH 12.8 and 13.3) by two complementary techniques. Using high performance ion exchange chromatography, evidence was found for the formation of complexes between Th(IV), Ca and ISA. In the presence of Ca, Th is assumed to coordinate with two ISA ligands and two Ca ions. The ratio between Th(IV) and ISA in this complex in the presence of Ca was confirmed by batch sorption experiments, in which the sorption of Th was studied as a function of the concentration of ISA. Moreover, it was shown in these experiments that, in the absence of Ca, a 1:1 Th:ISA complex is formed. Conditional stability constants for the formation of both complexes are calculated.

Introduction

In the planned repository for low and intermediate level waste in Switzerland substantial amounts of organic waste are cellulosic [1]. Under the alkaline conditions of the cementitious repository, cellulose degrades rapidly via a peeling off reaction [2]. The main degradation products are the *erythro-* and *threo-*form of 2,4,5-trihydroxy-2-hydroxymethyl-pentanoic acid, called α-isosaccharinic acid (further denoted as ISA) and β-isosaccharinic acid respectively (Fig. 1). Isosaccharinic acid belongs to the class of polyhydroxy ligands. These are known to form stable complexes with various metal cations, especially under alkaline conditions [3−5]. The formation of water soluble radio-nuclide complexes with isosaccharinic acid in a repository might therefore enhance the release of radionuclides to the geo- and biosphere.

Only indirect evidence for the formation of complexes with radionuclides and ISA at alkaline pH exists [2, 6−9]. It is therefore the aim of the present work to study the complexation of Th(IV) with ISA under alkaline conditions and to demonstrate the existence of Th-ISA complexes. Th(IV) is an ideal representative for safety-relevant tetravalent actinides such as U(IV) or Pu(IV). The experimental handling of Th(IV) is easier than of the latter two radionuclides, because Th(IV) is redox-insensitive. Moreover, the effect of Ca^{2+} on the complexation was studied, because the concentration of Ca^{2+} in a cementitious repository is high, owing to the presence of $Ca(OH)_2$ in cement. Two different techniques were applied: (i) high performance ion exchange chromatography (HPIEC) and (ii) a batch technique, in which the sorption equilibrium of Th(IV) on an ion exchange resin was investigated as a function of the concentration of ISA.

HPIEC method

Using HPIEC, the complexed Th species were separated from free ISA and hydrolysed Th. The total concentrations of Th, ISA and Ca were determined in the fraction containing the complexed Th species. The ratio of these three parameters can elucidate the stoichiometry of the complex formed. Briefly, the experiments were carried out as follows: a mixture of defined amounts of $Th(NO_3)_4$ (10^{-4} M) and ISA (10^{-2} M) was allowed to equilibrate at pH 12.8 (0.08 M NaOH). In order to study the influence of Ca, ISA was supplied either as the sodium salt (prepared by alkaline hydrolysis of ISA lactone in NaOH) or as the Ca salt. The solution was spiked with Th-234 and Ca-45. After six days of equilibration, the clear solution was injected into the HPIEC device (Dionex DX-500), equipped with a Carbopac PA-100 analytical column (Dionex) filled with an anion exchange resin. The eluent (0.08 M NaOH) was forced through the column at a flow rate of 1 ml/min. After passing through the column, the eluate was collected in 2 ml fractions and each fraction was analysed for Th, ISA and Ca. The
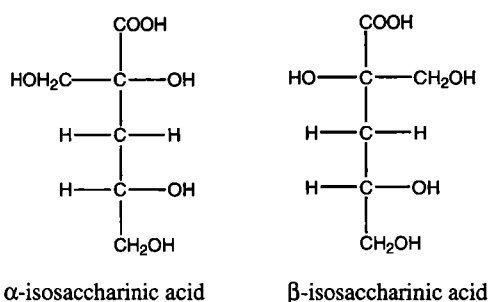

COOH
HOH₂C——C——OH
H——C——H
H——C——OH
CH₂OH

α-isosaccharinic acid

COOH
HO——C——CH₂OH
H——C——H
H——C——OH
CH₂OH

β-isosaccharinic acid

Fig. 1. Molecular structure of α- and β-isosaccharinic acid.

Table 1. The ratios of the total measured Th, ISA and Ca concentration in the fractions of the eluate from 0—4 min.

	average	std. dev.	number of exp.
ISA/Th	2.3	0.4	18
ISA/Ca	1.0	0.1	11
Ca/Th	2.4	0.5	11

total concentrations of Th and Ca were radiochemically determined. The activity of Th-234 was determined by measuring the Cerenkov radiation of its daughter isotope Pa-234m. ISA was determined using essentially the same HPIEC system as described, but with a pulsed amperometric detector connected (gold working electrode).

As had been shown in independent experiments, hydrolysed Th(IV) is completely retained by the HPIEC column in the absence of the ISA ligand. Further, Ca and free ISA are eluted at retention times longer than 4 min (data not shown). However, if the mixture of Th, Ca, and ISA is injected, Th and small amounts of ISA and Ca are eluted between 0 and 4 min. This is a direct indication that a complex between these ions is formed, which elutes during the first four minutes after injection. The stoichiometry of the complexes present in the fractions eluted from 0—4 min. in a series of replicates was calculated from the ratios of the total measured Th, ISA and Ca concentrations (Table 1). The ratio between ISA and Ca was found to be 1:1. Owing to the larger standard deviation, the ratio between. Th and ISA is less clear, but is probably near 1:2. These observations can be explained by the formation of a 1:2:2 Th:ISA:Ca complex.

If a mixture of Th and the sodium salt of ISA is injected, no Th is eluted from the column. This observation can be interpreted in two ways: (i) no complex between Th(IV) and ISA is formed or (ii) a complex is formed, however it dissociates completely when passing through the column. Independent of these interpretation possibilities, it can be stated that the presence of Ca^{2+} in a mixture of Th(IV) and ISA has a stabilising effect on possible complexes between these ions. Similar complexes between Ca^{2+}, Al(III) and the structurally related aldarate ligands were earlier described by Venema et al. [10].

Based on these results, two tentative general complexation reactions, relevant for Th(IV) speciation in the solutions injected to the HPIEC system, can be postulated. In the following equations, ISA denotes the a-isosaccharinate ion, i.e. with a deprotonated carboxylic group. Charges are omitted for simplicity.

$$Th + nISA \rightleftharpoons Th(ISA)_n + mH , \qquad (1)$$

$$Th + nISA + pCa \rightleftharpoons Th(ISA)_n(Ca)_p + mH . \qquad (2)$$

Eq. (1) describes the Th complexation in systems containing no Ca, whereas eq. (2) describes the systems

with Ca. The reasons for including the formation of protons are the hydrolysis of Th(IV) and the observation that the coordination of polyhydroxy ligands with higher charged cations at alkaline pH is accompanied by deprotonation of the coordinating hydroxo groups [4, 11]. Because the dissociation constants of these groups are unknown, it is of no use to further subdivide eqn's. (1) and (2) into deprotonation of the hydroxo groups of ISA and interaction of Th(IV) with the deprotonated ISA.

Batch method

In the batch sorption experiments, the distribution of Th(IV) between a solid and a liquid phase was investigated as a function of the concentration of ISA. This technique was used to further clarify the existence of Th-ISA complexes in the absence of Ca. In addition, this technique allows the calculation of thermodynamic stability data for the complexes formed, which is not possible for HPIEC owing to the possible changes of chemical equilibria involved therein.

For the present purpose, the sorption of Th(IV) on BioRad 50W-X2 cation exchange resin was measured as a function of the concentration of total ISA at pH 13.3 in the presence and absence of Ca. 15 ml aliquots of ISA in 0.3 M NaOH, spiked with Th-234 were added to 100 mg of resin. In some experiments, ISA was equilibrated with a 0.3 M NaOH solution saturated w.r.t. $Ca(CO)_2$ and spiked with Th-234. After equilibrating the systems for 3 days on a end-over-end shaker, the solid phase was separated from the solution by centrifuging at 48360 g for 30 min. The activity of Th-234 in the supernatant was radiochemically determined as described in the HPIEC experiment. The amount of sorbed Th was then calculated from the difference between this value and the total activity of Th added to the systems, taking into account the loss of Th by wall sorption.

The system obeys the required conditions for applying this batch technique: it is reasonable to assume that the reference sorption isotherm is linear in view of the low Th concentration ($\leq 10^{-15}$ M) and that the sorption of Th on the resin is reversible. Further, under the experimental conditions the resin is known to be chemically stable (manufacturer's specifications and reference [12]). Test experiments have shown the absence of sorption of ISA on the resin.

Based on the results obtained by HPIEC (eqn's. 1 and 2) the sorption distribution coefficients, K_d (ml/g), measured as a function of the ISA concentrations can be modeled [2] by

$$\log K_d = \log K_d^0 - \log \left(1 + \frac{\beta_1}{A \cdot [H]^m} \cdot [ISA]^n \right) \qquad (3)$$

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

$$\log K_d = \log K_d^0 - \log \left(1 + \frac{\beta_2 \cdot [Ca]^p}{A \cdot [H]^m} \cdot [ISA]^n \right) \qquad (4)$$
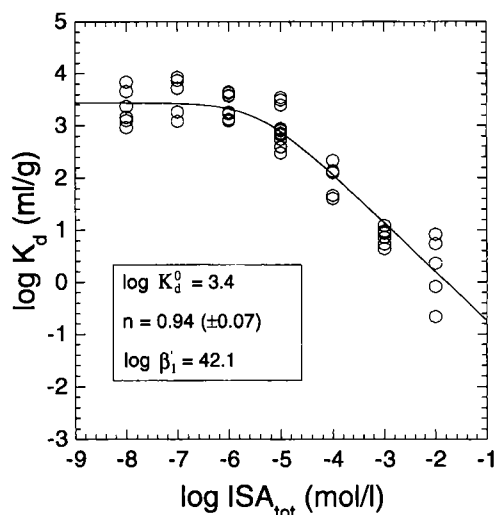
Fig. 2. Sorption of Th at pH 13.3 on an ion exchange resin at different ISA concentrations in the absence of Ca.
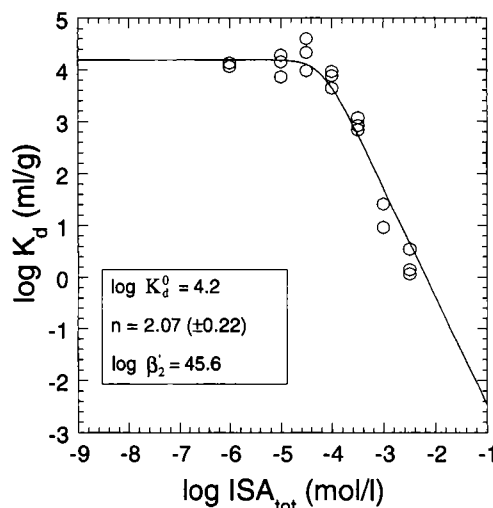

Fig. 3. Sorption of Th at pH 13.3 on an ion exchange resin at different ISA concentrations. The total Ca concentration in solution equals 0.7 mmol/l.

for the complexation reaction in the presence of Ca. Brackets denote molar concentrations of the species. β_1 and β_2 are the stability constants associated with eqn's. 1 and 2:

$$\beta_1 = \frac{[Th(ISA)_n] \cdot [H]^m}{[Th] \cdot [ISA]^n} \tag{5}$$

and

$$\beta_2 = \frac{[Th(ISA)_n(Ca)_p] \cdot [H]^m}{[Th] \cdot [Ca]^p \cdot [ISA]^n} \ . \tag{6}$$

A is a side reaction term for the hydrolysis of Th(IV) given by

$$A = 1 + \beta_4^{OH} \cdot [OH]^4 \tag{7}$$

with β_4^{OH} the only hydrolysis constant relevant for Th(IV)-speciation at alkaline pH [13]. K_d^0 is the sorption distribution coefficient measured in the absence of ISA.

Because the total concentration of Th is much smaller than the total concentration of ISA ([ISA]$_{tot}$), the concentration of free uncomplexed ISA can be approximated by [ISA]$_{tot}$. In view of the constant concentrations of Ca and protons used in the batch sorption experiments, eqn's. (3) and (4) can be simplified to:

$$\log K_d = \log K_d^0 - \log \left(1 + \frac{\beta_1'}{A} \cdot ([ISA]_{tot})^n\right) \tag{8}$$

and

$$\log K_d = \log K_d^0 - \log \left(1 + \frac{\beta_2'}{A} \cdot ([ISA]_{tot})^n\right) \tag{9}$$

with β_1' and β_2' being conditional stability constants defined as

$$\beta_1' = \frac{\beta_1}{[H]^m} \ , \tag{10}$$

$$\beta_2' = \frac{\beta_2 \cdot [Ca]^p}{[H]^m} \ . \tag{11}$$

The results of the batch sorption experiments are shown in Figs. 2 and 3. The main difference between the two systems is expressed by the slope of the curves obtained by fitting the experimental data to eqn's. (8) and (9). In this fitting procedure, β_1', β_2', K_d^0 and n are treated as adjustable parameters, whereas A is calculated using the data given by [13]. Using the specific ion interaction theory [14], these data measured at ionic strength of 3 M were recalculated to 0.3 M, which yielded $\log A_{(0.3\ M)} = 37.0$. The values of n shown in Fig's 2 and 3 equal ~ 1 in the absence of Ca and ~ 2, when Ca is added. These are indications of the formation of a 1:1 Th:ISA complex in systems without Ca and the formation of a 1:2 Th:ISA complex in systems with Ca. Note that, when setting n in the fitting procedure to exactly 1 or 2, respectively, the values of $\log \beta_1'$ and $\log \beta_2'$ do not change by more than 0.2 log-units.

$\log \beta_1'$ and $\log \beta_2'$ cannot be directly compared to related literature values. In the work of Wieland *et al.* [9], in which the sorption of Th(IV) on cement was studied as a function of the concentration of ISA, a stability constant, C, was calculated based on the formation of a hypothetical Th:ISA 1:2 complex, thus neglecting the participation of Ca present at a concentration of ~ 2 mM in cement pore water. This stability constant may be compared more or less to our β_2'/A values, because the concentration of Ca^{2+}, pH and ionic strength used here are quite similar to those given by Wieland *et al.* [9]. With this respect, the value reported here ($\log \beta_2'/A = 8.6$) is in fair agreement with $\log C = 8.7$ [9].

Conclusions

The present work directly shows the involvement of Ca in the complex formation between Th(IV) and ISA and the associated stoichiometry: namely, the coordi-

nation of one Th(IV) ion by two ISA ligands in the presence of Ca and a 1:1 Th(IV):ISA stoichiometry in the absence of Ca. The experimental techniques applied here are complementary. The HPIEC gives information about the species that are part of the complexes. However, due to the possible disintegration on the separation column of the equilibria relevant in solution, the technique cannot be applied as such to determine thermodynamic constants involved. The latter aspect, however, can be realised in the batch sorption experiments. Note that the equilibrium constants obtained here are conditional values that can be applied only to solutions of same pH, Ca concentration, etc., as used in the experiments. In order to obtain equilibrium constants that can be applied more universally, further experiments, in which pH and Ca^{2+} concentration are varied, are needed. Such experiments can elucidate the exact stoichiometry of the reactions involved in the formation of Th(IV)-ISA complexes, i.e. they allow the number of protons split off and the number of Ca^{2+} ions involved in complex formation to be calculated.

Acknowledgments

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