Thermodynamic Model for ThO2(am) Solubility in Isosaccharinate Solutions

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Abstract Extensive studies on ThO_2(am) solubility were carried out as functions of: 1) a wide range in isosaccharinate concentrations (0.0002 to 0.2 M) at fixed pH values of about 6 and 12; and 2) pH (ranging from 4.5 to 12) at fixed aqueous isosaccharinate concentrations of 0.008 M or 0.08 M to determine the aqueous complexes of isosaccharinate with Th(IV). The samples were equilibrated over periods ranging up to 69 days, and the data showed that steady-state/equilibrium concentrations in most cases were reached in <15 days. The data were interpreted using the SIT model, and required the inclusion of mixed hyddroxy-ISA complexes of Th [$Th(OH)ISA^{2+}$, $Th(OH)_3(ISA)_2^-$, and $Th(OH)_4(ISA)_2^{2}$] with $\log_{10} K^0 = 12.50 \pm 0.47$ for [$ThO_2(am) + 3H^+ + ISA^- = Th(OH)ISA^{2+} + H_2O$] , $\log_{10} K^0 = 4.41 \pm 0.47$ for [$ThO_2(am) + H^+ + 2ISA^- + H_2O = Th(OH)_3(ISA)_2^-$], and $\log_{10} K^0 = -3.18 \pm 0.47$ for [$ThO_2(am) + 2ISA^- + 2H_2O = Th(OH)_4(ISA)_2^{2-}$]. Predictions based on these Th-ISA complexes agreed closely with the extensive experimental data developed in this study as well as the very limited (only pH 8.3) data from liquid-liquid extractions recently reported in the literature.

Keywords Solubility, thermodynamics, ThO_2(am), isosaccharinate, thorium isosaccharinate complexes, complexation constants, thorium

1 Introduction

Isosaccharinic acid (2,4,5-trihydroxy-2hydroxymethyl-pentonic acid; represented here as HISA(aq)), a degradation product of cellulose disposed in low level radioactive waste geologic repositories, is known to form strong complexes with many metal ions including actinides [1]. Only very limited reliable data are available for isosaccharinate (ISA^-) complexes of thorium. Two types of data that are available for this system are 1) those that are based on sorption experiments under alkaline conditions [2-6] and 2) those based on liquid-liquid extractions [7, 8]. The data based on sorption experiments have recently been reviewed by Hummel et al. [1] who concluded that the entire data can be represented by [$Th(OH)_4(aq) + ISA^- = Th(OH)_{4-x}(ISA_{-xH}) + xH_2O$; $Th(OH)_4(aq) + 2ISA^- + Ca^{2+} = CaTh(OH)_{4-2y}(ISA_{-yH})(aq) + 2yH_2O$] and that the values of x and y in the above reactions cannot be determined by standard thermodynamic methods.

In two recent journal articles Allard and Ekberg [7, 8] reported Th-ISA complexes based on liquid-liquid extractions with 0.025M acetylacetone in toluene from 1.0 M $NaClO_4$ at a fixed $\log [H^+] \approx -8.3$ and at three different temperatures (15ºC, 25ºC, and 35ºC). Allard and Ekberg [8] report the data for all three temperatures, and Allard and Ekberg [7] deal exclusively with the data set for 25ºC. They reported values for complexation constants for three Th-ISA complexes ($Th(ISA)_n^{4-n}$, n varying from 1 to 3). The study appears to have been well carried out. However, several limitations are inherent in the experimental design and the data interpretation. The study was conducted at only one ionic strength (1.0 M $NaClO_4$) and independent values of ion-interaction parameters are not available; thus it is not possible to obtain the values of the equilibrium constants at zero ionic strength for application to determining thorium behavior in the low ionic strength groundwater prevalent at most repositories. The most serious limitation of the study is in the data interpretation. The authors interpreted their results using only $Th(ISA)_n^{4-n}$ species. Because the study was conducted at just one hydrogen ion concentration, it would be impossible to determine whether their experimental data could also have been interpreted equally well using mixed hydroxy-ISA complexes of thorium, especially considering that 1) thorium like other tetravalent actinides strongly hydrolyzes [9] even under fairly acidic conditions and 2) mixed hydroxy complexes containing ISA and other strongly complexing ligands (such as EDTA) have been reported for other tetravalent actinides [e.g., Np(IV) and Pu(IV)] [10, 11]. In addition, it is possible that the nature and type of dominant complexes are different not only at the H^+ concentrations other than the one investigated in their study but also at those used in their study.

To reliably predict environmental behavior of Th disposed in low-level waste repositories, it is necessary to have data on the nature of Th-ISA aqueous species and their complexation constants that will be applicable to a wide range in pH values and ISA concentrations. It is clear that the only reliable experimental study [8] containing useable data for the Th-ISA system is limited in several ways. Therefore, additional studies in this system are required 1) at relatively low ionic strengths and/or as a function of the ionic media, 2) in a wide range of pH values at different fixed ISA^- concentrations, and 3) in a wide range of ISA^- concentrations at different fixed pH values so as to be able to develop a reliable model applicable to a wide range of pH values and ISA concentrations. This study presents extensive data on ThO_2(am) solubility in relatively low ionic strength solutions as a function of a wide range in pH (varying from approximately 4.5 and 12) and ISA concentrations (varying up to 0.2 M) which are interpreted along with reinterpretation of the data reported in [8].

2 Materials and Methods

All experiments were conducted at room temperature (22º ± 2ºC) in a controlled atmosphere chamber containing Argon. Deionized water was used in all experiments. HCl stock solution and carbonate-free NaOH were used for pH adjustments where necessary.

The ThO_2(am) used in this study was obtained by titrating a concentrated Th stock solution, prepared from $Th(NO_3)_4 \cdot 4H_2O$ with carbonate-free NaOH to a pH value of about 10.5 and washing the resulting precipitate with deionized water to remove soluble Na and nitrate impurities.

A stock solution of sodium salt of α-isosaccharinate (NaISA) was prepared from $Ca(ISA)_2$(cr) using a modified version of the method [12] briefly described below. The $Ca(ISA)_2$(cr) used in this preparation was prepared as described in Rai et al. [13] and was characterized by X-ray diffraction. A 2.5 g portion of $Ca(ISA)_2$(cr) was reacted overnight with 25 mL of 0.35 M Na_2CO_3 in 0.01 M NaOH to precipitate Ca as $CaCO_3$, resulting in NaISA in the aqueous phase along with carbonate in excess of the amount needed to precipitate Ca. The aqueous phase was separated from $CaCO_3(s)$ by centrifugation. The pH value of this aqueous phase was adjusted to 5 with HCl to eliminate the excess carbonate. Chemical analysis of the aqueous phase showed isosaccharinate concentration of 0.466 M and Ca concentration of <0.0004 M.

Four sets of experiments were conducted to determine the influence of isosaccharinate on the solubility of $ThO_2(am)$. Sets I and II involved the solubility of $ThO_2(am)$ as a function of pH and time at fixed isosaccharinate concentrations of 0.008 M and 0.08 M. In Sets III and IV ThO(am) solubility was determined as a function of isosaccharinate concentrations and at fixed pH values of approximately 6 and 12.

The washed $ThO_2(am)$ precipitates containing 25 mg Th were added to 20 mL of appropriate NaISA solutions. The pH values of these suspensions were adjusted using HCl or NaOH to a range in values between approximately 4.5 and 12 for Sets I and II, and to approximately 6 for Set III and 12 for Set IV. The suspensions thus prepared were continuously agitated on a shaker and sampled at different equilibration periods ranging up to 69 days. At each equilibration period the pH values of the suspensions were measured using an Orion-Ross combination electrode calibrated against pH buffers covering the range in values of samples to be analyzed. The samples were centrifuged and an aliquot of the supernatant was withdrawn for filtration through Amicon Centricon-30 membrane filters with 40,000 MW cutoff and approximately 0.004 μm pore size. The filtrates were analyzed for thorium by inductively coupled plasma mass spectroscopy.

For these analyses the filtrates were diluted and acidified. The measured Th concentrations and pH values and the concentrations of other pertinent aqueous species (based on input values) at different equilibration periods are reported in Appendix Tables A.1 through A.4.

The data were interpreted using the Specific Ion-interaction Theory (SIT) described in many publications by the Nuclear Energy Agency of the Organization for Economic Co-Operation and Development (e.g., [9]). The base line thermodynamic data for Th and other species, some of the associated ion-interaction parameters, and the computerized SIT fitting code (NONLINT-SIT) used in these interpretations are described in [9] and/or [1].

3 Results and Discussion

Isosaccharinic acid in solution can exist in three different forms; isosaccharinic acid [HISA(aq)], isosaccharinate [ISA^-, a deprotonated HISA(aq)], and isosaccharinate-1,4-lactone [ISL(aq), a dehydration product of HISA(aq)]. The available thermodynamic data for these species have recently been reviewed by [1]. They concluded that due to the ambiguities in the lactonization constant [HISA(aq) = ISL(aq) + H_2O] ([10, 14]) and the need to confirm the value of intrinsic protonation constant ($\log_{10} K^0 = 3.27$) for [$H^+ + ISA^- = HISA(aq)$] based on NMR studies ([15]), only a composite protonation constant ($\log_{10} K^0 = 4.0 \pm 0.5$) for the reaction [$H^+ + ISA^- = HISA(aq)^*$, where $HISA(aq)^*$ equals HISA(aq) plus ISL(aq)] can be recommended. In addition to the $\log_{10} K^0 = 0.37 \pm 0.07$ for lactonization constant that we determined based on the intrinsic protonation constant value [15] and the fits to the solubility data of $Ca(ISA)_2(cr)$) [10], the only other value reported for this reaction is $\log_{10} K^0 = 0.84 \pm 0.04$ by [14]. The differences in these values result from the differences in the value of protonation constants used in these calculations. Values based on intrinsic constants were selected for interpretation of the data obtained in this study because they are based on structural information of the species and are obtained from relatively dilute solutions. These values dictate that the uncertainties in the formation of HISA(aq) and ISL(aq), based on the intrinsic constants and other values reported in the literature, will impact the ~pH 4 results in our study. Since a major portion of our investigation was conducted at pH values much greater than 4 where the dominant species amongst HISA(aq), ISA^-, and ISL(aq) is ISA^-, the uncertainties in the formation constant of HISA(aq) will have an insignificant effect on most of the results discussed in this study.

Although previous studies [9, 16] with $ThO_2(am)$ have shown that equilibrium in this system is reached rapidly in as little as 6 days, considerably longer equilibration periods were selected for this study. The equilibrium/steady state concentrations in the high fixed ISA set (0.08) as a function of pH and the variable NaISA sets at fixed pH values of about 6 and 12 show that steady state concentrations in all of these sets are reached in less than 15 days. It appears to have taken a little longer (<55 days) to reach steady state concentrations in the set with low NaISA (0.008 M) as a functions of pH.

A comparison of $ThO_2(am)$ solubility in the presence and absence of NaISA shows that the observed concentrations in the presence of NaISA are up to many orders of magnitude higher than in the absence of NaISA, indicating that the increase in solubility in the presence of NaISA must result from ISA complexes of thorium. As mentioned in the introduction, only one study reports values for Th-ISA complexes ([8]) using liquid-liquid extractions from 1.05 m $NaClO_4$ solutions. The values of ion interaction parameters for the reported complexes [$Th(ISA)_n^{4-}$] are not available to convert these constants to zero ionic strengths and thus use them to predict concentrations in our systems. However, using reasonable values of ion interaction parameters, the $\log_{10} \beta_n^0$ values for the formation of $Th(ISA)_n^{4-}$ with n varying from 1 to 3 were estimated (Table 1) and then used to caculate the $ThO_2(am)$ solubility under our experimental conditions. A comparison of these predictions shows that the predicted values for the fixed NaISA concentration sets as a function of pH in the relatively low pH region are up to several orders of magnitude higher and in the relavely high pH region are up to many orders of magnitude lower than those observed (Figure 1). The predicted concentrations for fixed pH sets as a function of NaISA are in all cases up to several orders of magnitude higher for the pH 6 set and lower for the pH 12 set (Figure 2). It should be noted that these differences are up to several orders of magnitude greater than what might be expected from uncertainties in the estimated $\log_{10} \beta_n^0$ values caused by using estimated ion-interaction parameters. In addition, the changes in predicted concentrations as a function of pH (Fig 1) and/or a function of NaISA concentrations at fixed pH values of about 6 or 12 (Figure 2) are drastically different than those observed, indicating that the model previously reported in the literature ([8]) cannot be correct.

3.1 Thermodynamic Interpretations of ThO_2(am) Solubility Data

To develop a reliable model for Th-ISA complexes several combinations of Th-ISA complexes involving monomeric, multi-ligand, and mixed hydroxy-ISA complexes were evaluated. The dominant types of aqueous complexes and their formation constants were first determined through thermodynamic analyses of ThO_2(am) solubility data in the fixed NaISA concentrations (0.008 m or 0.08 m) as functions of pH (Figure 3). These species and their formation constants were then tested to predict ThO_2(am) solubility as a function of NaISA concentration at fixed pH values of abut 6 or 12 (Figure 4). The model that best described the entire data included [$Th(OH)ISA^{2+}$, $Th(OH)_3(ISA)_2^-$, and $Th(OH)_4(ISA)_2^{2-}$] with the log K^0 values of 12.50 ± 0.47, 4.41 ± 0.47, and -3.18 ± 0.47 for reactions 1, 2, and 3, respectively. For these interpretations SIT ion interaction

$$ThO_2(am) + 3H^+ + ISA^- = Th(OH)ISA^{2+} + H_2O \quad (1)$$

$$ThO_2(am) + H^+ + 2ISA^- + H_2O = Th(OH)_3(ISA)_2^- \quad (2)$$

$$ThO_2(am) + 2ISA^- + 2H_2O = Th(OH)_4(ISA)_2^{2-} \quad (3)$$

parameters [$\varepsilon(Na^+, ISA^-) = -0.07$ from [1], and $\varepsilon(Na^+, Th(OH)_3(ISA)_2^-) = -0.07$ assumed to be identical to that for (Na^+, ISA^-)] were used. A range of $\varepsilon(Na^+, Th(OH)_4(ISA)_2^{2-})$ values from -0.12 to -0.57 were tried, but the fitted values were not significantly different from each other and the overall standard deviation in the entire fitted data varied only slightly (0.47 to 0.52). This is not surprising since the ionic strength and Na concentrations are relatively low, and the major effects on activity corrections result from the Debye- Huckel term included in the model rather than being due to the ion-interaction parameters. The concentrations predicted with this model (Table 2 and 3) agree closely with the observed concentrations in all of the sets (Figures 3 and 4) with the exception of a few data points at relatively high pH in the fixed 0.008 m NaISA concentration set (Figure 3).

Thermodynamic modeling cannot differentiate between the species $Th(OH)ISA^{2+}$, $Th(OH)_3(ISA)_2^-$ and $Th(OH)_4(ISA)_2^{2-}$ in reactions 1-3 and $Th(ISA_{-H})^{2+}$, $Th(ISA_{-H})(ISA_{-2H})^-$ and $Th(ISA_{-2H})_2^{2-}$, respectively. Therefore, the experimental data on the solubility of ThO_2(am) could have been equivalently modeled using the following reactions:

$$ThO_2(am) + 3H^+ + ISA^- = Th(ISA_{-H})^{2+} + 2H_2O$$

$$ThO_2(am) + H^+ + 2ISA^- = Th(ISA_{-H})(ISA_{-2H})^- + 2H_2O$$

$$ThO_2(am) + 2ISA^- = Th(ISA_{-2H})_2^{2-} + 2H_2O$$

The latter set of species represents chelate complexes between Th(IV) and isosaccharinate in which one or two alcohol hydroxyl groups are deprotonated in addition to the carboxylate group. Because our earlier NMR studies [15] show that deprotonation of the alcoholic OH groups in ISA does not occur below pH 12, we have chosen to represent Th-ISA complexes as reported in reactions 1-3. However, the pKa of the alcoholic OH groups could be lowered significantly due to their interaction with high charge density cations (e.g., Th^{4+}, UO_2^{2+}) as is suggested by recent study [17] of UO_2^{2+} with gluconate, a ligand similar to ISA in that gluconate contains multiple alcoholic OH groups and a carboxylate group. Therefore further studies to characterize the structure of Th(IV)-ISA complexes could help to determine which set of species represent the actual complexes in solution, but this is beyond the scope of the present work.

When the equilibrium reactions for the dissolution of ThO_2(am) (Eq. 1-3) are combined with the ThO_2(am) solubility product ($\log_{10} K_{sp}^0 = -46.7$) [9], they provide the logarithm of the equilibrium constant of 3.18 ± 0.47 for [$Th^{4+} + H_2O + ISA^- = Th(OH)ISA^{2+} + H^+$], -4.91 ± 0.47 for [$Th^{4+} + 3H_2O + 2ISA^- = Th(OH)_3(ISA)_2^- + 3H^+$], and - 12.49 ± 0.47 for [$Th^{4+} + 4H_2O + 2ISA^- = Th(OH)_4(ISA)_2^{2-} + 4H^+$]. No other thermodynamic data for mixed hydroxy-ISA complexes of thorium are available for comparison to the data developed in this study.

3.2 Thermodynamic Interpretations of the data from liquid-liquid extractions in 1.05 m $NaClO_4$

Although the predictions of Th concentrations based on the Allard and Ekberg's [8] model developed from liquid-liquid extractions are up to several orders of magnitude different than those we observed experimentally (Figures 1 and 2), it is of interest to determine whether the model developed in our study which contains mixed hydroxy-ISA complexes of Th [$Th(OH)_x(ISA)_y^{4-x-y}$] instead of $Th(ISA)_n^{4-n}$, the one proposed by Allard and Ekberg [8], can equally well explain their data. Allard and Ekberg [8] interpreted their data using Equation (4), slightly modified to exclude β_{101} which according to their data becomes only marginally important at extremely low ISA^- concentrations of <~10^{-5} m, and in their paper they have reported the values of $D_{Th,}$ λ_4, Aa^-,

$$D_{Th} = [\lambda_4 \beta_{140} (Aa^-)^4] / [1 + \beta_{140} (Aa^-)^4 + \beta_{102} (ISA^-)^2 + \beta_{103} (ISA^-)^3] \qquad (4)$$

β_{101}, β_{102}, β_{103}, and ISA^- at different temperatures. However, they did not report values for β_{140} at different temperatures which we estimated from their data (log β_{140} of 26.18, 27.20, and 26.0 at 15ºC, 25ºC, and 35ºC, respectively). These estimated values reproduced their predicted values very well when compared to their fitted values and as shown in Figure 5. We tested the ability of our model to accurately interpret liquid-liquid extraction data of Allard and Ekberg [8] using their equation (4) modified (Eq. 5) to

$$D_{Th} = [\lambda_4 \beta_{140} (Aa^-)^4] / [1 + \beta_{140} (Aa^-)^4 + (K_{Th(OH)4(ISA)2}{}^{2-} [ISA^-]^2) / (H^+)^4] \qquad (5)$$

include $K_{Th(OH)4(ISA)2}{}^{2-}$, a concentration equilibrium constant at 1.05 m ionic strength for the formation of $Th(OH)_4(ISA)_2{}^{2-}$ according to the reaction [$Th^{4+} + 4H_2O + 2ISA^- = Th(OH)_4(ISA)_2{}^{2-} + 4H^+$] (which based on our data is the only dominant species in the pH value (~8.3) of Allard and Ekberg's study). The reinterpretation of liquid-liquid extraction data required the inclusion of log $K_{Th(OH)4(ISA)2}{}^{2-}$ values of -15.3 ±0.4, -13.7 ± 0.4, and -14.4 ± 0.4 at 15ºC, 25ºC, and 35ºC, respectively. A few observations can be made regarding these calculated log $K_{Th(OH)4(ISA)2}{}^{2-}$ values: 1) as a result of non-systematic changes in β_{140} values used in [8], the calculated values do not systematically either decrease or increase with the increase or decrease in temperature, 2) the calculated log K value (-13.7 ± 0.4) at 25ºC and in 1.05 m ionic strength is close to the zero ionic strength value (log K^0 = -12.49 ± 0.47) fitted from our data and seems reasonable because the difference in these values may truly be due to the changes in activities of different species (see footnote 1), 3) the log $K_{Th(OH)4(ISA)2}{}^{2-}$ value (-13.7 ± 0.4) at 1.05 m ionic strength at 25ºC cannot be directly compared to the 22 ± 2º C value (-12.49 ± 0.47) at zero ionic strength determined from our study because SIT ion-interaction parameters for (Na^+,

$Th(OH)_4(ISA)_2^{2-}$) are not available at any temperature[1], nor can they be determined from the Allard and Ekberg data because the study was conducted at only one ionic strength, and 4) fitted log $K_{Th(OH)4(ISA)2}^{2-}$ values provide a close agreement between the experimental and calculated D_{Th} values as a function of NaISA concentrations at all temperatures (Figure 5); this agreement is as close as that reported by Allard and Ekberg [8] based on the inclusion of $Th(ISA)_n^{4-n}$ complexes. In conclusion, the predictions based on Allard and Ekberg's [8] model are completely at odds with our experimental data, but our model not only describes well the data obtained in our study but also describes their data well. Since Allard and Ekberg [8] conducted their study at only one pH, it was not possible for them to evaluate the mixed-hydorxy complexes of Th, the complexes that are dominant in a large range of pH values (4.5 to 12), and thus the disagreements are a result of poor selection of the concentration-controlling species. Fits to the Allard and Ekberg's [8] data are primarily dependent on the ISA concentration dependence of the species because the experiments were conducted at only one fixed pH value. Therefore it is not surprising that [$Th(OH)_4(ISA)_2^{2-}$], the dominant species in our model at pH ~ 8.3 that describes Allard and Ekberg's data well, is the species that increases Th concentrations by two orders of magnitude with each one order of magnitude increase in isosaccharinate concentration; in exactly the same manner as Allard and Ekberg's [8] model uses mostly [$Th(ISA)_2^{2+}$] to describe their data.

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[1] SIT ion-interaction parameter for (Na^+, $Th(OH)_4(ISA)_2^{2-}$) at approximately 25ºC can be estimated from the log K^0 value (-12.49 ±0.47), calculated log K value (-13.7 ±0.4) at 1.05 m $NaClO_4$, and the ε values [(Na^+, ClO_4^-) = 0.14 ± 0.02, (Na^+, ISA^-) = -0.07, (Th^{4+}, ClO_4^-) = 0.7 ± 0.1] reported in Hummel et al. (2005). The ε(Na^+, $Th(OH)_4(ISA)_2^{2-}$) = -0.57 ± 0.63 calculated in this manner has a relatively large uncertainty and thus cannot be used with any reliability. However, this value does point out that the log K value (-13.7 ±0.4) at 1.05 m $NaClO_4$ calculated from these data seems reasonable as the decrease in log K value going from 0 ionic strength to 1.05 m is smaller than dictated by the Debye-Huckel term alone.

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FIGURE LEGENDS

Figure 1. ThO_2(am) solubility as a function of pH and time and at a fixed NaISA concentration of 0.008 mol.kg^{-1} (top) or 0.08 mol.kg^{-1} (bottom). Solid line depicts predicted concentration based on the $Th(ISA)_n^{4-n}$ complexes reported by Allard and Ekberg [8] (Table 1) and the other appropriate thermodynamic data reported in Table 2 and 3. Dashed line depicts ThO_2(am) solubility based on the thermodynamic data reported in Tables 2 and 3 without any Th-ISA complexes.

Figure 2. ThO_2(am) solubility as a function of NaISA and time and at a fixed pH values of about 6 and 12, for actual pH values see Appendix Tables A.3 and A.4. Solid line depicts predicted concentration based on the $Th(ISA)_n^{4-n}$ complexes reported by Allard and Ekberg [8] (Table 1) and the other appropriate thermodynamic data reported in Tables 2 and 3.

Figure 3. ThO_2(am) solubility as a function of pH and time and at a fixed NaISA concentration of 0.008 mol.kg^{-1} (top) or 0.08 mol.kg^{-1} (bottom). Lines represent predicted concentrations using the thermodynamic data reported in Tables 2 and 3: *solid line* represents total Th concentration and *other lines* represent concentrations of different species as marked in the Figure.

Figure 4. ThO_2(am) solubility as a function of NaISA concentration and time and at a fixed of about 6 and 12, for actual pH values see appendix Tables A.3 and A.4. Lines represent predicted concentrations using the thermodynamic data reported in Tables 2 and 3: *solid line* represents total Th concentration and *other lines* represent concentrations of different species as marked in the Figure.

Figure 5. Observed [8] and predicted distribution coefficients ([D_{Th}]) for liquid-liquid extraction in1.05 mol.kg^{-1} $NaClO_4$ and at 15ºC, 25ºC, or 35ºC. Predicted ([D_{Th}] values based on data reported in Allard and Ekberg [8] including $Th(ISA)_n^{4-n}$ complexes (ALL/EKB model) are compared with the "This study's model" that included the formation constant for $Th(OH)_4(ISA)_2^{2-}$ according to the reaction [$Th^{4+} + 4H_2O + 2ISA^- = Th(OH)_4(ISA)_2^{2-} + 4H^+$] instead of for $Th(ISA)_n^{4-n}$ (see text for details).

TEXT TABLE HEADINGS

Table 1. ISA complexes of thorium based on the literature data

Table 2. Thermodynamic data used in calculations

Table 3. SIT ion-interaction parameters used in this study

APPENDIX TABLE HEADINGS

Table A1. Solubility of ThO_2(am), equilibrated for different periods, as a function of pH and at fixed NaISA concentration of 0.008 M

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Table A4. Solubility of ThO_2(am), equilibrated for different periods, as a function of NaISA concentration and at a fixed pH value of about 12

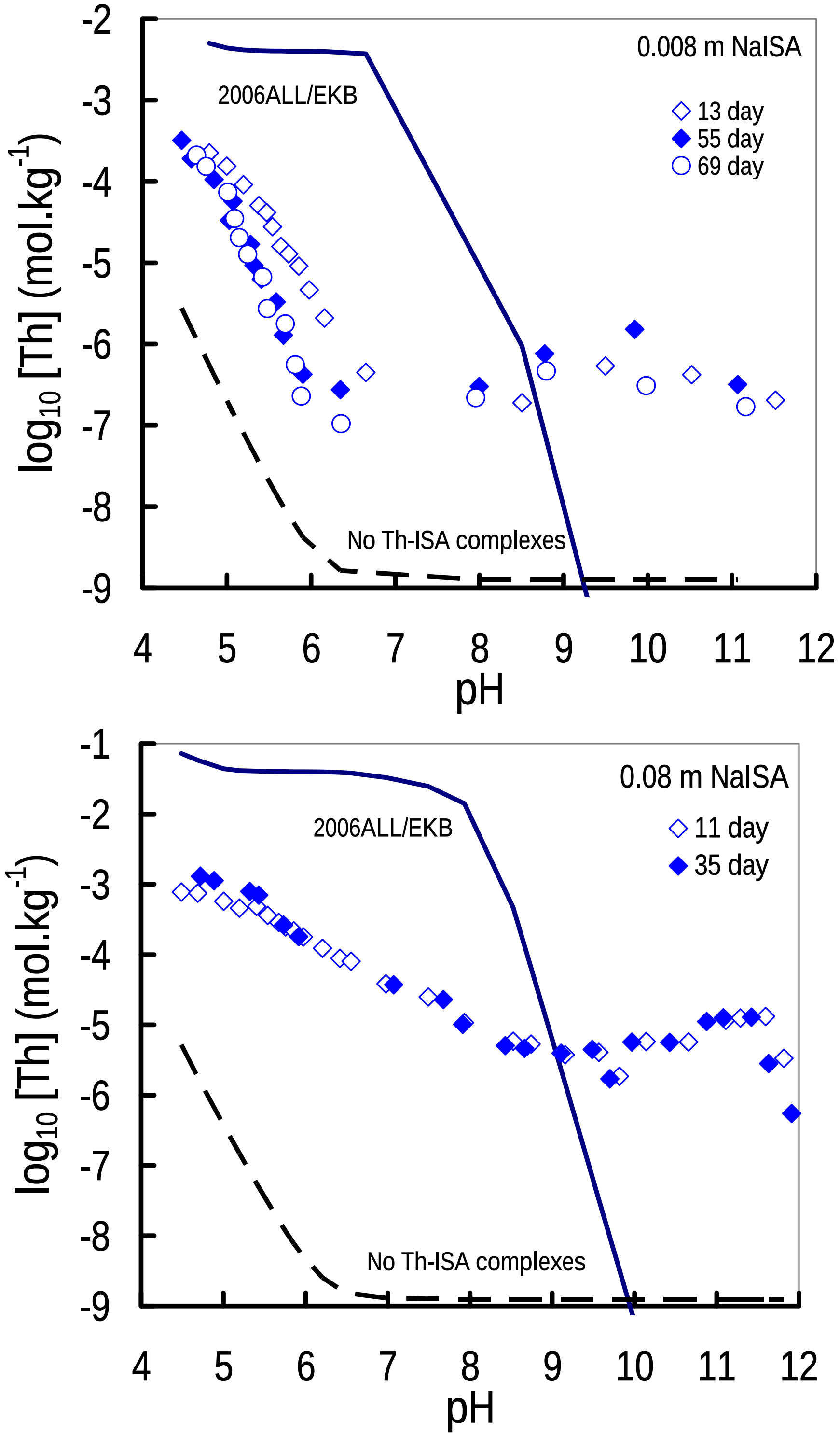

Figure 1. ThO_2(am) solubility as a function of pH and time and at a fixed NaISA concentration of 0.008 mol.kg^{-1} (top) or 0.08 mol.kg^{-1} (bottom). Solid line depicts predicted concentration based on the $Th(ISA)_n^{4-n}$ complexes reported by Allard and Ekberg [8] (Table 1) and the other appropriate thermodynamic data reported in Table 2 and 3. Dashed line depicts ThO_2(am) solubility based on the thermodynamic data reported in Tables 2 and 3 without any Th-ISA complexes.

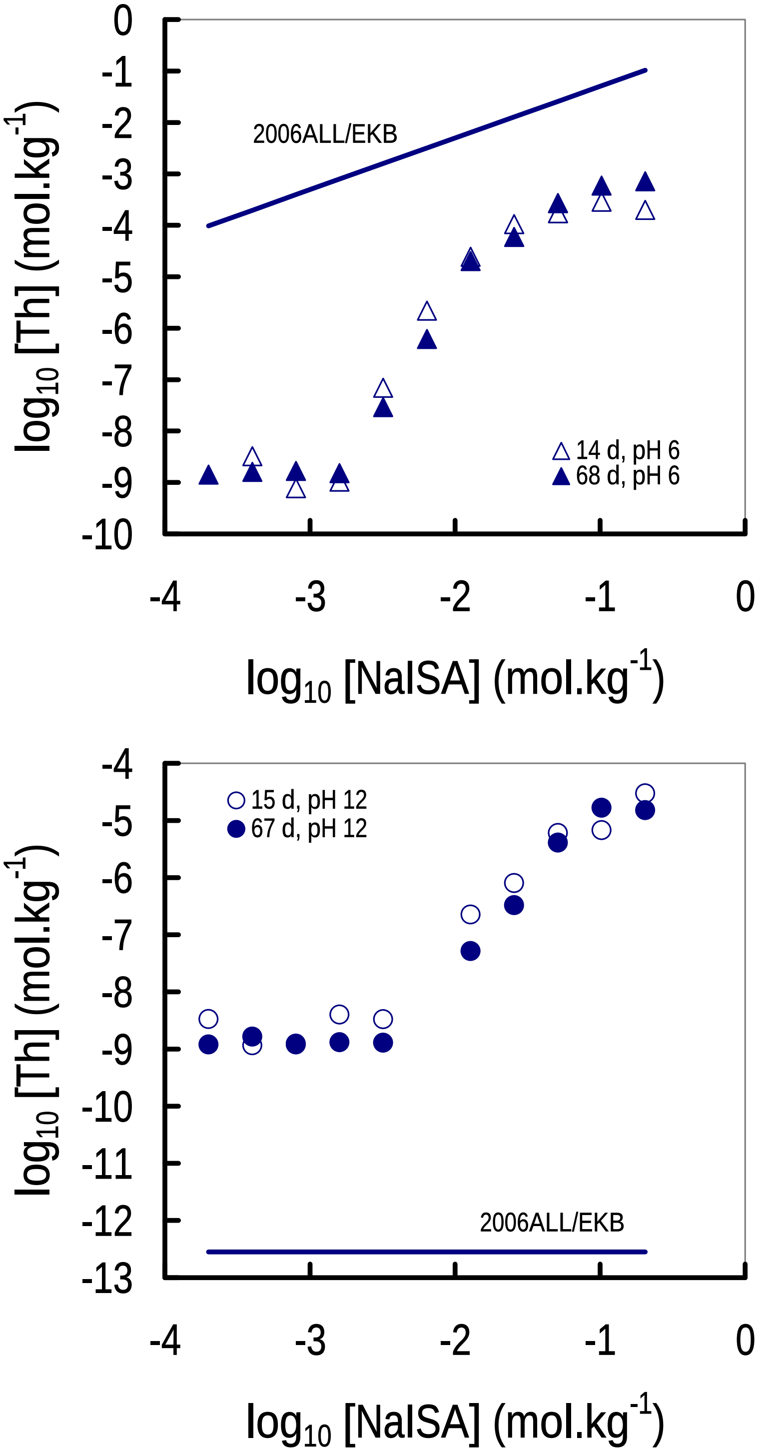

Figure 2. ThO_2(am) solubility as a function of NaISA and time and at a fixed pH values of about 6 and 12, for actual pH values see Appendix Tables A.3 and A.4. Solid line depicts predicted concentration based on the $Th(ISA)_n^{4-n}$ complexes reported by Allard and Ekberg [8] (Table 1) and the other appropriate thermodynamic data reported in Tables 2 and 3.

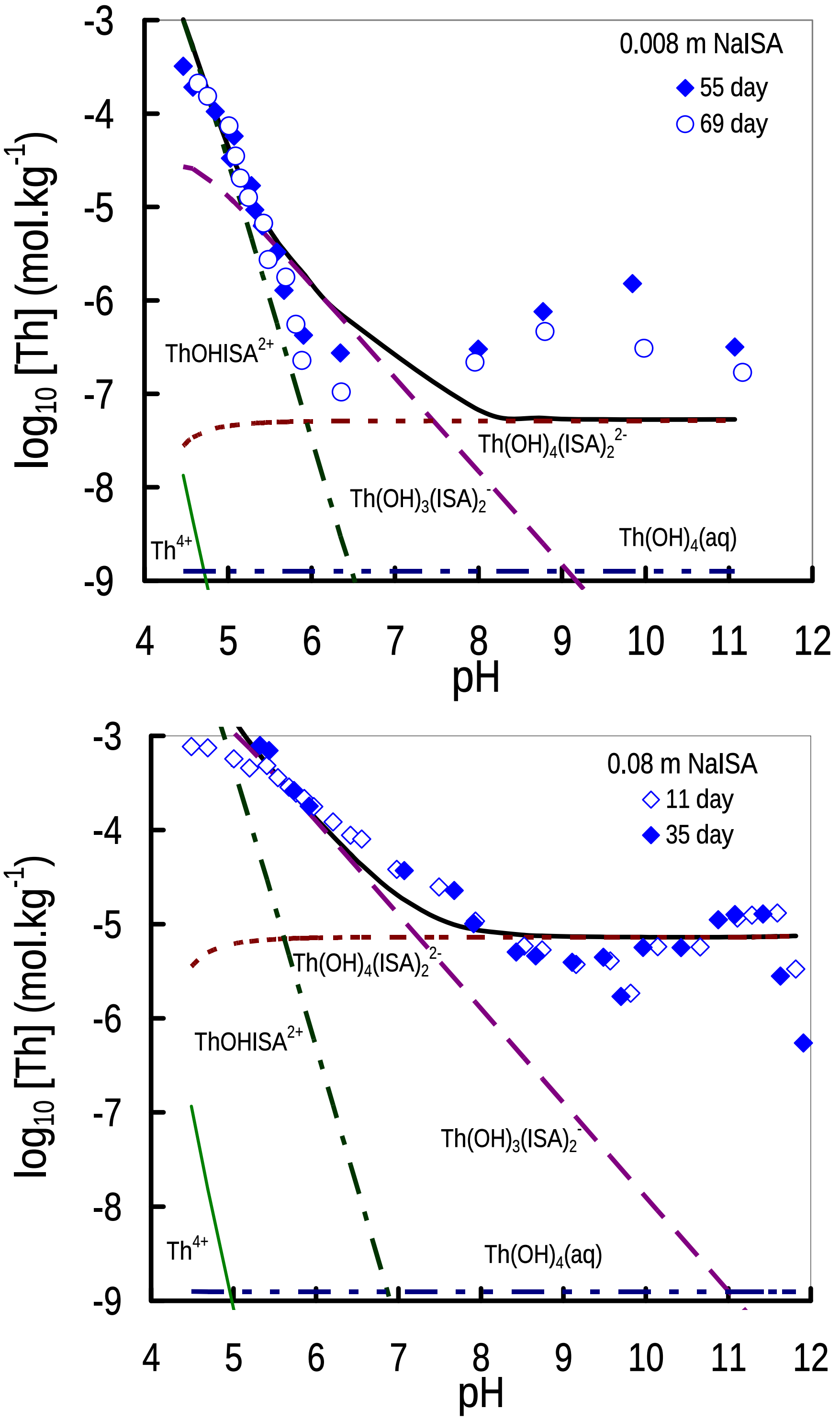

Figure 3. ThO_2(am) solubility as a function of pH and time and at a fixed NaISA concentration of 0.008 mol.kg^{-1} (top) or 0.08 mol.kg^{-1} (bottom). Lines represent predicted concentrations using the thermodynamic data reported in Tables 2 and 3: *solid line* represents total Th concentration and *other lines* represent concentrations of different species as marked in the Figure.

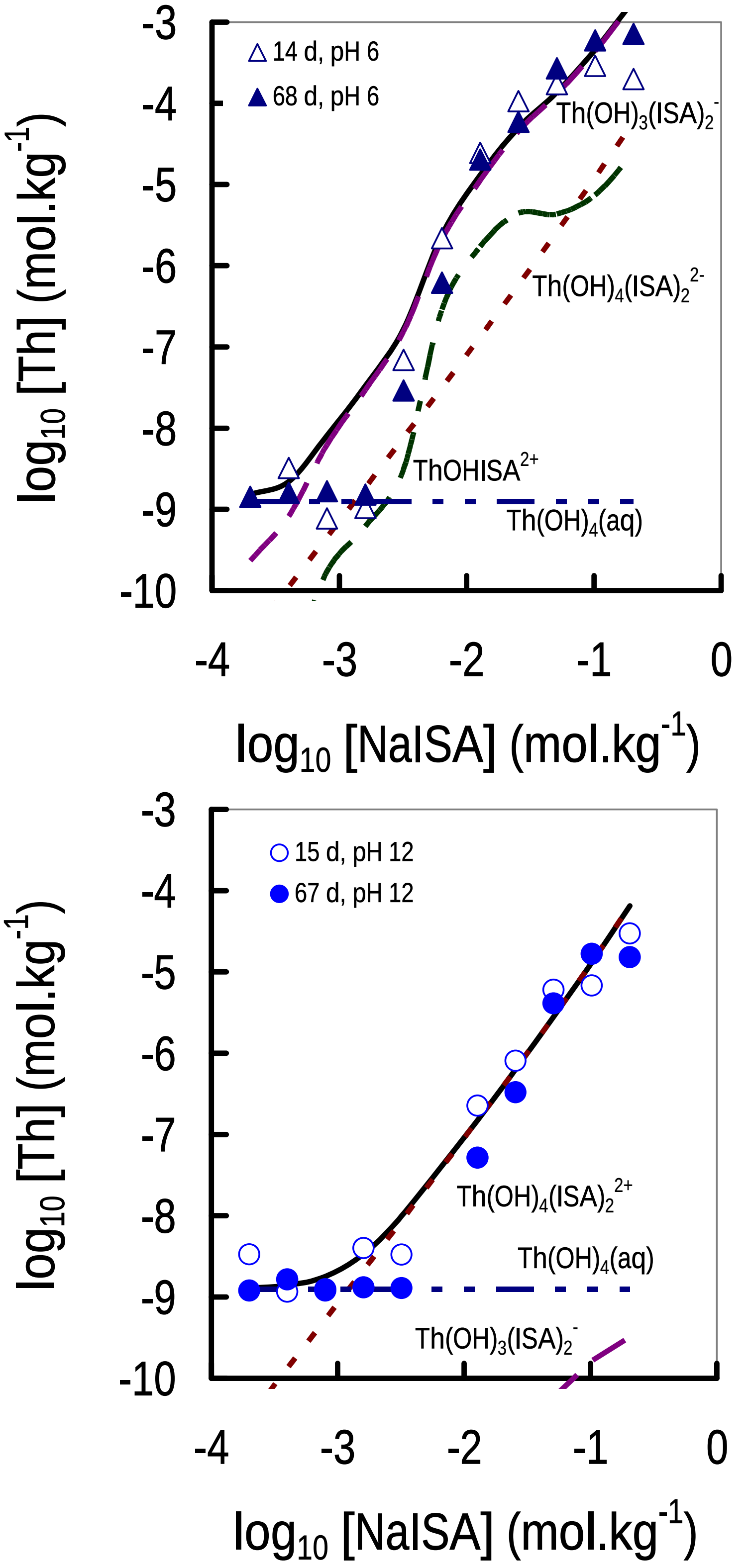

Figure 4. ThO_2(am) solubility as a function of NaISA concentration and time and at a fixed of about 6 and 12, for actual pH values see appendix Tables A.3 and A.4. Lines represent predicted concentrations using the thermodynamic data reported in Tables 2 and 3: *solid line* represents total Th concentration and *other lines* represent concentrations of different species as marked in the Figure.

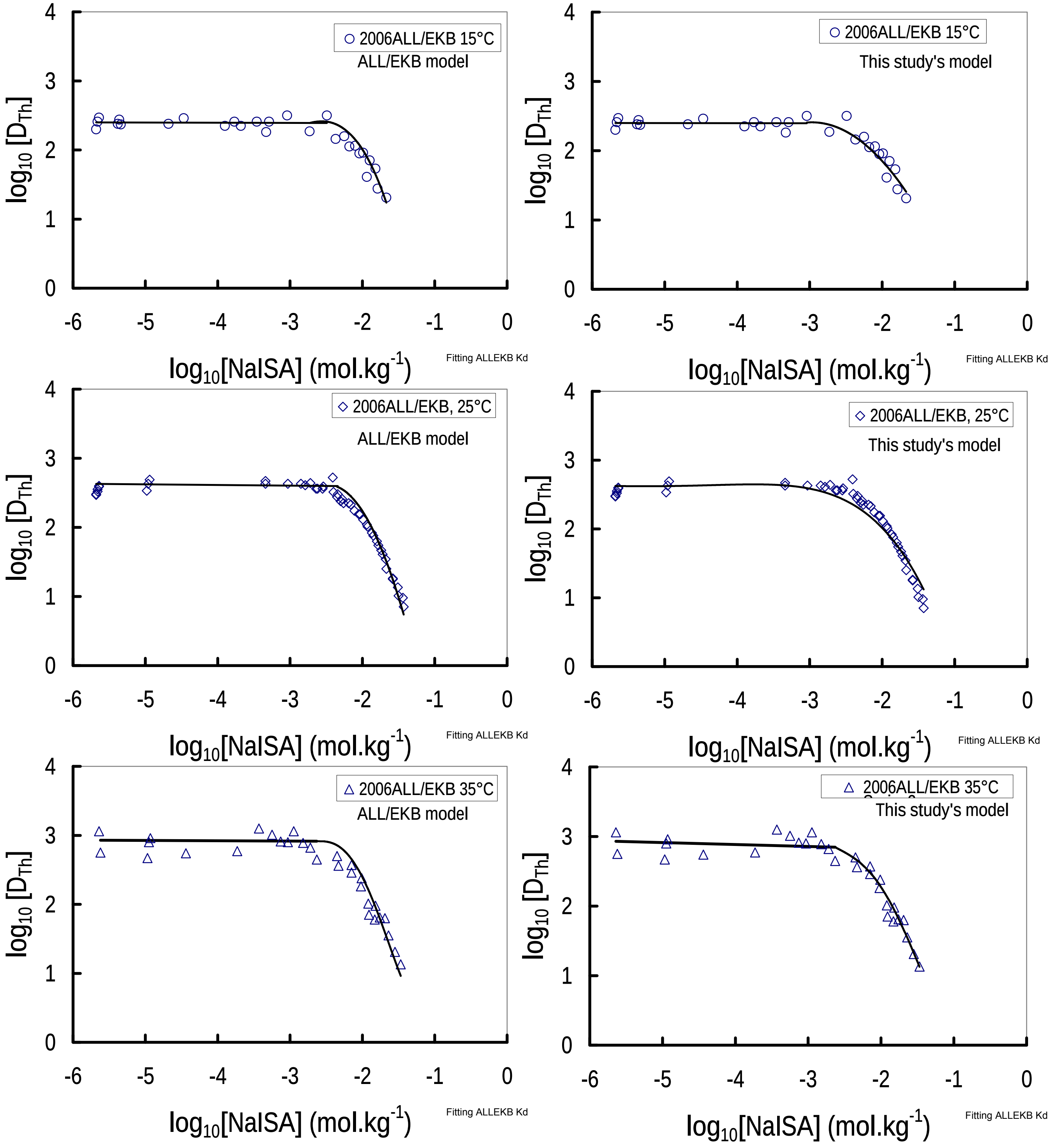

Figure 5. Observed [8] and predicted distribution coefficients ($[D_{Th}]$) for liquid-liquid extraction in1.05 mol.kg^{-1} $NaClO_4$ and at 15ºC, 25ºC, or 35ºC. Predicted ($[D_{Th}]$ values based on data reported in Allard and Ekberg [8] including $Th(ISA)_n^{4-n}$ complexes (ALL/EKB model) are compared with the "This study's model" that included the formation constant for $Th(OH)_4(ISA)_2^{2-}$ according to the reaction [$Th^{4+} + 4H_2O + 2ISA^- = Th(OH)_4(ISA)_2^{2-} + 4H^+$] instead of for $Th(ISA)_n^{4-n}$ (see text for details).

Table 1. ISA complexes of thorium based on the literature data

Stability Constants		I_M[b]	**Reference**
Parameter[a]	**Value**		
log β_1	12.56 ± 5.01	1.01	[8]
log β_2	19.38 + 0.35 / -0.95	1.01	[8]
log β_3	21.30 ± 0.26	1.01	[8]
log β_1^0	14.14 ± 5.01	0.0	This study[c]
log β_2^0	22.10 + 0.35/-0.95	0.0	This study[c]
log β_3^0	24.96 ± 0.26	0.0	This study[c]

[a] For the reactions [$Th^{4+} + nISA^- = Th(ISA)_n^{4-n}$].

[b] $NaClO_4$ as the medium.

[c] We calculated these values using the SIT model. The ε_1 value for (Th^{4+}, ClO_4^-) = 0.70 ± 0.10 is from Rand et al. [9], and for (Na^+, ClO_4^-) = 0.01 ± 0.10, and (Na^+, ISA^-) = -0.07 are from [1]. ε_1 values needed for ($Th(ISA)_n^{4-n}$, ClO_4^-) are not available. These calculations used the ε_1 values for ($ThISA^{3+}$, ClO_4^-) = 0.56, ($Th(ISA)_2^{2+}$, ClO_4^-) = 0.40, and ($Th(ISA)_3^+$, ClO_4^-) = 0.27, corresponding to the average values of similarly charged metal ions with ClO_4^- reported by NEA. It should be noted that because of the relatively high ionic strength used in this study the corrections to convert concentration constants to thermodynamic equilibrium constants are primarily due to the Debye-Huckel term. The contribution of the assumed ion interaction parameters is very small (-0.07, -0.17, and -0.05 for $Th(ISA)_n^{4-n}$ with n varying from 1 to 3 respectively), certainly much smaller than the standard deviation reported in the original numbers.

Table 2. Thermodynamic data used in calculations

Reaction	**log K^0**	**Reference**
$ThO_2(am) + 2H_2O = Th^{4+} + 4OH^-$	-46.7	[9]
$Th^{4+} + H_2O = ThOH^{3+} + H^+$	-2.50	[9]
$Th^{4+} + 2H_2O = Th(OH)_2^{2+} + 2H^+$	-6.2	[9]
$Th^{4+} + 4H_2O = Th(OH)_4(aq) + 4H^+$	<-18.21	This study
$2Th^{4+} + 2H_2O = Th_2(OH)_2^{6+} + 2H^+$	-5.90	[9]
$HISA(aq) = ISL(aq) + H_2O$	0.37 ± 0.07	[10]
$HISA(aq) = ISA^- + H^+$	-3.27 ± 0.02	[15]
$ThO_2(am) + 3H^+ + ISA^- = Th(OH)ISA^{2+} + H_2O$	12.50 ± 0.47	This study
$ThO_2(am) + H^+ + 2ISA^- + H_2O = Th(OH)_3(ISA)_2^-$	4.41 ± 0.47	This study
$ThO_2(am) + 2ISA^- + 2H_2O = Th(OH)_4(ISA)_2^{2-}$	-3.18 ± 0.47	This study

Table 3. SIT ion-interaction parameters used in this study

Species	**ε_1**	**Reference**
Na^+, ISA^-	-0.07	This study[a]
Na^+, $Th(OH)_3(ISA)_2^-$	-0.07	This study[b]
Na^+, $Th(OH)_4(ISA)_2^{2-}$	-0.12	This study[c]

[a] Calculated from values reported in [1]

[b] Assumed to be identical to Na^+, ISA^-

[c] Average of the values of Na^+ with divalent anions reported in Hummel et al. [1]

Table A1. Solubility of ThO_2(am), equilibrated for different periods, as a function of pH and at fixed NaISA concentration of 0.008 M

log ISA	log Na	13 days		55 days		69 days	
		pH	**log Th**	**pH**	**log Th**	**pH**	**log Th**
-2.097	-2.097	4.793	-3.648	4.464	-3.495	4.642	-3.677
-2.097	-2.097	4.999	-3.811	4.580	-3.718	4.754	-3.815
-2.097	-2.097	5.196	-4.038	4.848	-3.977	5.013	-4.133
-2.097	-2.097	5.380	-4.297	5.073	-4.243	5.092	-4.456
-2.097	-2.097	5.473	-4.382	5.029	-4.479	5.149	-4.690
-2.097	-2.097	5.542	-4.558	5.280	-4.773	5.247	-4.897
-2.097	-2.097	5.642	-4.799	5.321	-5.031	5.427	-5.175
-2.097	-2.097	5.734	-4.891	5.411	-5.203	5.482	-5.564
-2.097	-2.097	5.854	-5.042	5.585	-5.484	5.694	-5.751
-2.097	-2.097	5.978	-5.334	5.671	-5.892	5.814	-6.256
-2.097	-2.097	6.160	-5.680	5.903	-6.372	5.885	-6.643
-2.097	-2.097	6.651	-6.350	6.347	-6.563	6.357	-6.980
-2.097	-2.097	8.505	-6.724	7.997	-6.521	7.958	-6.661
-2.097	-2.095	9.494	-6.270	8.774	-6.120	8.796	-6.333
-2.097	-2.079	10.521	-6.379	9.844	-5.820	9.982	-6.513
-2.097	-1.948	11.515	-6.693	11.068	-6.499	11.164	-6.771

Table A2. Solubility of ThO_2(am), equilibrated for different periods, as a function of pH and at fixed NaISA concentration of 0.08 M

log ISA	log Na	11 days		35 days	
		pH	log Th	pH	log Th
-1.097	-1.097	4.488	-3.112	4.721	-2.885
-1.097	-1.097	4.688	-3.128	4.887	-2.950
-1.097	-1.097	5.004	-3.244		
-1.097	-1.097	5.194	-3.342	5.321	-3.103
-1.097	-1.097	5.404	-3.316	5.430	-3.156
-1.097	-1.097	5.538	-3.443		
-1.097	-1.097	5.673	-3.544	5.734	-3.581
-1.097	-1.097	5.757	-3.608		
-1.097	-1.097	5.857	-3.664	5.917	-3.746
-1.097	-1.097	5.972	-3.751		
-1.097	-1.097	6.206	-3.914		
-1.097	-1.097	6.418	-4.055		
-1.097	-1.097	6.554	-4.096		
-1.097	-1.097	6.979	-4.417	7.070	-4.431
-1.097	-1.097	7.493	-4.604	7.676	-4.642
-1.097	-1.097	7.932	-4.969	7.911	-4.994
-1.097	-1.097	8.524	-5.233	8.429	-5.297
-1.097	-1.097	8.743	-5.274	8.665	-5.337
-1.097	-1.097	9.156	-5.428	9.107	-5.404
-1.097	-1.097	9.568	-5.391	9.486	-5.352
-1.097	-1.097	9.817	-5.734	9.700	-5.769
-1.097	-1.096	10.144	-5.239	9.967	-5.246
-1.097	-1.094	10.658	-5.243	10.427	-5.250
-1.097	-1.090	11.112	-4.936	10.879	-4.953
-1.097	-1.076	11.594	-4.881	11.421	-4.892
-1.097	-1.086	11.288	-4.903	11.080	-4.899
-1.097	-1.046	11.817	-5.477	11.632	-5.551
-1.097	-1.000	12.245	-6.505	11.912	-6.263

Table A3. Solubility of ThO_2(am), equilibrated for different periods, as a function of NaISA concentration and at a fixed pH value of about 6

log ISA	**log Na**	**14 days**		**68 days**	
		pH	**log Th**	**pH**	**log Th**
-3.699	-3.699	6.18	-6.651	6.63	-8.846
-3.398	-3.398	6.238	-8.490	6.685	-8.796
-3.097	-3.097	6.153	-9.112	6.402	-8.777
-2.796	-2.796	6.115	-8.983	6.322	-8.818
-2.495	-2.495	6.058	-7.160	6.196	-7.537
-2.194	-2.194	5.776	-5.660	5.648	-6.207
-1.893	-1.893	5.681	-4.610	5.502	-4.693
-1.592	-1.592	5.654	-3.975	5.481	-4.228
-1.291	-1.291	5.654	-3.764	5.605	-3.568
-0.990	-0.990	5.45	-3.539	5.651	-3.226
-0.689	-0.689	5.45	-3.702	5.602	-3.145

Table A4. Solubility of ThO_2(am), equilibrated for different periods, as a function of NaISA concentration and at a fixed pH value of about 12

log ISA	**log Na**	**15 days**		**67 days**	
		pH	**log Th**	**pH**	**log Th**
-3.699	-1.991	12.215	-8.475	11.906	-8.921
-3.398	-1.983	12.315	-8.934	12.013	-8.783
-3.097	-1.967	12.254	-8.922	11.948	-8.904
-2.796	-1.936	12.275	-8.397	11.973	-8.883
-2.495	-1.879	12.242	-8.479	11.983	-8.890
-1.893	-1.642	12.208	-6.645	12.014	-7.285
-1.592	-1.449	12.130	-6.094	11.935	-6.482
-1.291	-1.213	12.103	-5.219	11.963	-5.388
-0.990	-0.949	12.076	-5.169	12.087	-4.778
-0.689	-0.668	12.019	-4.528	12.361	-4.820