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Environmental Mobility of Pu(IV) in the Presence of Ethylenediaminetetraacetic Acid: Myth or Reality?

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Abstract Ethylenediaminetetracetic acid (EDTA), which was co-disposed with Pu at several US Department of Energy sites, has been reported to enhance the solubility and transport of Pu. It is generally assumed that this enhanced transport of Pu in geologic environments is a result of complexation of Pu(IV) with EDTA. However, the fundamental basis for this assumption has never been fully explored. Whether EDTA can mobilize Pu(IV) in geologic environments is dependent on many factors, chief among them are not only the complexation constants of Pu with EDTA and dominant oxidation state and the nature of Pu solids, but also (1) the complexation constants of environmentally important metal ions (e.g., Fe, Al, Ca, Mg) that compete with Pu for EDTA and (2) EDTA interactions with the geomedia (e.g., adsorption, biodegradation) that reduce effective EDTA concentrations available for complexation. Extensive studies over a large range of pH values (1 to 14) and EDTA concentrations (0.0001 to 0.01 mol·L^{-1}) as a function of time were conducted on the solubility of 2-line ferrihydrite ($Fe(OH)_3(s)$), $PuO_2(am)$ in the presence of different concentrations of Ca ions, and mixtures of $PuO_2(am)$ and $Fe(OH)_3(s)$. The solubility data were interpreted using Pitzer's ion-interaction approach to determine/validate the solubility product of $Fe(OH)_3(s)$, the complexation constants of Pu(IV)-EDTA and Fe(III)-EDTA, and to determine the effect of EDTA in solubilizing Pu(IV) from $PuO_2(am)$ in the presence of Fe(III) compounds and aqueous Ca concentrations. Predictions based on these extensive fundamental data show that environmental mobility of Pu as a result of Pu(IV)-EDTA complexation as reported/implied in the literature is a myth rather than the reality. The data also show that in geologic environments where Pu(III) and Pu(V) are stable, the EDTA complexes of these oxidation states may play an important role in Pu mobility.

Keywords Thermodynamics · Solubility · Pu · EDTA · Pu EDTA complexes · Pitzer model · SIT model · $PuO_2(am)$ · Ferrihydrite solubility · Fe(III) EDTA complexes · $Fe(OH)_3(am)$

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1 Introduction

Ethylenediaminetetraacetic acid (EDTA) has been used in the nuclear industry as a decontaminating agent [1, 2], in defense production of Pu, and to process Pu-containing nuclear wastes [3]. The Pu-containing EDTA waste solutions have been either inadvertently or intentionally disposed in geologic environments. Inadvertent discharges into the ground have occurred as a result of leakages of high-level radioactive-waste tanks. As an example, Tank 241-T-106 at Hanford released 435,000 L of mixed radioactive waste containing Pu and EDTA into the subsurface [4] during 1973. A contaminant plume at this tank site extended to a depth of 33 m. Most of the Pu was found in sediments at 2 m below the tank, presumably due to the presence of insoluble particulate PuO_2, but a Pu spike was detected at a depth of 29 m [4]. Enhanced solubility and transport of Pu in groundwater has occurred at several sites in the DOE Complex [5, 6]. It is generally assumed that the enhanced mobility of Pu in geologic environments must result from Pu(IV)-EDTA complexes because, (1) EDTA is known to form very strong complexes with tetravalent Pu [7–10]; (2) in many instances significant amounts of tetravalent Pu was co-disposed with EDTA in geologic environments; (3) laboratory studies report that EDTA complexes of Pu(VI), Pu(V) and Pu(III), the only other environmentally important oxidation states, are not stable in oxygenated systems and that the dominant oxidation state of Pu in these systems is Pu(IV) [8–12]; and (4) it was previously intimated that Pu(III) spontaneously converts to Pu(IV) [13], although our recent data [14] shows that Pu(III) is a stable oxidation state under the reducing conditions prevalent in many geologic environments. Although limited mobility of Pu, in most cases co-disposed with EDTA, is reported [4–6], no definitive data pertaining to specific sites or geologic environments are available to support the generalization that Pu(IV)-EDTA complexes are responsible for this observed Pu mobility.

The mobility of Pu in geologic environments is dependent on many factors. Chief among these are the Pu oxidation state, pH, the presence and concentrations of strongly complexing ligands such as EDTA, and the presence and concentrations of metal ions such as Fe(III) and Ca(II) that compete with Pu for complexation with ligands. In order to evaluate whether Pu(IV)-EDTA complexes are responsible for enhanced Pu mobility, as the existing indirect evidence seem to indicate, reliable thermodynamic data for both EDTA complexes with Pu and competing metal ions are required to predict their concentrations and the competition of metal ions with Pu for EDTA. Much of the past data for EDTA complexes with metals of interest have been obtained through the use of spectroscopic, polarographic and potentiometric titrations, and ion-exchange techniques. One of the major difficulties in determining reliable values for strongly complexing species such as EDTA complexes of Pu(IV) or Fe(III) using the techniques listed above is that the activities of bare metal ions, which are needed to calculate equilibrium constants, cannot be reliably obtained. A recent critical review [15] of past data [8–10, 16] considered the existing data to be inadequate and did not select/recommend any values for Pu(IV)-EDTA complexes. Unfortunately, Hummel et al. [15] did not review the two most recent papers on this topic [7, 17]. Rai et al. [17] determined values of Pu(IV)-EDTA complexes by using $PuO_2(am)$ to fix the Pu^{4+} activity at a given pH. This study showed that Pu(IV) forms mixed hydroxy-EDTA complexes of the type $Pu(OH)_x(EDTA)^{-x}$ (with x varying from 1 to 3) which dominate in the environmental range of pH values. A more recent study [7] has supported the formation of these complexes. However, there is a disagreement between the thermodynamic models for Pu(IV)-EDTA systems presented in these two most recent studies [7, 17], discussed in detail in Sect. 3. In addition, the values of acidity constants for H_nEDTA^{n-4} (with n varying from 1 to 6) used in Rai et al. [17] and in Boukhalfa et al. [7] to interpret their data, differ markedly from each other and from the critically reviewed values presented in Hummel et al. [15]. Therefore, there is a need to reinterpret/discuss these data so that they are consistent with all of the available data for Pu(IV) [15, 18] and to define a Pu(IV)-EDTA model applicable to the environmental pH values.

Reliable values for Pu(IV)-EDTA complexes are needed to accurately predict Pu(IV) behavior in geologic environments containing competing ions such as Fe(III) and Ca(II), provided reliable complexation constant values are also available for EDTA complexes with the competing ions. However, there is a large uncertainty in the available values. This is especially true for Fe(III), which is expected to be one of the most important ions competing with Pu(IV) for EDTA, not only because it forms strong complexes with EDTA as does Pu(IV), but also because (1) it is ubiquitous in geologic environments, and (2) in the environmental pH range Fe(III) activities are expected to be over 17 orders of magnitude higher than that of Pu(IV), because Fe(III) has a higher $Fe(OH)_3$(am) solubility product than PuO_2(am). Much of the available data for Fe(III)-EDTA complexes are old, and an earlier critical review [19] based on these data listed tentative values for only two of the Fe(III)-EDTA complexes ($Fe(EDTA)^-$ and FeH(EDTA)(aq)). A more recent review of this system by the National Institute of Standards and Technology [20] reported selected values for equilibrium constants for a number of Fe(III)-EDTA complexes (Table 1). The standard error for different constants is reported to vary a great deal, up to three orders of magnitude (Table 1). Clearly, a large degree of uncertainty is expected in the predicted Pu behavior in the presence of Fe(III) when the existing data are used, especially for predictions in the alkaline region. Therefore, the studies described in this paper were conducted to develop a more reliable model for predicting Pu behavior in the presence of Fe(III) or Ca(II). These studies included (1) the solubility of well-characterized 2-line-ferrihydrite ($Fe(OH)_3$(s)) as a function of pH for determining the solubility product of this solid and for using this solid to fix the Fe(III) activity in experiments involving EDTA, (2) solubility of 2-line-ferrihydrite as a function of pH and at fixed EDTA concentrations of 0.0001 and 0.001 $mol{\cdot}L^{-1}$, and as a function of EDTA concentration at a fixed pH of ∼12, (3) solubility of PuO_2(am) in the presence of 2-line-ferrihydrite as a function of pH at fixed EDTA concentrations of 0.0032, 0.001 and 0.00032 $mol{\cdot}L^{-1}$, and (4) solubility of PuO_2(am) as a function of EDTA concentration at a fixed pH value of 9 and at several different fixed concentrations of Ca. These data

Table 1 Equilibrium constants for Fe(III) reactions with EDTA at 25 °C

Reaction	$\log_{10} K$	$\log_{10} K^\circ$	Reference
$Fe^{3+} + EDTA^{4-} \rightleftharpoons Fe(EDTA)^-$	25.1[a]	27.59 ± 0.03[c]	Smith et al. [20]
$Fe(EDTA)^- + H^+ \rightleftharpoons FeH(EDTA)(aq)$	1.3 ± 1[a]	1.503 ± 1[c]	Smith et al. [20]
$Fe^{3+} + EDTA^{4-} + H_2O \rightleftharpoons FeOH(EDTA)^{2-} + H^+$		19.76 ± 3[c]	Calc. from Smith et al. [20]
$FeOH(EDTA)^{2-} + H^+ \rightleftharpoons Fe(EDTA)^- + H_2O$	7.39 ± 3[a]	7.83 ± 3[c]	Smith et al. [20]
$2FeOH(EDTA)^{2-} \rightleftharpoons Fe_2(OH)_2(EDTA)_2^{4-}$	2.8 ± 2[b]	1.84 ± 2[c]	Smith et al. [20]

[a] Ionic strength of 0.1 $mol{\cdot}L^{-1}$ from $NaClO_4$ for the second reaction and KCl for others

[b] Ionic strength of 1.0 $mol{\cdot}L^{-1}$ from KCl

[c] $\log_{10} K^\circ$ value estimated by us using the SIT model with ion-interaction parameters values from Hummel et al. [15] ($\varepsilon(H^+, Cl^-) = (0.12 \pm 0.01)$; $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$; $\varepsilon(Fe(OH)EDTA^{2-}, K^+) = -(0.17 \pm 0.18)$ same as for $\varepsilon(H_2EDTA^{2-}, K^+)$; $\varepsilon(Fe^{3+}, Cl^-) = (0.23 \pm 0.02)$ and $\varepsilon(FeEDTA^-, K^+) = \varepsilon(FeEDTA^-, Na^+) = (0.01 \pm 0.16)$ same as for corresponding Am-species; $\varepsilon(Fe_2(OH)_2(EDTA)_2^{4-}, K^+) = \varepsilon(EDTA^{4-}, K^+) = (1.07 \pm 0.19)$)

helped to develop a more reliable model for the hydroxide/EDTA system involving Pu(IV)-Fe(III)-Ca(II) and have shown that Pu(IV)-EDTA complexes are not stable in the presence of Fe(III) and Ca. Therefore, Pu(IV)-EDTA complexes are very unlikely to be the species responsible for Pu mobility in geologic environments.

2 Methods and Materials

The PuO_2(am) used in this study was prepared according to the method described in Rai et al. [17]. Briefly, a Pu(IV) stock solution in HNO_3 was titrated with NaOH to a pH value of ∼10 to precipitate PuO_2(am), and the precipitate was allowed to age in the mother liquor for about two hours. The PuO_2(am) precipitate was washed twice with 20-mL aliquots of $pH = 9$ water to remove excess Na^+ and NO_3^- ions.

A 2-line ferrihydrite was prepared using the procedure discussed in Schwertmann and Cornell [21]. The x-ray diffraction analyses of the solid confirmed the presence of 2-line ferrihydrite (Fig. 1), represented in this paper as $Fe(OH)_3$(s). The solid thus prepared had a 333 $m^2 \cdot g^{-1}$ surface area.

A solution of 0.0983 $mol \cdot L^{-1}$ Na_2H_2EDTA in water was purchased from Aldrich. A standard stock solution of 6.96 $mol \cdot L^{-1}$ NaOH was prepared by dissolving solid NaOH in water and titrating it against standard HCl solutions. A standard 6.0 $mol \cdot L^{-1}$ HCl solution and concentrated HNO_3 used in the experiments were obtained from GFS. A 0.5 $mol \cdot L^{-1}$ thenoyltrifluoroacetone (TTA) in toluene was prepared from reagent-grade chemicals. A 0.5 $mol \cdot L^{-1}$ $CaCl_2$ solution was prepared using $CaCl_2$ purchased from Aldrich. Deionized water, which had been degassed by boiling and cooling in an Ar atmosphere, was used in all experiments.

2.1 Experimental Procedures

All experiments were conducted at room temperature (23 ± 2 °C) in an inert atmosphere (Ar at 99.99% with <10 ppm O_2) control chamber. The different sets of experiments conducted with $Fe(OH)_3$(s) and mixtures of $Fe(OH)_3$(s) and PuO_2(am) are described below.

2.1.1 Solubility of $Fe(OH)_3$(s) *in the Presence and Absence of* EDTA

The solubility of $Fe(OH)_3$(s) was determined in acidic to highly basic solutions ranging from 0.03 $mol \cdot L^{-1}$ HCl to 4 $mol \cdot L^{-1}$ NaOH and as a function of time. In these experiments,

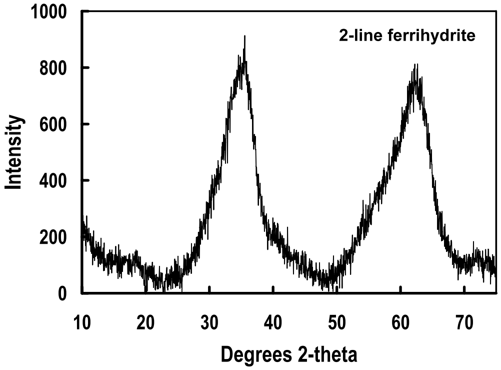

Fig. 1 X-ray diffraction pattern of $Fe(OH)_3$(s) (2-line ferrihydrite) using Cu-Kα radiation

approximately 10 mg of the solid was suspended in 35 mL of a given solution contained in a 50-mL plastic centrifuge tube. The pH values of solid/solution suspensions ranging from 1.5 to 12 were adjusted using HCl or NaOH. The suspensions representing hydrogen ion activities of $<10^{-12}$ mol·L^{-1} were prepared using standard NaOH solutions.

The solubility of $Fe(OH)_3(s)$ in the presence of EDTA was also determined. The sets of experiments with $Fe(OH)_3(s)$ in 35 mL solutions in 50-mL plastic centrifuge tubes in the presence of EDTA consisted of (1) acidic to highly basic solutions ranging from 0.03 mol·L^{-1} HCl to 4 mol·L^{-1} NaOH containing 0.0001 mol·L^{-1} EDTA, (2) pH 1.7 to 12 solutions, obtained with HCl or NaOH, containing 0.001 mol·L^{-1} EDTA, and (3) EDTA concentrations ranging from 0.0001 to 0.013 mol·L^{-1} at a fixed pH value of 12.

2.1.2 *Solubility of* PuO_2(am) *in the Presence of* EDTA *and* $Fe(OH)_3$(am) *or Fixed Concentrations of* Ca

Because of the possible adsorption of EDTA, especially in the relatively low pH regions, by PuO_2(am) or $Fe(OH)_3(s)$, the total amounts of these compounds remaining in each suspension after reaction with EDTA solutions in different sets were controlled at as low an amount as possible and at about 2 mg each. Each sample in each set contained approximately 2 mg of Pu as PuO_2(am), and each set contained different amounts of $Fe(OH)_3(s)$ and EDTA concentrations. The required amounts of PuO_2(am) and $Fe(OH)_3(s)$ were added to different 50-mL centrifuge tubes followed by 35 mL of specific concentrations of EDTA, and pH was adjusted. The different sets in this system consisted of (1) 2 mg of PuO_2(am), 3.5 mg of $Fe(OH)_3(s)$ and 0.00032 mol·L^{-1} EDTA adjusted to a range of pH values from 2.4 to 12.6, (2) two sets of 2 mg of PuO_2(am), 6.8 mg of $Fe(OH)_3(s)$ and 0.001 mol·L^{-1} EDTA adjusted to a range of pH values from 2 to 11.5, and (3) 2 mg of PuO_2(am), 17.2 mg of $Fe(OH)_3(s)$ and 0.0032 mol·L^{-1} EDTA adjusted to a range of pH values from 2.3 to 11.5. The data presented in Sect. 3 show that the measured Fe concentrations are almost identical to the amount of added EDTA, indicating that we were successful in controlling the EDTA adsorption by PuO_2(am) and $Fe(OH)_3(s)$ to an insignificant level.

To determine the competition of Ca with Pu(IV) for EDTA, five samples containing PuO_2(am) were equilibrated with different concentrations of EDTA at a pH of about 9 for 220 days, and were then spiked with different concentrations of Ca and equilibrated for an additional eight days (see Appendix for details).

2.1.3 *General Procedure*

All solid/solution suspensions were shaken at about 120 rpm on an orbital shaker. At different equilibration periods the pH values and, where appropriate, Eh values of the suspensions were measured. The pH values were measured with an Orion-Ross semimicro combination glass electrode calibrated against standard pH buffers covering a range in pH values of the samples. The Eh values were measured with a Broadly-James redox Pt Eh-electrode calibrated against standard quinhydrone redox buffers. The suspensions were centrifuged at 2000 g for about ten minutes. Supernatants were filtered through Amicon Centriplus (Amicon Corp., Lexington, Massachusetts) filters with 30,000 MW cutoff of approximately 0.0036-µm pore size. A 0.5-mL aliquot of the sample was passed through the filter to saturate any possible adsorption sites on the filter and filtration containers, and this filtrate was discarded before filtering an aliquot for analysis.

Iron concentrations in filtrates were determined using Inductively Coupled Plasma (ICP) emission spectroscopy and/or ICP mass spectroscopy. Aqueous phases were analyzed for total Pu by liquid scintillation counting using a Wallac 1414 WinSpectral and Packard Hionic

Fluor cocktail with a detection limit of approximately $10^{-9.8}$ mol·L^{-1} for ^{239}Pu. Because of the presence of high concentrations of Fe in the samples and because the total Pu concentrations in nearly all of the samples were below the detection limits for standard UV-Vis-NIR spectroscopy, oxidation states of Pu were determined using solvent extraction with thenoyltrifluoroacetone (TTA) in toluene [22]. All solvent extractions were completed in less than ten minutes. Pu(III) concentrations were also determined by a solvent extraction method described in Rai et al. [14]. This method involved quantifying Pu(IV) in one subsample by TTA extractions and Pu(IV) plus Pu(III) in another subsample by TTA extractions in the presence of $KBrO_3$, which oxidizes Pu(III) to Pu(IV) so that the total Pu(III) and Pu(IV) can be extracted as Pu(IV) by TTA. Potassium bromate is a mild oxidant which, in the short time required for extractions, rapidly oxidizes Pu(III) to Pu(IV); further oxidation to higher oxidation states is much slower [22, 23]. For this method, HCl was used to acidify the samples. The experimental verification of this method using stock solutions of different oxidation states is presented in Rai et al. [14]. The data presented in Rai et al. [14] indicate that up to about 38% of Pu(III) can be extracted as Pu(IV), thus the actual concentrations of Pu(III) in the samples may be much higher and of Pu(IV) much lower than that measured by this method. Even with these uncertainties in the determination of Pu(III), this is the only method that can be used to quantify Pu(III) present in such low concentrations. The concentrations of [Pu(V) + Pu(VI)] were estimated by subtracting the extracted Pu(IV) or [Pu(III) + Pu(IV)] from the total Pu. Analytical errors in all cases are estimated to be less than 10%. The analytical data for all of the sets are reported in their entirety in the Appendix Tables 8 through 13. The raw data were obtained in molar concentration units (mol·L^{-1}). However, these numbers are represented in molal concentration units (mol·kg^{-1} H_2O): neglecting to make proper corrections for converting molar to molal concentrations will introduce an error of less than 2% in all samples, which is far less than the analytical errors and thus no such corrections were made.

2.1.4 *Thermodynamic Models*

The ion-interaction model of Pitzer and co-workers [24, 25] was used extensively to interpret the solubility data. This aqueous thermodynamic model emphasizes a detailed description of the specific ion interactions in the solution. Effects of specific ion interactions on excess solution Gibbs energy are contained in expressions for the activity coefficients. The activity coefficients can be expressed in a virial-type expansion as

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{DH}} + \sum_j \beta_{ij}(I) m_j + \sum_j \sum_k C_{ijk} m_j m_k + \cdots \tag{1}$$

where m is the molality, γ_i^{DH} is a modified Debye-Hückel activity coefficient that is a universal function of ionic strength, and $\beta_{ij}(I)$ and C_{ijk} are specific for each ion interaction and are functions of ionic strength. The third virial coefficient, C, is understood to be independent of ionic strength. A detailed description of the exact form of Eq. 1 was published in Felmy and Weare [26] and Felmy et al. [27]. Although relatively dilute electrolytes, with the exception of a few samples in high base, were used in this study, extensive Pitzer ion-interaction parameters for EDTA in NaCl solutions valid from dilute to concentrated NaCl are available [28, 29], which in combination with data on Pu(IV)-EDTA complexes we reported previously [17], can be used to interpret our data. We used the Pitzer ion-interaction codes, INSIGHT [30] and NONLIN, which use Pitzer equations for estimating activity coefficients and calculate chemical equilibria involving multiple solid and aqueous species.

Hummel et al. [15] have recently presented extensive data on EDTA complexes of many metal ions using the SIT model. It is therefore of interest to interpret the data obtained in this study with the SIT model to compare to the interpretations with the Pitzer model. For this purpose, the NONLINT-SIT model with the acidity constants of EDTA and SIT ion-interaction parameters of Na-EDTA reported in Hummel et al. [15] along with a few estimated values was used to determine complexation constants of reactions involving Pu and EDTA.

2.1.5 *Computational Methods*

Ab initio molecular orbital calculations were performed on two monomeric Pu(IV)-EDTA species to determine the structures of these complexes and to address the effect of hydrolysis on complex stability. The methods and results of these calculations are discussed in Appendix B.

3 Results and Discussion

Thermodynamic data on Fe(III) solids and aqueous species in the presence and absence of EDTA are discussed first, followed by PuO_2(am) solubility behavior in the presence of EDTA and $Fe(OH)_3$(s) or different Ca(II) concentrations.

3.1 $Fe(OH)_3$(s) Solubility in Highly Acidic to Basic Solutions and in the Absence of EDTA

The solubility of $Fe(OH)_3$(s) was determined from a large number of samples ranging from highly acidic to basic solutions (varying from 0.1 $mol{\cdot}L^{-1}$ HCl to 4.0 $mol{\cdot}L^{-1}$ NaOH) which were equilibrated over a long period (ranging up to 264 days). Because of the very poor detection limits for the analytical methods currently available and used in this study, meaningful Fe concentrations data are available primarily in the very acidic range (pH values of $< \sim 4$) where $Fe(OH)_3$(s) solubility is relatively high (Fig. 2a). The similarity of Fe concentrations as a function of pH at 26-day and 264-day equilibration periods indicates that a steady-state concentration appeared to have been reached very quickly (<26 days) (Fig. 2a). Although equilibrium in these studies was approached only from the undersaturation direction, the facts that, (1) a very long equilibration period (far beyond that generally required for reaching steady-state concentrations) was used in this study, (2) the solubility product of $Fe(OH)_3$(s) calculated from these data is consistent, across a large range of pH values, with the predicted $Fe(OH)_3$(s) solubility in the presence of EDTA and with the available thermodynamic data for the $FeEDTA^-$ complex (discussed later), and (3) almost all amorphous materials similar to $Fe(OH)_3$(s) (e.g., $Cr(OH)_3$(am), Rai et al. [31–33]) reach equilibrium within much shorter equilibration periods than used in this study, show that the observed solubility can be considered to be a result of an equilibrium phenomenon.

In a first attempt to interpret these data and develop a thermodynamic model for this system, it was assumed that the thermodynamic data given by Smith et al. [20] for the Fe(III)-hydroxide system (Table 2) is applicable and that the values for Pitzer ion-interaction parameters reported in Table 3 for the Fe-OH species are reliable. Predictions based on these data provided total Fe(III) concentrations which were approximately 1.5 orders of magnitude higher than the experimental concentrations determined in this study in the acidic region. Apparently the solubility product or the $\Delta_f G^\circ_m/RT$ value of the $Fe(OH)_3$(s) used in this

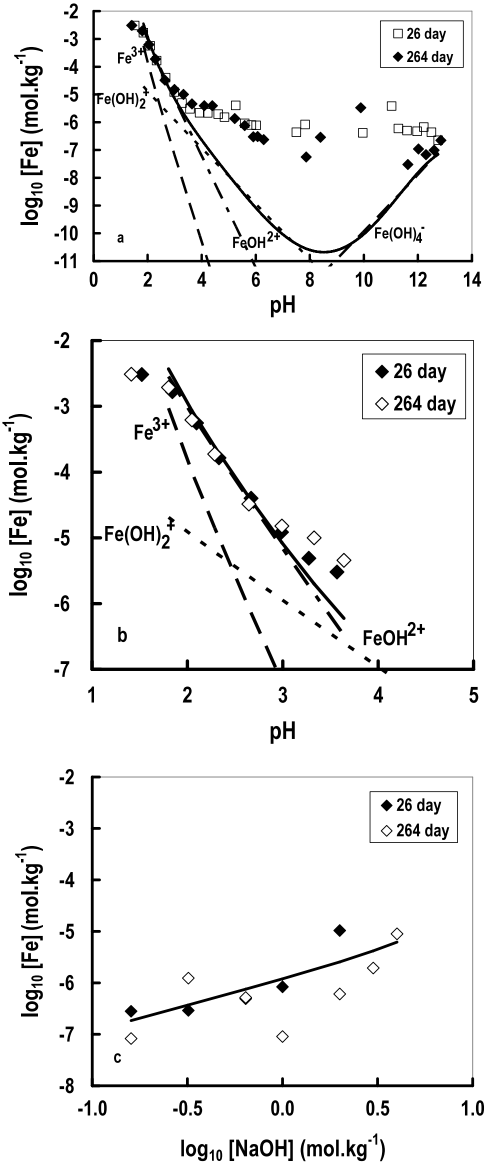

Fig. 2 Solubility of $Fe(OH)_3(s)$ as a function of pH and time (**a**) and (**b**) and NaOH and time (**c**). *Lines* represent predicted concentrations using the thermodynamic data reported in Tables 2 and 3: *solid lines* represent total Fe concentrations; *other lines* represent concentrations of different species as marked in the figure

study is lower than that of the solid phase reported in Smith et al. [20]. Because of detection limit problems and/or the presence of a minute amount of small particles of higher solubility in the bulk ferrihydrite phase at intermediate pH values (about 5 to 12) and considerable variation in ionic strength in the highly alkaline region (>0.1 mol·kg^{-1} OH^-), the data in the acidic region (pH values of about <4) are best suited to determining the $\Delta_f G^\circ_m/RT$ value or the solubility product value of the $Fe(OH)_3(s)$, where $FeOH^{2+}$ is the only expected dominant species. Since the ionic strength in these solutions is relatively low, it is expected that ignoring the ion-interaction parameters, reliable values for which are currently unavailable, will not significantly affect the calculated $\Delta_f G^\circ_m/RT$ value for $Fe(OH)_3(s)$. In

Table 2 Dimensionless standard molar Gibbs energies of formation ($\Delta_f G^\circ_m/RT$) of the important species used in calculations.[a] Note that the values of all species involving EDTA are relative to each other based on the convention that $\Delta_f G^\circ_m/RT$ (H_4EDTA(aq)) is set equal to zero

Species	$\Delta_f G^\circ_m/RT$	Reference
Fe^{3+}	-6.567 ± 0.444	Parker and Khodakovskii [36]
$Fe(OH)^{2+}$	-100.196	Smith et al. [20][b]
$Fe(OH)_2^+$	-187.317	Smith et al. [20][b]
$Fe(OH)_4^-$	-339.516	Smith et al. [20][b]
$Fe_2(OH)_2^{4+}$	-197.891	Smith et al. [20][b,c]
$Fe_3(OH)_4^{5+}$	-387.879	Smith et al. [20][b,c]
$FeEDTA^-$	-16.329	Smith et al. [20][d]
Fe(H)EDTA(aq)	-19.815	Smith et al. [20][d]
$Fe(OH)EDTA^{2-}$	-98.809 ± 0.521	This study
	-93.990	Smith et al. [20][d]
$Fe_2(OH)_2(EDTA)_2^{4-}$	-192.551	Smith et al. [20][c,d]
$Fe(OH)_3(s)$	-289.747 ± 1.134	This study
	-286.212	Smith et al. [20][b]
H_6EDTA^{2+}	-1.842	Calculated[e]
H_5EDTA^+	-2.993	Calculated[e]
H_4EDTA(aq)	0.00	Calculated[e]
H_3EDTA^-	5.135	Calculated[e]
H_2EDTA^{2-}	12.388	Calculated[e]
$HEDTA^{3-}$	28.046	Calculated[e]
$EDTA^{4-}$	53.927	Calculated[e]
$NaEDTA^{3-}$	-58.190	Calculated[e]
Ca^{2+}	-222.998	Guillaumont et al. [18]
$CaEDTA^{2-}$	-197.531	Based on Felmy and Mason [28][f]
$PuO_2(am)$	-389.541	Calculated[g]
Pu^{4+}	-192.817	Guillaumont et al. [18]

[a] The $\Delta_f G^\circ_m/RT$ values for Pu^{3+}, $PuOH^{3+}$, $Pu(OH)_2^{2+}$, $Pu(OH)_3^+$, $Pu(OH)_4$(aq), and Na^+ from Guillaumont et al. [18], and the values for $Ca(H)EDTA^-$, and $PuEDTA^-$, Pu(H)EDTA(aq) used in calculations were calculated from the $\log_{10} K^\circ$ values for these species reported in Hummel et al. [15] and the associated data listed in this table

[b] Based on the average values of equilibrium constants for the formation of the given species reported in this publication

[c] Species not important in the environmental range of pH values, see text for details

[d] The average values of concentration equilibrium constants reported in this reference, converted to zero ionic strength using the SIT model (see Table 1), were combined with other data reported in this table to obtain calculated $\Delta_f G^\circ_m/RT$ values

[e] Calculated from $\log_{10} K^\circ$ values reported by Hummel et al. [15]

[f] Calculated from $\log_{10} K^\circ$ value of 12.36 for the formation of this species reported in Felmy and Mason [28] and from the other data reported in this table

[g] Calculated from $\log_{10} K^\circ$ value and the other data reported in Guillaumont et al. [18]

Table 2 (*Continued*)

Species	$\Delta_f G^\circ_m/RT$	Reference
$Pu(OH)EDTA^-$	-290.276 ± 0.672	This study
$Pu(OH)_2EDTA^{2-}$	-374.460 ± 0.672	This study
$Pu(OH)_3EDTA^{3-}$	-448.209 ± 0.672	This study
$H_2O(l)$	-95.661	Guillaumont et al. [18]
OH^-	-63.421	Guillaumont et al. [18]

agreement with this expectation, inclusion of estimated values of ion-interaction parameters (Table 3) provided a $\Delta_f G^\circ_m/RT$ value for $Fe(OH)_3(s)$ of $-(289.747 \pm 1.134)$ and an essentially identical value $-(289.810 \pm 1.134)$ without these parameters which described the low-pH-experimental data well (Fig. 2a and 2b). These analyses also show that the dominant species in the low pH region (<4, Fig. 2a and 2b) are Fe^{3+} and $Fe(OH)^{2+}$ and in the high pH region (>13, Fig. 2c) is $Fe(OH)_4^-$ and that the uncertainty in the $\Delta_f G^\circ_m/RT$ values associated with these species is much smaller than reported in Smith et al. [20]. The $\log_{10} K^\circ$ value of $-(40.35 \pm 0.5)$ is calculated from our data, as compared to the value of $-(38.8 \pm 2)$ reported in Smith et al. [20], for the following solubility reaction 2.

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+} + 3OH^- \tag{2}$$

In addition, the interpretation of our data does not require the inclusion of any other species, and the existence or importance of these other hydrolyses species (i.e., $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$) cannot be vouched for. Because of detection limit problems and the ionic strengths that are variable and reach as high as 4 $mol \cdot kg^{-1}$ in highly alkaline conditions (Fig. 2c), development of a reliable model for the highly alkaline conditions from these data is problematic. However, comparisons of the experimental and predicted concentrations in equilibrium with $Fe(OH)_3(s)$ in the basic region shows that there is reasonable agreement when a $\Delta_f G^\circ_m/RT$ value for $Fe(OH)_3(s)$ calculated in this study is used in conjunction with an average $\Delta_f G^\circ_m/RT$ value for $Fe(OH)_4^-$ from Smith et al. [20].

3.2 $Fe(OH)_3(s)$ Solubility in Highly Acidic to Basic Solutions Containing EDTA

To further verify the solubility product for $Fe(OH)_3(s)$ and to develop a reliable model for Fe(III)-EDTA complexes, studies on the solubility of $Fe(OH)_3(s)$ as a function of pH at fixed concentrations of 0.0001 and 0.001 $mol \cdot L^{-1}$ EDTA, and as a function of EDTA concentrations at a fixed pH of ~12 were conducted (Fig. 3). The observed Fe concentrations (Fig. 3a and 3b) at fixed concentrations of EDTA (0.0001 or 0.001 $mol \cdot kg^{-1}$) in equilibrium with $Fe(OH)_3(s)$ and with pH increasing from ~2 to ~13 show: (1) a decrease in Fe concentrations at pH values of $< \sim 2.5$, (2) nearly constant Fe concentrations at the intermediate pH values of between approximately 2 and 11, and (3) a decrease in Fe concentrations in the alkaline region followed by concentrations that are at detection limits and an indication of an increase in concentrations in the highly alkaline region. The Fe concentrations at a fixed pH value of ~12 increase by an order of magnitude with about an order of magnitude increase in EDTA concentrations. The comparisons of observed Fe concentrations in equilibrium with $Fe(OH)_3(s)$ in the presence and absence of EDTA (Figs. 2 and 3) show that the Fe concentrations are similar to each other in the very acidic ($pH < \sim 2$) and very basic ($pH > \sim 12$) regions but are up to several orders of magnitude higher in the intermediate

Table 3 Pitzer ion-interaction parameters used in this study[a]

Binary parameters Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Reference
Fe^{3+}-$C1^{-}$	0.736	5.2553	0.00	−0.0451	This study[b]
$FeOH^{2+}$-Cl^{-}	0.3359	1.5323	0.00	−0.00861	This study[c]
Na^{+}-$Fe(OH)_4^{-}$	0.045	0.31	0.00	−0.003	This study[d]
Na^{+}-$EDTA^{4-}$	1.1	15.60	0.00	0.001	Felmy and Mason [28]
Na^{+}-$(H)EDTA^{3-}$	0.59	5.39	0.00	0.00	This study[e]
Na^{+}-$Pu(OH)_3EDTA^{3-}$	0.59	5.39	0.00	0.00	This study[e]
Na^{+}-$NaEDTA^{3-}$	0.59	5.39	0.00	0.00	Felmy and Mason [28]
Na^{+}-H_2EDTA^{2-}	−0.1262	1.74	0.00	0.054	Pokrovsky et al. [29]
Na^{+}-$Pu(OH)_2EDTA^{2-}$	−0.1262	1.74	0.00	0.054	This study[f]
Na^{+}-$CaEDTA^{2-}$	0.30	0.00	0.00	0.1131	Felmy and Mason [28]
Na^{+}-H_3EDTA^{-}	−0.2345	0.29	0.00	0.059	Pokrovsky et al. [29]
Na^{+}-$Pu(OH)EDTA^{-}$	−0.2345	0.29	0.00	0.059	This study[g]
Na^{+}-$Ca(H)EDTA^{-}$	−0.2345	0.29	0.00	0.059	This study[g]
Na^{+}-OH^{-}	0.0864	0.253	0.00	0.0044	Harvie et al. [37]
Na^{+}-$C1^{-}$	0.0765	0.2664	0.00	0.00127	Harvie et al. [37]
H^{+}-$C1^{-}$	0.1775	0.2945	0.00	0.0008	Harvie et al. [37]
Ternary parameters					
H^{+}-Na^{+}	0.036				Harvie et al. [37]
H^{+}-Na^{+}–$C1^{-}$	−0.004				Harvie et al. [37]
$C1^{-}$-OH^{-}	−0.05				Harvie et al. [37]
$C1^{-}$-OH^{-}-Na^{+}	−0.006				Harvie et al. [37]
OH^{-}-$Fe(OH)_4^{-}$	0.014				This study[d]
OH^{-}-$Fe(OH)_4^{-}$-Na^{+}	−0.0048				This study[d]

[a] Ion-interaction parameters for negatively charged Pu(IV)-EDTA, Pu(III)-EDTA and Fe(III)-EDTA species with Na^{+} were assumed to be equal to the parameters for Na^{+} with $EDTA^{x-}$ of the same charge as the above-mentioned species (e.g., the ion-interaction parameters for (Na^{+}, $Pu(OH)EDTA^{-}$) were set equal to those for (Na^{+}, H_3EDTA^{-}))

[b] It was assumed that the parameters for Cr^{3+}-Cl^{-} reported by Pitzer [24] are applicable to this system; a reasonable assumption. However, the chloride concentrations in most of the samples are low, primarily from the HC1 used in adjusting pH values, the parameters involving $C1^{-}$ do not figure significantly in calculations, but were included in the model for completeness

[c] It was assumed that the parameters for Fe^{2+}-Cl^{-} reported by Pitzer [24] are applicable to this system

[d] It was assumed that the parameters identical to the corresponding Al(III) and Cr(III) species reported by Wesolowski [38] and Rai et al. [31] are applicable to this system

[e] Assumed to be identical to Na^{+}-$NaEDTA^{3-}$ reported by Felmy and Mason [28]

[f] Assumed to be identical to Na^{+}-H_2EDTA^{2-} reported by Pokrovsky et al. [29]

[g] Assumed to be identical to Na^{+}-H_3EDTA^{-} reported by Pokrovsky et al. [29]

pH regions in the presence of EDTA. These comparisons indicate that the increase in Fe concentrations in the intermediate pH values must result from the complexation of Fe with EDTA.

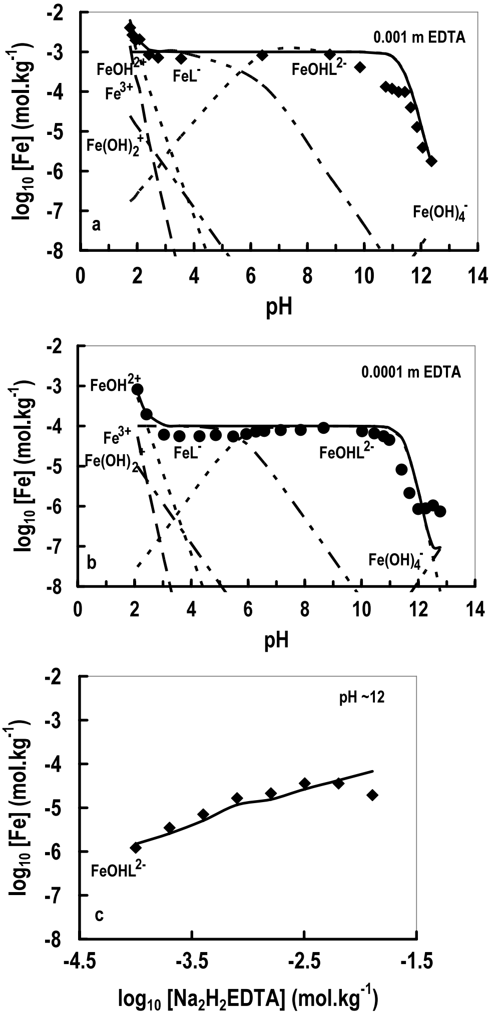

Fig. 3 Solubility of $Fe(OH)_3(s)$ as a function of pH and EDTA (L) concentrations at different equilibration periods (8 day for (**a**), 27 day for (**b**), and 8 day for (**c**). *Lines* represent predicted concentrations using the thermodynamic data reported in Tables 2 and 3 with $\Delta_f G^\circ_m/RT$ values for $Fe(OH)_3(s)$, FeL^- and $FeOHL^{2-}$ from this study and other values from Smith et al. [20]: *solid lines* represent total Fe concentrations; *other lines* represent concentrations of different species as marked in the figure

In an attempt to interpret these data and to determine the values for various Fe(III)-EDTA complexes, the $\Delta_f G^\circ_m/RT$ values of the Fe-OH discussed above were combined with values of the EDTA species based on Hummel et al. [15] and the estimated Pitzer ion-interaction parameters for these various species as listed in Table 3. Several different species ($FeEDTA^-$, FeHEDTA(aq), $Fe(OH)EDTA^{2-}$, $Fe_2(OH)_2(EDTA)_2^{4-}$), as recommended by Smith et al. [20] based on their review of the literature data, were tried to fit these data. No region of dominance for FeHEDTA(aq) and $Fe_2(OH)_2(EDTA)_2^{4-}$ species is found in our experimental data. In addition to the Fe(III)-OH model described above, only two species ($FeEDTA^-$ and $Fe(OH)EDTA^{2-}$) with $\Delta_f G^\circ_m/RT$ values of -16.329 and $-(98.809 \pm 0.521)$, respectively, are required to fit these extensive data (Fig. 3). These data provide $\log_{10} K^\circ$ values of (27.66 ± 0.21) and (21.935 ± 0.226) for reactions 3 and 4, respectively. The Fe-OH-EDTA model containing these data

$$Fe^{3+} + EDTA^{4-} \rightleftharpoons Fe(EDTA)^- \tag{3}$$

$$Fe^{3+} + EDTA^{4-} + H_2O \rightleftharpoons FeOH(EDTA)^{2-} + H^+ \qquad (4)$$

provide a close agreement between the experimental and predicted concentrations for the $Fe(OH)_3(s)$ solubility at: (1) fixed EDTA concentrations of 0.0001 or 0.001 $mol{\cdot}kg^{-1}$ EDTA and at pH values of between approximately 2 and 12 (Fig. 3a and 3b), and (2) a fixed pH value of about 12 and as a function of EDTA concentrations varying from about 0.0001 to 0.0128 $mol{\cdot}kg^{-1}$ (Fig. 3c). This agreement re-attests to the reliability of the Fe-OH system model developed above including the solubility product of $Fe(OH)_3(s)$, especially in light of the similarity of the Fe(III)-EDTA complexation constant value determined in this study and that recommended by Anderegg [19] and Smith et al. [20], as discussed below.

Values of equilibrium constants for the formation of Fe(III)-EDTA complexes at zero ionic strength are not available for comparison with the values determined in this study, although complexation constant values involving $FeEDTA^-$, FeHEDTA(aq), $Fe(OH)EDTA^{2-}$ and $Fe_2(OH)_2(EDTA)_2^{4-}$ at 0.1 and/or 1.0 $mol{\cdot}L^{-1}$ are available [20] (Table 1). Because of the unavailability of the ion-interaction parameters for the specific species involved and up to plus/minus three orders of magnitude reported variability in the equilibrium constant values (Table 1), it is difficult to obtain reliable equilibrium constant values at zero ionic strength from these data. However, literature data for $FeEDTA^-$ and $Fe(OH)EDTA^{2-}$ at relatively low ionic strength (0.1 $mol{\cdot}kg^{-1}$) are available. The use of estimated ion-interaction parameters in place of actual parameters to convert concentration constants to thermodynamic constants will not introduce a large degree of error as compared to the errors already reported, especially for $Fe(OH)EDTA^{2-}$. The SIT model was used to convert the concentration constants [20] for reactions (3 and 4) involving $FeEDTA^-$ and $Fe(OH)EDTA^{2-}$ to thermodynamic constants at zero ionic strength. For these calculations the estimated values of SIT parameters ε_{ij} as listed in Table 1 were used to calculate: (1) the $\log_{10} K^\circ$ value of (27.59 ± 0.03) for reaction 3, which is essentially identical to the value (27.66 ± 0.21) that describes the data well in this study, and (2) the $\log_{10} K^\circ$ value of (19.76 ± 3) for reaction 4. The $\log_{10} K^\circ$ value for reaction 4 determined in this study (21.935 ± 0.226), although it falls within the range of values calculated above from the literature data (19.83 ± 3), is much more precise and differs from the average literature value by about 2.1 $\log_{10}$ units. The close agreement between our experimental data and the model excluding FeHEDTA(aq) and $Fe_2(OH)_2(EDTA)_2^{4-}$, discussed above, leaves no doubt that these latter species have no region of importance in the pH range 2 to 12. Although there is a large degree of uncertainty in the equilibrium constants recommended by Smith et al. [20] for FeHEDTA(aq) and $Fe_2(OH)_2(EDTA)_2^{4-}$, predicted concentrations of these species (not depicted graphically) based on the average values are up to several orders of magnitude lower than those for the dominant species reported in Fig. 3a and 3b, consistent with the conclusion drawn from the data in this study.

3.3 Pu Behavior in the Presence of EDTA

It is important to have a reliable model of Pu behavior in the presence of EDTA (in this case Pu(IV), as this is the oxidation state implicated in the literature to be the complexed and mobile species) under environmental conditions. To do this, accurate thermodynamic data are required not only for Pu but also for all of the other ions (as for example Fe, Al, Ca, Mg) that compete with Pu for complexation with EDTA. Having discussed and verified/developed reliable thermodynamic data for Fe, we now focus on Pu(IV)-EDTA complexes.

A recent critical review of EDTA complexes of Pu(IV) by NEA [15] did not select any values because of the poor quality of data. However, they overlooked two publications [7, 17] that dealt with Pu(IV)-EDTA complexes. Boukhalfa et al. [7] used a combination of techniques (spectrophotometry in very acidic and high ionic strength solutions,

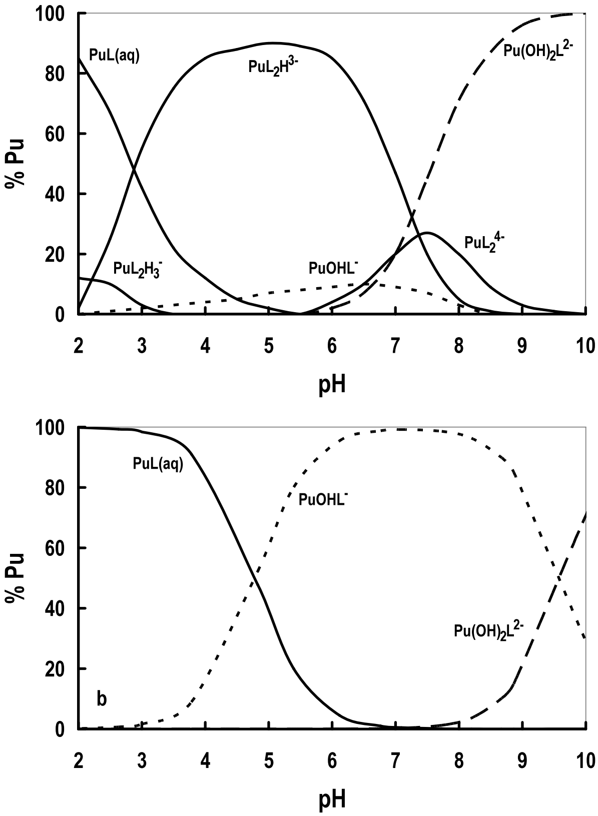

Fig. 4 *Top* figure from Boukhalfa et al. [7] after their Fig. 5, where the authors used concentration constants at different ionic strengths reported in Table 4. *Bottom* figure based on equilibrium with PuO_2(am) and 0.0001 mol·L^{-1} Na_2H_2EDTA at different pH values using the equilibrium constants reported by Boukhalfa et al. [7] converted to zero ionic strength with the SIT model (Table 4). In addition, the Pitzer ion-interaction parameters for various species with Na^+ were assumed to be identical to those for the same charged EDTA (L) species with Na^+ (see Table 3)

and potentiometry and voltammetry in 0.1 mol·L^{-1} $NaNO_3$ solutions), whereas the Rai et al. [17] investigations involved solubility studies in very dilute solutions in a pH range from about 1 to 12.

Many of the conclusions Boukhalfa et al. [7] drew based on the model they used for calculating the dominant species in different pH regions (their Fig. 5, see Fig. 4a) are very uncertain. They combined equilibrium constants at 1.0 mol·L^{-1} ionic strength with equilibrium constants at 0.1 mol·L^{-1} ionic strength without correcting these values and without considering activity coefficients for different species, many of which are highly charged, in developing their Fig. 5. The values of the EDTA acidity constants they used for interpretations are up to about 1.8 orders of magnitude different than the values recently recommended by Hummel et al. [15]. When care is taken to (1) convert their equilibrium constants to zero ionic strengths using the SIT model (Table 4), (2) calculate the solubility of PuO_2(am) in 0.0001 mol·kg^{-1} Na_2H_2EDTA as a function of pH using the data presented in NEA publications [15, 18], and (3) use the proper ion-interaction parameters for the aqueous species; the dominant species diagram based on their data is drastically different than the one they presented (compare Fig. 4a and 4b). For examples, our calculations based on their data show that (1) from very acidic solutions to pH values of up to about 4.8, the dominant species is PuEDTA(aq) as opposed to pH values of up to about 3 as they report, and (2) $Pu(EDTA)_2H^{3-}$, which is the dominant species between pH values of about 3 and 7 in their paper, is no longer even significant.

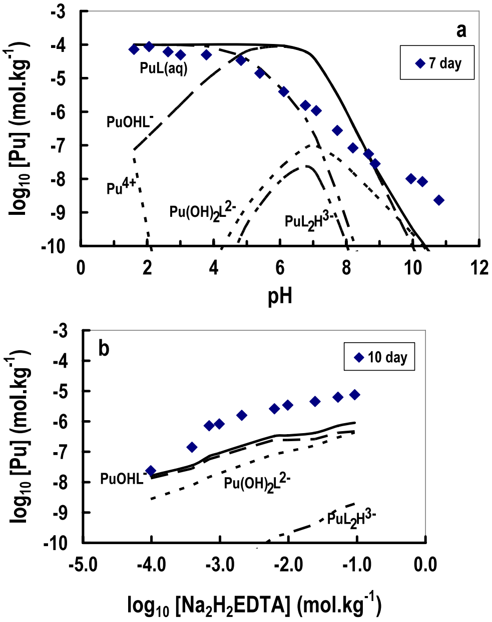

Fig. 5 Solubility of PuO_2(am) as a function of pH and EDTA (L) concentrations (0.0001 mol·L^{-1} for Fig. 5a and as noted for Fig. 5b) at different equilibration periods (from Rai et al. [17]). *Lines* represent predicted concentrations using the Pu-EDTA constants based on zero ionic strength data of Boukhalfa et al. [7] reported in Table 4 with $\Delta_f G^\circ_m/RT$ values for PuO_2(am), Pu^{4+}, and hydrolyses species from Guillaumont et al. [18] and the Pitzer ion-interaction parameters for various Pu-EDTA species assumed to be identical to the similarly charged EDTA species with Na^+ reported in Table 3. *Solid lines* represent predicted total Pu concentrations; *other lines* represent concentrations of different species as marked in the figure

Table 4 Values of equilibrium constants for various Pu(IV)-EDTA species based on Boukhalfa et al. [7]

Reaction	Medium	$\log_{10} K$	$\log_{10} K^\circ$
$Pu^{4+} + EDTA^{4-} \rightleftharpoons PuEDTA(aq)$	1.0 mol·L^{-1} (NaCl,HClO$_4$)	26.44 ± 0.2[a]	32.47 ± 0.2[b]
$Pu^{4+} + 2EDTA^{4-} \rightleftharpoons Pu(EDTA)_2^{4-}$	0.1 mol·L^{-1} NaNO$_3$	35.39 ± 0.15[a]	38.84 ± 0.15[c]
$Pu^{4+} + 2EDTA^{4-} + H^+ \rightleftharpoons Pu(EDTA)_2H^{3-}$	0.1 mol·L^{-1} NaNO$_3$	42.75 ± 0.13[a]	47.018 ± 0.13[c]
$Pu^{4+} + 2EDTA^{4-} + 3H^+ \rightleftharpoons Pu(EDTA)_2H_3^-$	0.1 mol·L^{-1} NaNO$_3$	47.39 ± 1.0[a]	52.71 ± 1.0[c]
$Pu^{4+} + EDTA^{4-} + OH^- \rightleftharpoons Pu(OH)EDTA^-$	0.1 mol·L^{-1} NaNO$_3$	35.76 ± 0.86[a]	39.17 ± 0.86[c]
$Pu^{4+} + EDTA^{4-} + 2OH^- \rightleftharpoons Pu(OH)_2EDTA^{2-}$	0.1 mol·L^{-1} NaNO$_3$	42.85 ± 0.1[a]	46.03 ± 0.1[c]

[a] Values from Boukhalfa et al. [7]

[b] Personal communication with Dr. Hakim Boukhalfa on January 26, 2007, LANL; value based on extrapolations with SIT model

[c] Values calculated by us with the SIT model using $\varepsilon(H^+, NO_3^-) = (0.07 \pm 0.01)$, $\varepsilon(Na^+, EDTA^{4-}) = (0.32 \pm 0.14)$, and $\varepsilon(Na^+, OH^-) = (0.04 \pm 0.01)$ from Hummel et al. [15]; assuming $\varepsilon(Pu^{4+}, NO_3^-) = (0.11 \pm 0.02)$ is identical to $\varepsilon(Th^{4+}, NO_3^-)$, and that the values for $\varepsilon(Na^+, Pu(EDTA)_2^{4-})$, $\varepsilon(Na^+, Pu(EDTA)_2H^{3-})$, $\varepsilon(Na^+, Pu(EDTA)_2H_3^-)$, $\varepsilon(Na^+, Pu(OH)EDTA^-)$ and $\varepsilon(Na^+, Pu(OH)_2EDTA^{2-})$ are identical to the corresponding EDTA species of the same charge with Na^+ quoted in Hummel et al. [15]

One of the main objectives of studies to determine Pu-EDTA complexes is to be able to predict Pu behavior in natural systems. Raw experimental data on PuO_2(am) solubility [17] as a function of pH and EDTA concentrations are available to compare predictions based on the Boukhalfa et al. [7] model. When these comparisons are made (Fig. 5) they show that the Pu-EDTA model they present does not agree with the experimental solubility data and their model over-predicts the concentrations in the pH $<\sim 8.5$ region. They present convincing evidence for the existence of PuEDTA species in very acidic ($\sim 0.9\ \text{mol}\cdot\text{L}^{-1}$ $HClO_4$) and high ionic strength solutions ($1.0\ \text{mol}\cdot\text{L}^{-1}$). However, these species over-predict the PuO_2(am) solubility in low ionic strength solutions at relatively high pH values; this suggests that the value they quote for the formation of PuEDTA(aq) is too high. Based on potentiometric titrations, Boukhalfa et al. [7] have reported a large number of other complexes (Pu(EDTA)_2^{4-}, $\text{Pu(EDTA)}_2\text{H}^{3-}$, $\text{Pu(EDTA)}_2\text{H}_3^{-}$, Pu(OH)EDTA^{-}, $\text{Pu(OH)}_2\text{EDTA}^{2-}$). With the exception of Pu(OH)EDTA^{-}, which appears important in a large range of pH values ($\sim$4.8–9.5), and $\text{Pu(OH)}_2\text{EDTA}^{2-}$, which is dominant at pH values $>\sim 9.5$ (Figs. 4b and 5a), the other complexes contribute very little, if any, to the total predicted concentrations. This observation, combined with the difficulties of studying the Pu(IV) system potentiometrically [17], makes it difficult to verify the existence of these other species. The Boukhalfa et al. [7] model under-predicts PuO_2(am) solubility as a function of EDTA concentration at a fixed pH value of ~ 9 (Fig. 5b). The main conclusions we can draw from the Boukhalfa et al. [7] data (Fig. 5b) are that PuEDTA(aq) species may be important in very acidic solutions, such as those ($0.9\ \text{mol}\cdot\text{L}^{-1}\ \text{H}^+$) investigated in their study, and other species of importance with increasing pH include Pu(OH)EDTA^{-} and $\text{Pu(OH)}_2\text{EDTA}^{2-}$ (Figs. 4b and 5). Boukhalfa et al. [7] report that $\text{Pu(OH)}_3\text{EDTA}^{3-}$ is expected to be important at pH values >8.5. The value of the equilibrium constant for the formation of PuEDTA(aq) reported by these authors is too high, and this may in turn have impacted the calculated values for other constants as well.

In order to develop a thermodynamic model consistent with the critically reviewed data for the Pu-OH system [18] and the acidity constants for EDTA species [15], the Rai et al. [17] data on the solubility of PuO_2(am) as a function of pH and EDTA concentrations were reinterpreted while keeping in mind the information presented in Boukhalfa et al. [7]. Our calculations show that when $\Delta_f G^\circ_m/RT$ values of PuEDTA(aq), Pu(OH)EDTA^{-}, $\text{Pu(OH)}_2\text{EDTA}^{2-}$ and $\text{Pu(OH)}_3\text{EDTA}^{3-}$ are simultaneously determined to fit the solubility data [17], PuEDTA(aq) species never become dominant, consistent with the discussion in Rai et al. [17]. These results indicate that the $\log_{10} K^\circ$ value for the formation of PuEDTA(aq) [$\text{Pu}^{4+} + \text{EDTA}^{4-} \rightleftharpoons \text{PuEDTA(aq)}$] is ≤ 26.36, and if these species are important, they are only important at pH values ≤ 1.6. The recalculated $\Delta_f G^\circ_m/RT$ values of Pu(OH)EDTA^{-}, $\text{Pu(OH)}_2\text{EDTA}^{2-}$ and $\text{Pu(OH)}_3\text{EDTA}^{3-}$ were found to be $-(290.276 \pm 0.672)$, $-(374.460 \pm 0.672)$ and $-(448.209 \pm 0.672)$, respectively. The Rai et al. [17] data were also interpreted using the NONLINT-SIT model instead of the Pitzer model. The SIT modeling provided $\Delta_f G^\circ_m/RT$ values for the above species that are very similar[1] to the values obtained using the Pitzer model. The $\Delta_f G^\circ_m/RT$ values determined above provide $\log_{10} K^\circ$ values for the PuO_2(am) dissolution reactions (Eq. 5 for x varying from 1 to 3)

$$[\text{PuO}_2(\text{am}) + \text{EDTA}^{4-} + (4-x)\text{H}^+ \rightleftharpoons \text{Pu(OH)}_x\text{EDTA}^{x-} + (2-x)\text{H}_2\text{O}] \qquad (5)$$

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[1] The SIT modeling provided $\Delta_f G^\circ_m/RT$ values of $-(290.825 \pm 0.650)$, $-(373.843 \pm 0.650)$ and $-(447.335 \pm 0.650)$ for Pu(OH)EDTA^{-}, $\text{Pu(OH)}_2\text{EDTA}^{2-}$, and $\text{Pu(OH)}_3\text{EDTA}^{3-}$, respectively. The following SIT ion interaction parameters from Hummel et al. [15] were used for these calculations: $\varepsilon(\text{H}^+, \text{Cl}^-) = 0.12$, $\varepsilon(\text{Na}^+, \text{Cl}^-) = 0.03$, $\varepsilon(\text{Na}^+, \text{OH}^-) = 0.04$, $\varepsilon(\text{Na}^+, \text{EDTA}^{4-}) = 0.32$, $\varepsilon(\text{Na}^+, \text{HEDTA}^{3-}) = -0.1$, $\varepsilon(\text{Na}^+, \text{H}_2\text{EDTA}^{2-}) = -0.37$, $\varepsilon(\text{Na}^+, \text{H}_3\text{EDTA}^-) = -0.33$, $\varepsilon(\text{H}_5\text{EDTA}^+, \text{Cl}^-) = -0.23$, $\varepsilon(\text{Pu}^{4+}, \text{Cl}^-) = 0.37$. In addition, it was assumed that (1) $\varepsilon(\text{Na}^+, \text{Pu(OH)}_3\text{EDTA}^{3-})$ and $\varepsilon(\text{Na}^+, \text{NaEDTA}^{3-})$ equal $\varepsilon(\text{Na}^+, \text{HEDTA}^{3-})$, (2) $\varepsilon(\text{Na}^+, \text{Pu(OH)}_2\text{EDTA}^{2-})$ equals $\varepsilon(\text{Na}^+, \text{H}_2\text{EDTA}^{2-})$, and (3) $\varepsilon(\text{Na}^+, \text{Pu(OH)EDTA}^-)$ equals $\varepsilon(\text{Na}^+, \text{H}_3\text{EDTA}^-)$.

of (21.855 ± 0.292), (16.871 ± 0.292) and (7.354 ± 0.292) for the formation of $Pu(OH)EDTA^{-}$, $Pu(OH)_2EDTA^{2-}$ and $Pu(OH)_3EDTA^{3-}$, respectively. These values are consistently about half an order of magnitude higher than those reported in Rai et al. [17] and primarily result from the differences in acidity constants of EDTA used in the present study. These solubility reactions, when combined with the solubility product [18] of PuO_2(am), provide values for the $\log_{10} K^\circ$ for the formation of $Pu(OH)_nEDTA^{n-}$ [$Pu^{4+} + EDTA^{4-} + n OH^- \rightleftharpoons Pu(OH)_nEDTA^{n-}$] with $n = 1, 2$, or 3 of (38.203 ± 0.292), (47.220 ± 0.292) and (51.705 ± 0.292), respectively.

It is logical that mixed hydroxy-EDTA complexes, rather than PuEDTA(aq), are dominant in the entire pH range investigated by Rai et al. [17] because (1) Pu(IV) interacts very strongly with hydroxide (in 1.0 $mol\cdot L^{-1}$ $HClO_4$ about 30% of the Pu(IV) is hydrolyzed according to the data selected by Guillaumont et al. [18]) and (2) as the pH increases hydroxide out-competes EDTA for complexation with Pu as shown by changes in total soluble Pu concentrations in equilibrium with PuO_2(am) from a nearly constant Pu concentration at pH $\sim <4$ to an orders of magnitude decrease as the pH increases beyond 4 (Fig. 6). A close agreement is observed (Fig. 6) between the Pu concentrations predicted by the model described above and the experimental PuO_2(am) solubility as a function of pH and EDTA concentrations reported in Rai et al. [17]. We therefore conclude that the model, involving only $Pu(OH)EDTA^{-}$, $Pu(OH)_2EDTA^{2-}$, and $Pu(OH)_3EDTA^{3-}$ along with the other auxiliary data presented in this paper, provides reliable predictions of PuO_2(am) solubility in a wide range of pH and EDTA concentrations.

To the best of our knowledge, no experimental or theoretical molecular structures for mixed hydroxyl-EDTA complexes of Pu are currently available. Therefore, ab initio calculations reported in Appendix B were performed to better understand the structure and effects of hydrolysis on the stability of Pu(IV)-EDTA complexes. These data are not very conclusive but in general indicate that mixed hydroxy-EDTA complexes of Pu(IV) are favored at higher pH values, consistent with the thermodynamic interpretations of the solubility data.

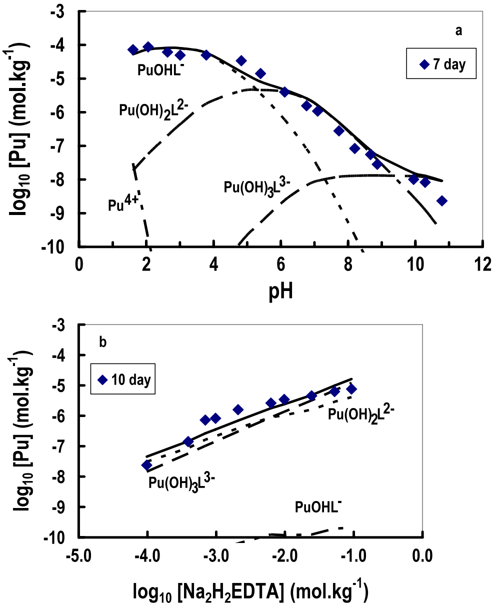

Fig. 6 Solubility of PuO_2(am) as a function of pH and EDTA (L) concentrations (0.0001 $mol\cdot L^{-1}$ for Fig. 6a and as noted for Fig. 6b) at different equilibration periods (from Rai et al. [17]). *Lines* represent predicted concentrations using the thermodynamic data developed in this study combined with the data reported in Guillaumont et al. [18] and Hummel et al. [15] and reported in Tables 2 and 3: *solid lines* represent predicted total Pu concentrations; *other lines* represent concentrations of different species as marked in the figure

3.4 Predicting Pu Behavior in the Presence of Fe(III) and Ca(II)

Based on the thermodynamic data developed/discussed above for the Fe(III) and Pu(IV) systems, predictions of the solubility of PuO_2(am) as a function of pH and in the presence of $Fe(OH)_3$(s) and 0.001 mol·kg^{-1} EDTA were made (Fig. 7). These calculations show (Fig. 7 and Table 5) that almost the entire amount of EDTA added was complexed with Fe(III) species and that the predicted Pu(IV) concentrations in the environmental range of pH values (∼4 to 10) are extremely low and near the detection limit for Pu(IV).

Reliable data for Ca-EDTA complexes are available in the literature [15, 28]. The reported values for the CaEDTA^{2-} complex are similar in these publications but the value from Felmy and Mason [15, 28] was used because these authors also report the necessary Pitzer

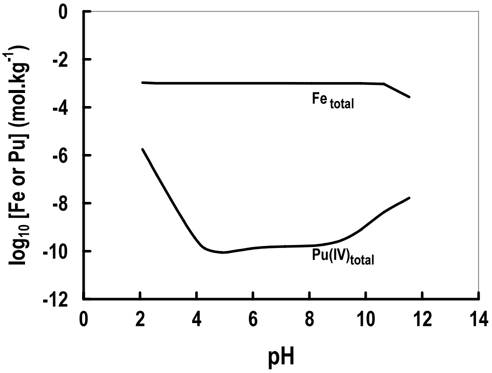

Fig. 7 Solubility of mixtures of PuO_2(am) and $Fe(OH)_3$(s) in the presence of 0.001 mol·kg^{-1} Na_2H_2EDTA as a function of pH. *Lines* represent total predicted Fe(III) and Pu(IV) concentrations using the thermodynamic data developed in this study combined with the data reported in Guillaumont et al. [18] and Hummel et al. [15] and reported in Tables 2 and 3

Table 5 Concentration of free-EDTA (all uncomplexed EDTA species) in solution after reaction of 0.001 mol·kg^{-1} of Na_2H_2EDTA with $Fe(OH)_3$(s) at different pH values

pH	$\log_{10}[H_n EDTA^{n-4}]_{free}$ (mol·kg^{-1})
2.1	−10.2
2.6	−10.2
3.1	−10.1
3.5	−10.1
3.9	−9.9
4.3	−9.7
4.9	−9.3
5.4	−8.9
5.9	−8.6
6.4	−8.4
7.1	−8.0
8.1	−7.1
8.5	−6.7
8.9	−6.3
9.2	−6.0
9.4	−5.8
9.8	−5.4
10.6	−4.4
11.5	−3.2

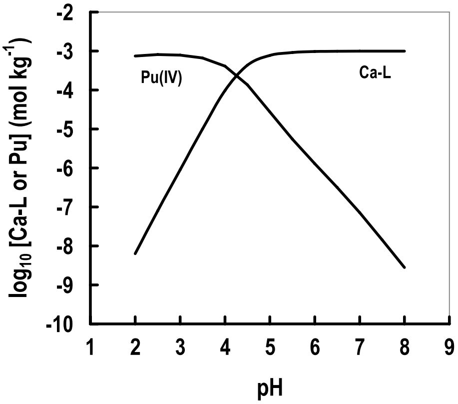

Fig. 8 Solubility of PuO_2(am) in the presence of 0.001 mol·kg^{-1} Na_2H_2EDTA and 0.001 mol·kg^{-1} Ca^{2+} as a function of pH. Lines represent total predicted Pu(IV) and Ca-EDTA (Ca-L) concentrations using the thermodynamic data developed in this study combined with a $CaEDTA^{2-}$ value from Felmy and Mason [28] and the other data reported in Guillaumont et al. [18] and Hummel et al. [15] reported in Tables 2 and 3

ion-interaction parameters needed for modeling. Therefore, predictions were also made for PuO_2(am) solubility as a function of pH in the presence of 0.001 mol·L^{-1} Ca^{2+} and total EDTA concentrations using the thermodynamic data for Pu-EDTA complexes obtained in this study and the CaEDTA data mentioned above (Fig. 8). These predictions show that Ca out-competes Pu(IV) for EDTA complexes in the environmental range of pH values. This is because Ca^{2+} has many orders of magnitude higher activity than Pu^{4+}, a sufficient amount higher that it even overcomes the Pu(IV)-EDTA complexation constant that is >10 orders of magnitude higher than that of Ca-EDTA.

3.5 Experimental Verification of Predictive Models

A limited verification of the Pu-Ca system model was done in which PuO_2(am) samples equilibrated for a long period (10 to 220 days) at a pH value of nine and in EDTA solutions with concentrations varying from ∼0.001 to 0.006 mol·L^{-1} were spiked with relatively low levels of soluble Ca varying from 0.001 to 0.02 mol·L^{-1} and further equilibrated for eight days (Fig. 9). The addition of Ca decreased the PuO_2(am) solubility in all the samples containing <0.008 mol·L^{-1} Na_2H_2EDTA by over an order of magnitude. The thermodynamic model of the system showed that these changes in PuO_2(am) solubility are predictable and are consistent with the thermodynamic data presented in this paper (Fig. 9). The reasons for disagreement at Na_2H_2EDTA concentrations >0.008 mol·L^{-1} are not known.

Studies were conducted on PuO_2(am) solubility in the presence of $Fe(OH)_3$(s) as a function of pH and at EDTA concentrations of 0.0031, 0.001 or 0.00031 mol·L^{-1}. The conclusions that can be drawn from these separate sets are identical; therefore the results for only the 0.001 mol·L^{-1} EDTA set are discussed. The measured and predicted concentrations of Pu(IV) and Fe(III) are reported in Fig. 10. The measured and predicted total Fe(III) concentrations are almost identical to each other and to the amount of EDTA added to the samples in the pH range between two and eight. The measured total Pu concentrations over a large range in pH values are orders of magnitude higher than the Pu(IV) concentrations predicted by the modeling parameters (Tables 2 and 3) in equilibrium with PuO_2(am) (Fig. 10). The oxidation state analysis of the Pu solutions indicated the presence of significant concentrations of Pu(III) at pH values < ∼8 and of Pu(V)/Pu(VI) (most likely Pu(V)) at pH values > ∼8. The estimated Pu(IV) concentrations are at odds with the thermodynamic predictions. The mere fact that measurable concentrations of Pu(III) are found is significant. It should be mentioned that accurate quantification of Pu(III) is problematic because Pu(III) can convert

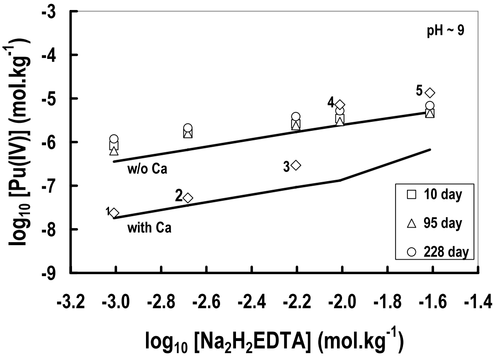

Fig. 9 Solubility of PuO_2 (am) as a function of EDTA concentrations in the absence of Ca (10, 95, 228 day equilibration periods) and in the presence of Ca ($\log_{10}[Ca] = -3.03$ for data point 1, -2.70 for data point 2, -2.23 for data point 3, -2.03 for data point 4, and -1.67 for data point 5, initially without Ca for 220 days and then re-equilibrated for an additional 8 days after addition of Ca). Lines represent predicted concentrations using thermodynamic data reported in Tables 2 and 3

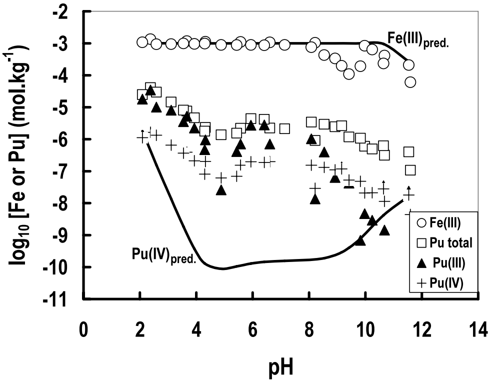

Fig. 10 Solubility of mixtures of PuO_2(am) and $Fe(OH)_3$(s) in the presence of 0.001 mol·kg^{-1} Na_2H_2EDTA as a function of pH for two different sets equilibrated for 12 or 156 days. *Lines* represent total predicted Fe(III) and Pu(IV) concentrations using the thermodynamic data developed in this study combined with the data reported in Guillaumont et al. [18] and Hummel et al. [15] and reported in Tables 2 and 3. Note that there is a close agreement between the experimental and predicted concentrations of Fe(III) but the predicted and experimental Pu(IV) concentrations do not agree in most cases. This is discussed at length in the text and is likely due to the fact that the measured Pu(IV) concentrations are an experimental artifact

to Pu(IV) during extractions (especially in this case where the solutions are dilute and reducing agents were not added intentionally) and thereby decrease the amount of Pu(III) and increase the amount of Pu(IV) measured compared to what is actually present in the samples (also see discussion on this topic in Sect. 2). Therefore, the Pu(IV)/Fe(III) model cannot be verified directly from these results. However, because almost all of the added EDTA is complexed by Fe(III) in experiments involving $Fe(OH)_3$(s) + PuO_2(am) (Fig. 10 and Table 5), very little free EDTA remains ($<10^{-7}$ mol·kg^{-1}, at all pH values less than ~8.1, out of a total of 10^{-3} EDTA initially added) for complexing with Pu(IV). Thus, the solubility of PuO_2(am) in this pH region that includes the pH region of environmental importance should be very similar to PuO_2(am) solubility in the absence of EDTA. There is absolutely no doubt that if the tetravalent oxidation state of Pu could be effectively controlled or quantified, there would be complete agreement between the measured and predicted Pu(IV) concentrations.

It was puzzling, however, that significant concentrations of Pu(III) were detected even though no reducing agents were added to the system. We believe this reduction occurred as a result of a small percentage of Fe(II) impurities in the $Fe(OH)_3$(s) solid used in equilibrations. We have recently shown [14] that Fe(II) can effectively reduce Pu(IV) to Pu(III) in the experimental range of pH values used in this study. The analysis of the $Fe(OH)_3$(s) solid showed the presence of 3.15% of Fe(II). Based on the amount of the $Fe(OH)_3$(s) solid added to each sample (5.34 mg per 35 mL), the amount of total Fe(II) (4.5×10^{-5} mol·kg^{-1}), if all is assumed to dissolve, exceeds in all cases the total soluble Pu concentration, indicating that there is a sufficient amount of Fe(II) present in each sample to reduce Pu(IV) to Pu(III). The reason that significant concentrations of Pu(III) are found only at pH values $< \sim 8$ may be that Fe(II) is not stable at higher pH values in the presence of O_2(gas) [34] and was most likely oxidized to Fe(III) by the trace of O_2(gas) impurities in Ar(gas) used for atmospheric control during equilibration.

Since it is somewhat problematic to accurately determine Pu(III) concentrations, we used the measured pe values to check whether they are low enough to be consistent with the presence of Pu(III) in solution. In these calculations pe and pH, and concentrations of EDTA, Fe, total Pu and other ions present in solution were the input values. Using the thermodynamic model for Fe(III), Pu(IV), Pu(III), Pu(V) and Pu(VI)[2] in the OH-EDTA systems we calculated the total concentrations and thus the percentage of Pu(III), Pu(IV), Pu(V) and Pu(VI) in equilibrium with PuO_2(am) and $Fe(OH)_3$(s) for a few selected low pH samples (where the measured Pu(III) concentrations were high and the measured pe values were expected to be reliable) (Table 6). The Pu(III) concentrations thus predicted (Table 6) show that the measured pe values are consistent with the presence of Pu(III), further substantiating that the dominant oxidation state must be Pu(III) in these low pH value samples. It should also be pointed out that under reducing conditions (e.g., in the presence or Fe(II), hydroquinone, and Fe powder [14, 27] and those observed here) where the Pu^{3+} activity in equilibrium with PuO_2(am) is many orders of magnitude higher than that of Fe^{3+} in equilibrium with $Fe(OH)_3$(s), one has to expect a large solubility increase by Pu(III)-EDTA complexes. However, it was not possible to relate the observed Pu(III)/Pu(V) concentrations (Fig. 10) to

Table 6 Predicted oxidation state of Pu in selected samples from [PuO_2(am) + $Fe(OH)_3$(s)] equilibrated in 0.001 mol·kg^{-1} EDTA, see text for details

Experimental data			Predicted % Pu(III)
pH	Pe	% Pu(III)	
2.09	12.7	79	98
2.58	12.2	37	98
3.11	11.3	60	68
3.54	10.5	47	59
3.93	9.4	51	72

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[2] Tables 2 and 3; Pu(V) and Pu(VI) bare ion values from Guillaumont et al. [18]; and assuming that the values for Pu(V)-EDTA complexes are identical to those for Np(V)-EDTA complexes and the values for Pu(VI)-EDTA complexes are identical to those for U(VI)-EDTA complexes reported in Hummel et al. [15] and with the assumption that the Pitzer ion-interaction parameters for these species with Na^+ are identical to the similarly charged species reported in Table 3.

specific reactions[3] because of the unavailability of key thermodynamic data for Pu oxidation states other than Pu(IV), potential uncertainties in measured redox potentials/oxidation states, possible presence of Pu(IV) polymers/colloids, and/or unavailability of the specific amounts of Fe(II) that reacted with PuO_2(am) at different pH values.

3.6 Conclusions

Thermodynamic data for Pu(IV)/Fe(III)/Ca hydroxide and EDTA systems were developed and verified. A summary of only the important reactions involving $Fe(OH)_3$(s), Fe(III)-EDTA and Pu(IV)-EDTA recommended in this study is presented in Table 7. The main conclusion that can be drawn from these data is that in the presence of $Fe(OH)_3$(s) or at relatively low Ca concentrations, EDTA is primarily complexed with Fe(III) or Ca(II) and is unavailable for complexation with Pu(IV). The predicted Pu(IV) concentrations in natural systems are expected to be even many orders of magnitude lower than those discussed above when considering (1) the total amount of EDTA disposed in geologic environments is

Table 7 Summary of only the important reactions involving Fe(III)-OH, Fe(III)-EDTA, and Pu(IV)-EDTA recommended and specifically verified in this study as compared to those reported in the literature[a]

Reaction	$\log_{10} K^\circ$	Reference
$Fe(OH)_3(s) \rightleftharpoons Fe^{3+} + 3OH^-$	-40.35 ± 0.5	This study
	-38.8 ± 2	Smith et al. [20]
$Fe^{3+} + OH^- \rightleftharpoons FeOH^{2+}$	11.81 ± 0.5	This study[b]
	11.81 ± 3	Smith et al. [20]
$Fe^{3+} + EDTA^{4-} \rightleftharpoons Fe(EDTA)^-$	27.66 ± 0.209	This study[b]
	27.59 ± 0.03[c]	Smith et al. [20]
$Fe^{3+} + EDTA^{4-} + H_2O \rightleftharpoons FeOH(EDTA)^{2-} + H^+$	21.935 ± 0.226	This study
	19.76 ± 3	Calc. from Smith et al. [20]
$Pu^{4+} + EDTA^{4-} + OH^- \rightleftharpoons Pu(OH)EDTA^-$	38.203 ± 0.292	This study[d]
	39.17 ± 0.86	Boukhalfa et al. [7][e]
$Pu^{4+} + EDTA^{4-} + 2OH^- \rightleftharpoons Pu(OH)_2EDTA^{2-}$	47.220 ± 0.292	This study[d]
	46.03 ± 0.1	Boukhalfa et al. [7][e]
$Pu^{4+} + EDTA^{4-} + 3OH^- \rightleftharpoons Pu(OH)_3EDTA^{3-}$	51.705 ± 0.292	This study[d]

[a] Values of equilibrium constants for other relevant reactions can be calculated from the $\Delta_f G^\circ_m/RT$ values quoted in Table 2 from the equation: $[-\ln K^\circ = \Sigma(\Delta_f G^\circ_m/RT)_{\text{products}} - \Sigma(\Delta_f G^\circ_m/RT)_{\text{reactants}}]$

[b] Our results are consistent with the average values reported by Smith et al. [20]

[c] The uncertainty based only on the uncertainties in the SIT ion-interaction parameters

[d] The values of equilibrium constants for the formation of $Pu(OH)_nEDTA^{n-}$ with n varying from 1 to 3 when determined using the SIT model are similar to those in this table based on Pitzer model and are (38.441 ± 0.282), (46.952 ± 0.282) and (51.326 ± 0.282), respectively. For details see text

[e] The values are based on EDTA acidity constants used by Boukhalfa et al. [7] which differ by up to about 1.8 $\log_{10}$ units from those used in this study and reported in Hummel et al. [15]. Therefore, these values will change if calculated with EDTA acidity constants reported in Hummel et al. [15]

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[3] One of the reviewers wondered, based on an agreement for a pH = 11.5 data point, if equilibrium with $PuO_{2.5}$(s, hyd) [35] might explain the observed Pu(V) concentrations at pH >8: thermodynamic modeling of the data showed that this was not the case for a large range of pH values (6–10).

generally two to three orders of magnitude lower in concentration than assumed in these calculations, (2) other competing ions that are ubiquitous in the natural systems (e.g., Al, Mg and other metals) will also compete with Pu(IV) for EDTA complexation in a similar fashion as shown for Fe(III) and Ca, (3) EDTA can be strongly adsorbed by various soil components (e.g., $Fe(OH)_3(s)$), especially at low pH values, and (4) EDTA disposed in geologic environments may be biodegraded. These factors will lower the effective EDTA concentration available for complexing with Pu(IV). Therefore, and contrary to implications in the literature, we can conclude that Pu(IV)-EDTA will not be the mobile species in the environment and that Pu(IV)-EDTA as the environmentally mobile species is a myth rather than reality.

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Appendix A

Experimental raw data obtained in this study are reported in Tables 8 through 13.

Table 8 Solubility of $Fe(OH)_3(am)$ at different pH values equilibrated for 26 and 264 days

Na ($mol\cdot kg^{-1}$)	26 day		264 day	
	pH	$\log_{10}$[Fe] ($mol\cdot kg^{-1}$)	pH	$\log_{10}$[Fe] ($mol\cdot kg^{-1}$)
0.000	1.522	−2.516	1.412	−2.512
0.000	1.844	−2.777	1.803	−2.711
0.000	2.097	−3.252	2.048	−3.206
0.000	2.332	−3.783	2.286	−3.726
0.000	2.668	−4.397	2.645	−4.486
0.000	2.987	−4.913	2.991	−4.821
0.000	3.273	−5.311	3.329	−4.999
0.000	3.569	−5.519	3.642	−5.341
0.000	3.925	−5.661	4.096	−5.405
0.000	4.225	−5.664	4.394	−5.405
0.000	4.616	−5.709	NV	NV
0.000	4.845	−5.816	5.226	−5.866
0.000	5.262	−5.392	5.592	−6.117
0.000	5.594	−6.039	5.911	−6.523
0.000	5.840	−6.099	6.072	−6.513
0.000	6.018	−6.111	6.295	−6.625
0.000	7.504	−6.361	7.868	−7.249
0.000	7.831	−6.081	8.394	−6.544

Table 8 (*Continued*)

Na (mol·kg^{-1})	26 day		264 day	
	pH	$\log_{10}$[Fe] (mol·kg^{-1})	pH	$\log_{10}$[Fe] (mol·kg^{-1})
0.000	9.964	−6.385	9.887	−5.480
0.001	11.030	−5.418	NV	NV
0.002	11.280	−6.225	NV	NV
0.004	11.600	−6.302	11.630	−7.521
0.010	11.970	−6.325	12.020	−6.963
0.020	12.220	−6.176	12.300	−7.169
0.040	12.500	−6.361	12.600	−7.010
0.080	12.750	−6.651	12.850	−6.652

NV = no value

Table 9 Solubility of $Fe(OH)_3$(am) in different concentrations of NaOH equilibrated for 26 and 264 days

$\log_{10}$[NaOH] (mol·kg^{-1})	26 day	264 day
	$\log_{10}$[Fe] (mol·kg^{-1})	$\log_{10}$[Fe] (mol·kg^{-1})
−0.796	−6.552	−7.082
−0.495	−6.536	−5.909
−0.194	−6.308	−6.285
0.000	−6.078	−7.043
0.301	−4.983	−6.218
0.477	NV	−5.711
0.602	NV	−5.047

NV = no value

Appendix B

Computational methods and the results obtained with these analyses, to determine the structures of $Pu(OH)_x EDTA^{x-}$ complexes, are discussed in this appendix.

Computational Methods

Ab initio molecular orbital calculations were performed on two monomeric Pu(IV)-EDTA species to determine the structures of these complexes and to address the effect of hydrolysis on complex stability. The structures of $Pu(H_2O)EDTA$ ($PuC_{10}H_{14}N_2O_9^0$) and $Pu(OH)EDTA^-$($PuC_{10}H_{13}N_2O_9^-$) were energy minimized in the gas phase without symmetry constraint at the spin-restricted Hartree-Fock (RHF) level of theory and the density functional theory (DFT) level of theory using the hybrid functional B3LYP [39]. The Stuttgart relativistic small-core (RSC) electron core pseudopotential basis set was used for the Pu atom [40]; the 3-21G basis set was used for H, C, N, and O atoms [41]. The initial structure for $Pu(H_2O)EDTA$ was taken from the crystal structure of Ti(IV)-EDTA solid-phase hydrate [42]; a water proton was removed to create the initial structure for $Pu(OH)EDTA^-$. Wavefunctions and structures from the RHF optimized clusters were used as inputs for optimization at the DFT level. All calculations were performed using the software NWChem [43] version 4.7.

Table 10 Solubility of $Fe(OH)_3$(am) in the presence of 0.0001 mol·kg^{-1} EDTA equilibrated for 27 days and in 0.001 mol·kg^{-1} EDTA equilibrated for eight days

0.0001 mol·kg^{-1} EDTA			0.001 mol·kg^{-1} EDTA		
pH	log$_{10}$ (mol·kg^{-1})		pH	log$_{10}$ (mol·kg^{-1})	
	Na	Fe		Na	Fe
2.103	−3.699	−3.087	1.749	−2.699	−2.390
2.422	−3.699	−3.710	1.835	−2.699	−2.574
3.038	−3.699	−4.218	1.944	−2.443	−2.707
3.583	−3.699	−4.254	2.082	−1.785	−2.685
4.291	−3.699	−4.254	2.413	−2.699	−3.072
4.863	−3.699	−4.225	2.734	−2.699	−3.145
5.479	−3.699	−4.260	3.546	−2.699	−3.169
5.940	−3.699	−4.200	6.407	−2.665	−3.086
6.278	−3.699	−4.139	8.789	−2.699	−3.066
6.571	−3.699	−4.124	9.849	−2.578	−3.384
7.152	−3.699	−4.104	10.760	−2.145	−3.877
7.858	−3.699	−4.097	10.980	−2.090	−3.928
8.663	−3.699	−4.046	11.210	−2.027	−4.006
10.020	−3.516	−4.130	11.430	−1.998	−4.006
10.450	−3.319	−4.185	11.640	−1.933	−4.398
10.780	−3.095	−4.254	11.860	−1.828	−4.890
10.980	−2.836	−4.348	12.060	−1.666	−5.409
11.410	−2.569	−5.088	12.370	−1.548	−5.749
11.690	−2.284	−5.670			
12.000	−2.000	−6.072			
12.260	−1.699	−6.053			
12.520	−1.398	−5.983			
12.770	−1.097	−6.130			

Results of Computations

We focused these calculations on the simplest of the species, namely $Pu(H_2O)EDTA$ and $Pu(OH)EDTA^-$, which because of their stoichiometry bear strong resemblance to a Ti(IV)-EDTA complex, the molecular structure of which is already known [42]. In the Ti(IV) complex, the metal atom resides in the cavity of a seven-coordinate pentagonal bipyramid bound to two ethylenediamine nitrogen atoms, four carboxylate oxygen atoms and one oxygen from a water ligand. First shell Pu(IV) coordination numbers to water oxygen and/or ligands bearing oxo groups are capable of becoming as high as 11–12 for Pu(IV)-nitrate complexes [44] and 10 for Pu(IV)-carbonate complexes [45]. In the absence of more comprehensive information on this topic, we limited the current computational investigation to the question of whether or not Pu(IV) and Ti(IV) could possess analogous structures. Although the Pu(IV) and Ti(IV) ions have substantially different ionic radii, it is reasonable to hypothesize that the equivalent Pu complex could be stable due to a similar electrostatic charge distribution. Geometry optimization of the $Pu(H_2O)EDTA$ and $Pu(OH)EDTA^-$ complexes at the RHF and DFT levels of theory suggest seven coordination is retained in the case of the Pu atom in the metal site (Fig. 11a). Calculated bond distances are given in Table 14. Predicted Pu-O

Table 11 Solubility of $Fe(OH)_3$(am) in different concentrations of EDTA equilibrated for eight days

pH	$\log_{10}$ (mol·kg^{-1})		
	Na	EDTA	Fe
12.026	−1.772	−4.000	−5.914
12.046	−1.758	−3.699	−5.457
12.040	−1.741	−3.398	−5.153
12.003	−1.722	−3.097	−4.782
12.048	−1.648	−2.796	−4.672
12.028	−1.549	−2.495	−4.444
12.001	−1.429	−2.194	−4.446
11.931	−1.236	−1.893	−4.712

Table 12 Solubility of PuO_2(am) in the presence of Na_2H_2EDTA and in the presence and absence of Ca at different equilibration periods (top half of the table without Ca, bottom half with Ca)

$\log_{10}[Na_2H_2EDTA]$ (mol·kg^{-1})	10 days		95 days		228 days	
	pH	$\log_{10}$[Pu(IV)] (mol·kg^{-1})	pH	$\log_{10}$[Pu(IV)] (mol·kg^{-1})	pH	$\log_{10}$[Pu(IV)] (mol·kg^{-1})
−3.009	8.983	−6.081	8.763	−6.199	8.995	−5.927
−2.682	8.979	−5.799	8.828	−5.804	9.019	−5.676
−2.205	8.955	−5.583	8.999	−5.623	9.005	−5.414
−2.011	8.999	−5.461	9.046	−5.527	8.999	−5.283
−1.613	9.053	−5.342	9.108	−5.341	9.027	−5.165

$\log_{10}[Na_2H_2EDTA]$ (mol·kg^{-1})	$\log_{10}$ [Ca] (mol·kg^{-1})	8 days[a]	
		pH	$\log_{10}$[Pu(IV)] (mol·kg^{-1})
−3.009	−3.032	9.031	−7.624
−2.682	−2.703	8.988	−7.281
−2.205	−2.227	8.998	−6.531
−2.011	−2.033	9.023	−5.142
−1.613	−1.670	9.035	−4.872

[a] The samples in the upper half of the table were spiked with Ca after they were equilibrated for 220 days. They were then re-equilibrated for an additional eight days

bond distances to EDTA oxygen atoms at the DFT level of theory average 2.163 Å, significantly shorter than those measured for carbonate [45] whereas the predicted distance to water oxygen (2.405 Å) agrees very well with measurements (2.38 Å) [44]. Comparison of the $Pu(H_2O)EDTA$ and $Pu(OH)EDTA^-$ complexes at the DFT level of theory shows that the effect of hydrolysis at the water ligand is to increase all Pu-N and Pu-O bonds by approximately 0.12 and 0.07 Å, respectively, while shortening the bond to water oxygen by 0.31 Å (Fig. 11b). This effect is expected given the increased electron density donated to the Pu atom by the hydroxyl ligand relative to water. Lengthening of the Pu-N and Pu-O (carboxylate) bonds with the change in the complex from $PuEDTA(H_2O)$ to $Pu(OH)EDTA^-$ reflects weakening of the Pu interaction with the EDTA ligand. With respect to the possible existence of more hydrolyzed species such as $Pu(OH)_2EDTA^{2-}$ and $Pu(OH)_3EDTA^{3-}$, it is

Table 13 Solubility of PuO_2(am) in the presence of $Fe(OH)_3$(am) and 0.001 $mol\cdot kg^{-1}$ Na_2H_2EDTA at twelve day equilibration period

pH	pe	Concentrations in $\log_{10}$ ($mol\cdot kg^{-1}$)			% of toal Pu		
		Cl	Fe	Pu_{Total}	Pu(III)	Pu(IV)	[Pu(V) + Pu(VI)]
2.085	12.73	−2.113	−2.968	−4.604	72.0	4.5	23.6
2.584	12.23	−2.465	−3.027	−4.528	34.1	18.7	47.2
3.107	11.31	−2.784	−3.026	−4.837	55.5	15.2	29.4
3.544	10.48	−3.034	−3.003	−5.091	43.5	26.4	30.1
3.93	9.44	−2.921	−3.019	−5.329	47.8	21.2	31.0
4.301	8.82	−3.002	−3.008	−5.746	26.3	31.3	42.4
4.881	8.26	−3.042	−3.053	−5.861	1.9	39.9	58.2
5.431	6.56	−3.085	−3.055	−5.811	26.6	11.8	61.6
5.936	4.82	−3.076	−3.052	−5.358	62.6	9.8	27.6
6.412	4.32	−3.026	−3.063	−5.379	66.9	4.4	28.6
7.136	4.26	−3.026	−3.054	−5.675	NV	NV	NV
8.082	3.88	−3.132	−3.121	−5.465	30.2	33.5	36.3
8.537	3.56	−3.386	−3.366	−5.533	13.6	49.0	37.4
8.925	3.13	−3.535	−3.474	−5.610	2.6	54.6	42.8
9.158	2.85	−3.812	−3.704	−5.580	5.2	51.3	43.5
9.419	2.76	−4.766	−3.962	−5.928	3.6	32.4	64.0
9.825	2.61	−3.988	−3.717	−5.969	0.1	36.3	63.7
10.641	2.35	−3.511	−3.628	−6.204	5.6	16.5	77.9
11.539	1.92	NV	−3.681	−6.396	5.9	4.7	89.3

NV = no value

Table 14 Bond distances (Å) calculated at the Hartree-Fock (RHF) and hybrid density functional theory (B3LYP) level for 1:1 Pu(EDTA) species in the gas phase. A relativistic small-core (RSC) electron core pseudopotential basis set was used for the Pu atom and the 3–21G basis set was used for other atom types. See Fig. 11 for atom labeling. Atom O5 is the water/hydroxyl oxygen atom

Bond	Bond distances (Å) for different models and species			
	RHF/Stuttgart RSC/3-21G		B3LYP/Stuttgart RSC/3-21G	
	$PuEDTA(H_2O)^0$	$Pu(OH)EDTA^-$	$PuEDTA(H_2O)^0$	$Pu(OH)EDTA^-$
Pu-N1	2.575	2.738	2.566	2.703
Pu-N2	2.578	2.708	2.576	2.676
Pu-O1	2.147	2.234	2.162	2.260
Pu-O2	2.143	2.196	2.169	2.226
Pu-O3	2.168	2.229	2.169	2.234
Pu-O4	2.168	2.220	2.153	2.201
Pu-O5	2.416	2.096	2.405	2.093

therefore reasonable to speculate that the Pu-N and Pu-O bonds are more labile at higher pH, thereby making these Pu coordination sites more accessible for competition by additional hydroxyls. Given the higher coordination numbers expected for Pu(IV), it is also possible that binding of additional water and/or hydroxyls without severing other first shell bonds is

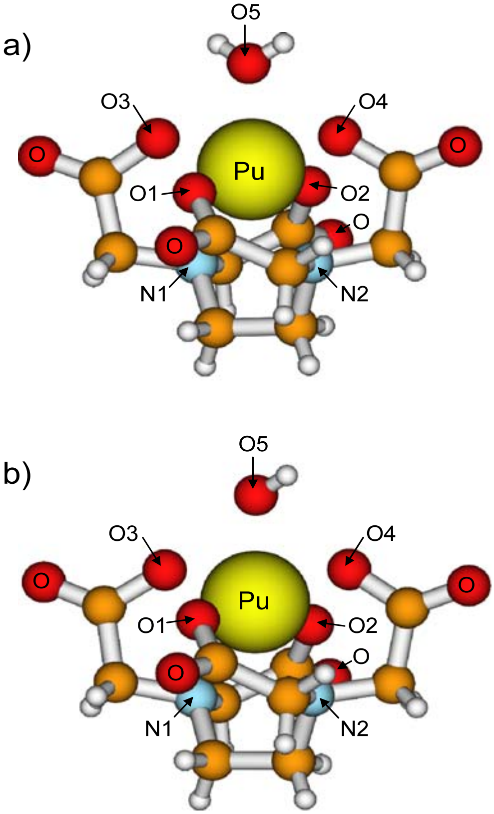

Fig. 11 Ball-and-stick models of the (**a**) PuEDTA(H$_2$O) and (**b**) Pu(OH)EDTA$^-$ complexes after energy minimization at the DFT level of theory. In both cases, the Pu atom is in seven coordination. All plutonium, oxygen, and plutonium atoms are labeled. The unlabeled smaller balls are hydrogen and the larger are carbon atoms. Atom numbering corresponds to tabulated bond-length data listed in Table 14

energetically favorable. Although beyond the scope of the ab initio calculations applied in this work, the existence of the higher hydrolysis species involving two and three hydroxyls combined with weaker association to the EDTA ligand is plausible by this reasoning, consistent with the experimental solubility data (Fig. 6) and the thermodynamic interpretations discussed in the text Sect. 3.3.

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