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Modeling of Pu(IV) Extraction by Tri-*n*-butyl Phosphate from Acidic Nitrate Media Containing Acetohydroxamic Acid

Peter Tkac,*[†,‡] Alena Paulenova,[§] George F. Vandegrift,[‡] and John F. Krebs[‡]

Radiation Center, Oregon State University, Corvallis, Oregon 97331-5903, Argonne National Laboratory, Chemical Sciences and Engineering Division, Argonne, Illinois 60439-4837, and Department of Nuclear Engineering and Radiation Health Physics, Oregon State University, Corvallis, Oregon 97331-5903

The presence of acetohydroxamic acid (HAHA), proposed as a holding-back compound for the PUREX process, significantly decreases extraction of Pu by tri-*n*-butyl phosphate (TBP) due to the formation of strong Pu(IV)−hydroxamate complexes. From the fitting of experimental distribution ratios of Pu, two Pu(IV) species were proposed to be present in the organic phase. The contribution of $Pu(NO_3)_4(TBP)_2$ species is relevant only at very low concentrations of HAHA or its absence, while under higher concentrations of HAHA, the mono- and diacetohydroxamate complexes, $Pu(AHA)(NO_3)_3(TBP)_2$ and $Pu(AHA)_2(NO_3)_2(TBP)_2$, are the main extracted species. A thermodynamic model describing the speciation of tetravalent plutonium in aqueous solutions of nitric acid and acetohydroxamic acid and its distribution with 0.30 volume fraction tri-*n*-butyl phosphate in *n*-dodecane is presented.

Introduction

One of the possible solutions to facilitate separation of plutonium and neptunium from uranium in a modified PUREX process is the introduction of a hydrophilic ligand with a strong complexation affinity toward tetravalent Pu and Np in the aqueous phase that would greatly diminish their extractability. Effective hold-back ligands should meet required criteria such as strong complexation of tetravalent actinides in nitric acid media, low extractability, low material corrosion activity, and commercial availability where the ligand does not induce the formation of precipitates, does not evolve gaseous or volatile products, and has good chemical and radiolytic stability. Several salt-free reagents to separate Pu and Np from U have been proposed and tested, including carboxylic derivates of hydroxylamine such as acetohydroxamic acid (HAHA) or formohydroxamic acid (FHA).[1] In the past decade a number of papers relevant to the extraction of Pu(IV) by tri-*n*-butyl phosphate (TBP) from HNO_3 in the absence and presence of HAHA have been published.[1−12] Recently, a model of the extraction of Pu(IV)[11] and Np(IV)[13] by TBP from various aqueous nitrate concentrations in the absence of HAHA has been developed. Because of the complex chemistry of plutonium and neptunium at lower nitric acid concentrations, such as disproportionation of Pu(IV), hydrolysis of Pu(IV) and Np(IV), and possible formation of colloids, these extraction models are mainly applicable at higher nitric acid concentrations. Hydrolysis and disproportionation can significantly affect the distribution ratios by TBP as has been demonstrated recently for extraction of Pu(IV).[10] On the other hand, at high aqueous HNO_3 concentrations, when $TBP \cdot HNO_3$ adducts become dominant, the formation of $M(NO_3)_4(TBP)(TBP \cdot HNO_3)$ species was also proposed for tetravalent Pu and Np.[11,13,14]

In the presence of hydroxamic acids the distribution ratios for tetravalent Pu and Np by TBP drops significantly due to the formation of strong metal(IV)−hydroxamate complexes.[3,6,8,10,15] Although the metal complexes with FHA and HAHA are rather hydrophilic in character compared to benzohydroxamate complexes, it has been previously reported that, in the presence of HAHA, coextraction of acetohydroxamate complexes of U(VI),[16,17] Mo(VI),[18] Pu(IV),[8] and Np(IV)[19] by TBP is possible. Therefore, to successfully predict distribution ratios of Pu(IV) in the presence of HAHA, a more thorough design of an extraction model is very important. Using the concept developed in our earlier work[11] for the calculation of distribution ratios of Pu(IV), we have approached the modeling of extraction of Pu by TBP in the presence of HAHA, considering coextraction of the Pu-AHA species. In this paper, we present a computational model for the calculation of distribution ratios of Pu(IV) in the system containing nitric acid and additional nitrate $LiNO_3$, HAHA, and 0.30 volume fraction TBP in *n*-dodecane by applying the mean activity coefficients of aqueous ionic species and critically selected stability constants. The calculated values of the Pu(IV) distribution ratio are compared with our experimental results and previously reported experimental data[6] for a set of various concentrations of HAHA, HNO_3, and $LiNO_3$. Several organic Pu species are proposed and discussed.

Experimental Section

Safety Notes. Pu-239 is an α-emitting radioactive isotope. Working with radioactive isotopes requires appropriate precautions and experimental procedures developed for operations with ionizing radiation.

Reagents. All chemical reagents used in this work were of analytical reagent grade purity and used without further purifica-

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* Corresponding author. E-mail: tkac@anl.gov. Tel.: 630-252-7542.

[†] Radiation Center, Oregon State University. Current address: Argonne National Laboratory.

[‡] Argonne National Laboratory.

[§] Department of Nuclear Engineering and Radiation Health Physics, Oregon State University.

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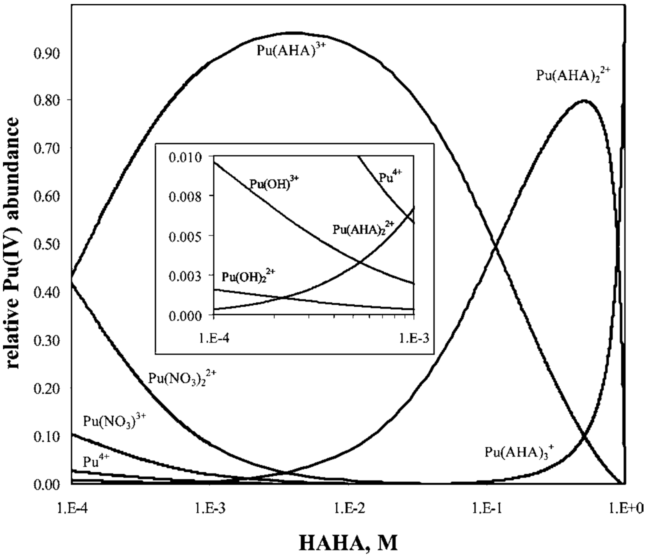

Figure 1. Speciation diagram of Pu(IV) ($1 \cdot 10^{-7}$ mol·L^{-1}) in the presence of 1 mol·L^{-1} HNO_3 and various HAHA concentrations. Inset shows the presence of hydrolyzed Pu(IV) species at low HAHA concentrations.

tion. All aqueous solutions were prepared with deionized water with a resistivity of ≥ 18 MΩ·cm.

Pu-239 was obtained from Argonne National Laboratory in the chloride form and dissolved in reagent grade (0.67 volume fraction) HNO_3. It was then evaporated to dryness and redissolved in 4 mol·L^{-1} HNO_3, which produced a mixture of tetravalent and hexavalent oxidation states. Pu(VI) was reduced to Pu(IV) by addition of a small molar excess of acidified hydrogen peroxide and heated for 30 min at 40 °C. After reduction of Pu(VI), a few crystals of solid $NaNO_2$ were added to maintain the Pu in the tetravalent oxidation state. The Am-241 impurity was removed by anion-exchange chromatography (Dowex 1X-4). Am was washed out with 7 mol·L^{-1} HNO_3, and Pu(IV) was eluted with 0.36 mol·L^{-1} HCl. The solution of Pu(IV) in HCl was evaporated to dryness and redissolved in nitric acid. The purity of the tetravalent oxidation state of Pu was confirmed to be >99.5 % by extraction with 0.5 mol·L^{-1} thenoyl trifluoroacetone[20] (TTA) in xylene from 1 mol·L^{-1} nitric acid.

Solvent Extraction. All extraction experiments were performed with TBP diluted with *n*-dodecane to 1.1 mol·L^{-1} (0.30 volume fraction). Before its use, the TBP/dodecane solution was pre-equilibrated with an aqueous phase containing HNO_3 and $LiNO_3$, except for the addition of the tracer Pu(IV) and HAHA, having the same concentration as the final aqueous phase for which distribution ratios were measured. Extraction of HAHA by TBP can be considered negligible as reported elsewhere.[17] Aqueous solutions were prepared by addition of Pu(IV) stock solution in 1 mol·L^{-1} HNO_3, stock solutions of HNO_3 and $LiNO_3$ in desired ratios, with the HAHA being added last before mixing the aqueous and organic phases. Distribution ratios for Pu(IV) (initially at $\sim 1 \cdot 10^{-7}$ mol·L^{-1}) were measured in batch experiments; samples were rigorously agitated in plastic extraction vials using a vortex mixer at a 1:1 organic/aqueous volume ratio for 4 min at ambient temperature conditions (22 ± 2 °C). After agitation, phases were separated after a short period of centrifugation, and aliquots from both the organic and the aqueous phases were taken to measure the equilibrium concentrations of the metal using liquid scintillation counting with an Ultima Gold scintillation cocktail (100 μL aliquot in 5 mL of scintillation cocktail). For the second extraction, the extraction procedure was repeated with the aqueous phase from the first extraction with an addition of a fresh portion of the organic phase containing no Pu. Distribution ratios of plutonium were calculated as the ratio of the total equilibrium analytical concentrations of Pu in the organic and aqueous phase and are presented as an average of at least two values.

Results and Discussion

Speciation of Pu in the Presence of HAHA. Addition of HAHA to the aqueous solution containing Pu(IV) in nitric acid causes significant changes in the speciation of plutonium. The formation of complexes between Pu(IV) and HAHA is greatly affected by the acidity of the solution. Besides promoting destructive acidic hydrolysis of HAHA, acidity also defines the speciation of the acetohydroxamate species, no matter which of the Pu(IV)-mono-, di-, or triacetohydroxamate complexes predominate. Because of the strong complexation affinity of HAHA toward metals, the presence of HAHA suppresses the hydrolysis and disproportionation reaction of Pu(IV) expected at lower acidity by forming acetohydroxamate complexes:

$$\mathrm{Pu(OH)^{3+} + HAHA \leftrightarrow Pu(AHA)^{3+} + H_2O} \qquad (1)$$

where AHA refers to the dissociated and HAHA the protonated (nondissociated) form of HAHA. To predict the behavior of Pu in a two-phase system containing H^+/NO_3^-, AHA, and TBP, identification of all Pu species in the aqueous phase is essential. The stability constants for Pu(IV) hydroxo and nitrate complexes used for the speciation of aqueous Pu species were obtained from our previous publication,[11] where an extensive discussion for their selection is given. The stability constants $\log \beta_1 = 14.2$, $\log \beta_2 = 24.1$, and $\log \beta_3 = 32.2$ for Pu(IV)−acetohydroxamate complexes $Pu(AHA)^{3+}$, $Pu(AHA)_2^{2+}$, and $Pu(AHA)_3^{+}$ together with the dissociation constant of HAHA (p$K_a = 9.02$) were determined by Carrott et al.[6] The speciation diagram of Pu(IV) species in the presence of HAHA (Figure 1) reveals that under the conditions investigated in this study the acetohydroxamate complexes of Pu predominate over the whole range. Even at very high acidity (6 mol·L^{-1} HNO_3) and in the presence of 0.4 mol·L^{-1} HAHA, the predominant species are $Pu(AHA)^{3+}$ and $Pu(AHA)_2^{2+}$.[8] An excess of HAHA favors formation of the di- and triacetohydroxamate complexes; however, it has to be noted that the speciation diagram shows Pu species formed immediately after addition of HAHA and their concentrations decrease markedly due to the relatively fast reaction of the acidic hydrolysis of HAHA.[21,22] This acidic hydrolysis is an irreversible destructive process that leads to the formation of hydroxylamine and acetic acid as degradation products. Besides the hydrolysis of HAHA, another reaction that affects the speciation of Pu is the relatively slow reduction of Pu(IV) by HAHA to Pu(III).[23,24]

In our recent work,[24] for the conditions with a low HAHA/Pu ratio, it was determined that at least three different reactions are responsible for the reduction and oxidation of Pu in the presence of HAHA and HNO_3. Monoacetohydroxamate complexes decompose by a second-order reaction mechanism with respect to its own concentration and lead to the formation of Pu(III). At low HAHA concentrations, a two-electron reduction of noncomplexed Pu(IV) with HAHA also occurs. The produced Pu(III) is unstable and slowly reoxidizes back to Pu(IV), which, at the point when all of the HAHA has decomposed, can be catalyzed by the presence of nitrous acid. On the other hand, for a higher HAHA/Pu ratio, as was proposed earlier by Carrott et al.,[23] the reduction of Pu(IV) is characterized by a variable induction period, during which no Pu(III) is formed until at some point near a 1:1 HAHA/Pu ratio; some free Pu^{4+} is released from the complex, and the reduction of Pu(IV) with HAHA is initiated. Therefore, at a high HAHA/Pu ratio, which is relevant to our study, the reduction of Pu(IV) by hydroxamic acid after a short contact time is negligible, and the distribution ratios of Pu should be unaffected.

Modeling the Distribution Ratio of Pu(IV) between AHA/H^+/NO_3^- and 0.30 Volume Fraction TBP. Prior to consideration of the extraction of Pu(IV) species by TBP, it is important to understand that the essential factors controlling the transfer of metal from the aqueous to the organic phase are the concentrations of “free” TBP, which is available for complexation. Even under conditions with tracer concentrations of Pu, the concentration of free TBP plays an important role. TBP extracts HNO_3 very well, and at about (6 to 7) mol·L^{-1} aqueous concentration of nitric acid, the 0.30 volume fraction TBP is fully associated with nitric acid. The equilibrium of HNO_3 between the aqueous and the organic (TBP/*n*-dodecane) phases was successfully modeled by Chaiko and Vandegrift,[25] and the proposed organic species between TBP and HNO_3 were included in our model as discussed previously.[11] The extraction experiments of tetravalent plutonium were examined for several concentration combinations of HNO_3, $LiNO_3$, and HAHA. Distribution ratios obtained using a trace concentration of ^{239}Pu(IV) ($1 \cdot 10^{-7}$ mol·L^{-1}) were compared with data reported by Carrott et al.[6] for various Pu concentrations. No significant variation in the distribution ratios for the trace amount of Pu (Figure 2, squares) and the literature data[6] for extraction experiments with a concentration of Pu up to 33.57 g·L^{-1} (Figure 2, circles) was observed. Also, the extraction data for 0.4 mol·L^{-1} HAHA and 1 mol·L^{-1} HNO_3 system are in good accordance with data reported by Carrott et al.[6] for 0.5 mol·L^{-1} HAHA and 1 mol·L^{-1} HNO_3 system, confirming the fact that at high HAHA/Pu ratios, the effect of the HAHA concentration on the distribution ratio of Pu(IV) is not very significant.[8] The extraction yield of Pu(IV) from HNO_3 by TBP increases with increasing nitric acid concentration and decreases with increasing HAHA concentration due to formation of hydrophilic Pu−acetohydroxamate complexes formed in the aqueous phase. Although HAHA lowers distribution ratios of Pu(IV) significantly, some portion of Pu(IV)-mono- and diacetohydroxamate can be extracted by TBP as previously confirmed by vis-NIR (visible-near infrared) spectroscopy.[8]

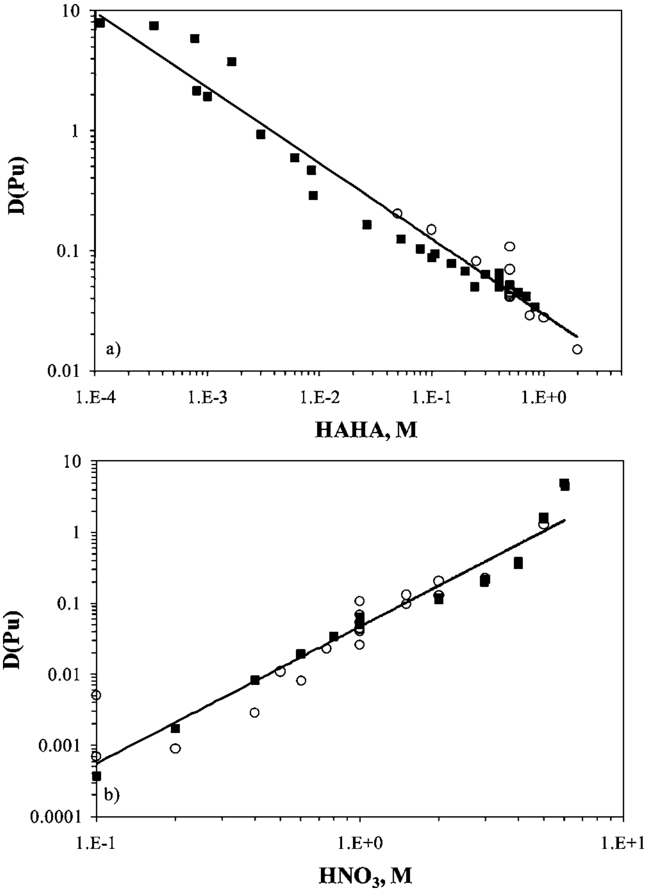

Figure 2. Distribution ratios of Pu from various concentrations of HAHA and HNO_3. (a) ■, 1 mol·L^{-1} HNO_3 and ($1.1 \cdot 10^{-4}$ to 0.833) mol·L^{-1} HAHA; ○, 1 mol·L^{-1} HNO_3 and (0.05 to 2) mol·L^{-1} HAHA, data from ref 6 at macro concentrations of Pu. (b) ■, 0.4 mol·L^{-1} HAHA and (0.1 to 6) mol·L^{-1} HNO_3; ○, 0.5 mol·L^{-1} HAHA and (0.1 to 5) mol·L^{-1} HNO_3, data from ref 6 at macro concentrations of Pu.

Therefore, to successfully predict the extraction of Pu from various initial aqueous concentrations of H^+, NO_3^-, and HAHA, Pu species containing AHA in the organic phase, $Pu(AHA)_x(NO_3)_{4-x}(TBP)_2$, should be considered.

The distribution ratio D of Pu(IV) in the absence of HAHA was defined[11] earlier:

$$D_{Pu(IV)} = \frac{\overline{[Pu(IV)]_T}}{[Pu(IV)]_T} = \frac{\overline{[Pu(NO_3)_4 \cdot TBP_2} + \overline{[Pu(NO_3)_4 \cdot TBP_2 \cdot HNO_3}}{[Pu(IV)]_T} \tag{2}$$

where the subscript symbol *T* represents the analytical total concentration of metal, and the overbar represents extracted organic species. Generally, for a wide region of hydrogen- and nitrate-ion concentrations, the aqueous concentration of $[Pu(IV)]_T$ can be expressed using the hydrolysis and nitrate-complex stability constants:

$$[Pu(IV)]_T = [Pu^{4+}(H_2O)_n] \cdot \left(1 + \frac{K_{H1}}{\{H^+\} \cdot \{H_2O\}} + \frac{K_{H2}}{(\{H^+\} \cdot \{H_2O\})^2} + \frac{\beta_{1N} \cdot \{NO_3^-\}}{\{H_2O\}^2} + \frac{\beta_{2N} \cdot \{NO_3^-\}^2}{\{H_2O\}^4}\right) \tag{3}$$

where {} indicate activities of relevant species, K_H and β_N are the hydrolysis and stability constants of Pu(IV) with nitrate, respectively.

The second and fourth powers of water activities indicate that from $Pu^{4+}(H_2O)_n$ two molecules of water are replaced by one molecule of bidentate nitrate. The extraction constants $K_1 = 1.06 \cdot 10^5 \pm 1.1 \cdot 10^4$ for $Pu(NO_3)_4(TBP)_2$ and $K_2 = 2.12 \cdot 10^4 \pm 5.0 \cdot 10^3$ for $Pu(NO_3)_4(TBP)(TBP \cdot HNO_3)$ were reported previously.[11]

In the presence of HAHA, besides the complexation of Pu in the aqueous phase with acetohydroxamate and nitrate, the following extraction equilibria can also occur:

$$Pu^{4+}(H_2O)_n + AHA^- + 3NO_3^- + \overline{2TBP} \Leftrightarrow \overline{Pu(AHA)(NO_3)_3(TBP)_2} + nH_2O \quad (4)$$

$$Pu^{4+}(H_2O)_n + 2AHA^- + 2NO_3^- + \overline{2TBP} \Leftrightarrow \overline{Pu(AHA)_2(NO_3)_2(TBP)_2} + nH_2O \quad (5)$$

Therefore in the presence of HAHA, the total concentration of Pu(IV) in aqueous phase can be described as:

$$[Pu(IV)]_T = [Pu^{4+}(H_2O)_n] \cdot \left(1 + \frac{K_{H1}}{\{H^+\} \cdot \{H_2O\}} + \frac{K_{H2}}{(\{H^+\} \cdot \{H_2O\})^2} + \frac{\beta_{1N} \cdot \{NO_3^-\}}{\{H_2O\}^2} + \frac{\beta_{2N} \cdot \{NO_3^-\}^2}{\{H_2O\}^4} + \frac{\beta_1 \cdot \{AHA^-\}}{\{H_2O\}^2} + \frac{\beta_2 \cdot \{AHA^-\}^2}{\{H_2O\}^4} + \frac{\beta_3 \cdot \{AHA^-\}^3}{\{H_2O\}^6}\right) \quad (6)$$

where β_{1-3} are the stability constants of Pu(IV)−acetohydroxamate complexes. Again, it was assumed that two molecules of water are replaced by one molecule of a bidentate acetohydroxamate. Previously,[8] it was suggested that two Pu(IV)−acetohydroxamate complexes can be present in TBP after extraction from the HNO_3/HAHA system. The extraction constants for eqs 4 and 5 can be expressed as follows:

$$K_3 = \frac{\overline{[Pu(AHA)(NO_3)_3(TBP)_2} \cdot [H_2O]^n}{[Pu^{4+}(H_2O)_n] \cdot [AHA^-] \cdot [NO_3^-]^3 \cdot [TBP]^2} \cdot \frac{\overline{\gamma_{Pu(AHA)(NO_3)_3 \cdot TBP_2}} \cdot (\gamma_{H_2O})^n}{\gamma_{Pu^{4+}(H_2O)_n} \cdot (\gamma_{AHA^-}) \cdot (\gamma_{NO_3^-})^3 \cdot \overline{(\gamma_{TBP})^2}} \quad (7)$$

$$K_4 = \frac{\overline{[Pu(AHA)_2(NO_3)_2(TBP)_2} \cdot [H_2O]^n}{[Pu^{4+}(H_2O)_n] \cdot [AHA^-]^2 \cdot [NO_3^-]^2 \cdot \overline{[TBP]^2}} \cdot \frac{\overline{\gamma_{Pu(AHA)_2(NO_3)_2 \cdot TBP_2}} \cdot (\gamma_{H_2O})^n}{\gamma_{Pu^{4+}(H_2O)_n} \cdot (\gamma_{AHA^-})^2 \cdot (\gamma_{NO_3^-})^2 \cdot \overline{(\gamma_{TBP})^2}} \quad (8)$$

where $[AHA^-]$ is the concentration of the free acetohydroxamate anion, $\gamma(H_2O)$, $\gamma(Pu^{4+})$, $\gamma(AHA^-)$, and $\gamma(NO_3^-)$ are the activity coefficients of the aqueous species, and $\gamma(Pu(AHA)(NO_3)_3(TBP)_2)$, $\gamma(Pu(AHA)_2(NO_3)_2(TBP)_2)$, and $\gamma(TBP)$ are the activity coefficients of the species in the organic phase. It was assumed that the activity coefficients of neutral species in the organic phase are equal to one. Since the dissociation constant K_a of HAHA is very low ($pK_a = 9.02$), the concentration of acetohydroxamate anion [AHA] is very low and therefore considered to be equal to its activity {AHA}. The mean activity coefficients of the hydrogen ion, nitrate ion, and water were calculated using Bromley's method of activity coefficients. The activity coefficients of Pu^{4+} in the nitrate system were calculated by the SIT approach as reported previously[11] using the interaction parameter $\Delta\varepsilon(Pu^{4+}, NO_3^-) = 0.31$, adopting the value recently determined for Th^{4+} in nitrate media by Neck et al.[26]

To predict the extraction of Pu(IV)−acetohydroxamate complexes by TBP, it is important to understand that the presence of Pu−AHA species in the organic phase is directly associated with their concentration in the aqueous phase. Including four extraction constants K_3 and K_4 defined above (eqs 7 and 8) and K_1 and K_2 for $Pu(NO_3)_4(TBP)_2$ and $Pu(NO_3)_4(TBP)(TBP \cdot HNO_3)$ species determined in previous work,[11] the distribution ratio for Pu(IV) in the presence of HAHA can be expressed by eq 9.

$$D_{Pu(IV)} = \frac{\overline{[Pu(IV)]_T}}{[Pu(IV)]_T} = \frac{\overline{[Pu(NO_3)_4 \cdot TBP_2]} + \overline{[Pu(NO_3)_4 \cdot TBP_2 \cdot HNO_3]} + \overline{[Pu(AHA)(NO_3)_3 \cdot TBP_2]} + \overline{[Pu(AHA)_2(NO_3)_2 \cdot TBP_2]}}{[Pu^{4+}(H_2O)_n] + [Pu(OH)^{3+}] + [Pu(OH)_2^{2+}] + [Pu(NO_3)^{3+}] + [Pu(NO_3)_2^{2+}] + [Pu(AHA)^{3+}] + [Pu(AHA)_2^{2+}]}$$
$$= \frac{\gamma_{Pu^{4+}} \cdot \overline{[TBP]}_f^2 \cdot ((K_1 \cdot \{NO_3^-\}^4 + K_2 \cdot \{NO_3^-\}^5 \cdot \{H^+\}) \cdot \{H_2O\}^{-n} + K_3 \cdot \{NO_3^-\}^3 \cdot \{AHA\} \cdot \beta_1 + K_4 \cdot \{NO_3^-\}^2 \cdot \{AHA\}^2 \cdot \beta_2))}{\left(1 + \frac{K_{H1}}{\{H^+\} \cdot \{H_2O\}} + \frac{K_{H2}}{(\{H^+\} \cdot \{H_2O\})^2} + \frac{\beta_{1N} \cdot \{NO_3^-\}}{\{H_2O\}^2} + \frac{\beta_{2N} \cdot \{NO_3^-\}^2}{\{H_2O\}^4} + \frac{\beta_1 \cdot \{AHA\}}{\{H_2O\}^2} + \frac{\beta_2 \cdot \{AHA\}^2}{\{H_2O\}^4} + \frac{\beta_3 \cdot \{AHA\}^3}{\{H_2O\}^6}\right) \cdot \{H_2O\}^n} \quad (9)$$

It should be noted that this proposed model for the calculation of the distribution ratios of Pu in the presence of H^+/NO_3^-/HAHA is based on several assumptions. The stability constants for Pu−AHA complexes were not adjusted to changing ionic strength due to the unavailability of thermodynamic data for the interaction parameter for Pu^{4+} in the presence of HNO_3 and HAHA. Furthermore, the model adopts the values of activity coefficients for aqueous Pu^{4+} species calculated using the interaction parameter determined for Th^{4+} in nitrate media.[26] In addition, introducing HAHA affects the speciation of Pu(IV) in the aqueous phase considerably and almost certainly affects the activity coefficient of Pu^{4+} as well. However, because of lack of reliable literature data, this interaction was avoided in this work.

The calculated distribution ratio (eq 9) was found by optimizing the values of extraction constants K_3 and K_4 with minimum differences between the calculated and the experimentally observed distribution ratios resolved using the Microsoft Excel Solver plug-in. The solver was set to find minimum differences between the calculated and the experimentally observed distribution ratios (maximum R^2) by changing the values of the extraction constants K_3 and K_4. A comparison of the experimental data with the values of the distribution ratio of Pu(IV) calculated by eq 9 using the extraction constants $K_3 = 695$ for the $Pu(AHA)(NO_3)_3 \cdot TBP_2$ and $K_4 = 35.2$ for the $Pu(AHA)_2(NO_3)_2(TBP)_2$ species provided a very good fit [$R^2 = 0.985$ (Figure 3)].

From the comparison of calculated and experimental data of Pu distribution ratios, the presence of $Pu(NO_3)_4 \cdot TBP_2$ and $Pu(NO_3)_4(TBP)(TBP \cdot HNO_3)$ species under the conditions when HAHA was present can be considered to be negligible. The data acquired by the fitting procedure suggest that the major species extracted in the presence of HAHA is $Pu(AHA)(NO_3)_3(TBP)_2$. The contribution of the $Pu(AHA)_2(NO_3)_2(TBP)_2$ species to the total distribution ratio of Pu is relevant mostly at high HAHA concentration. These results are in good accordance with the data obtained previously by vis-NIR spectroscopy.[8] Figure 4 shows the comparison of the

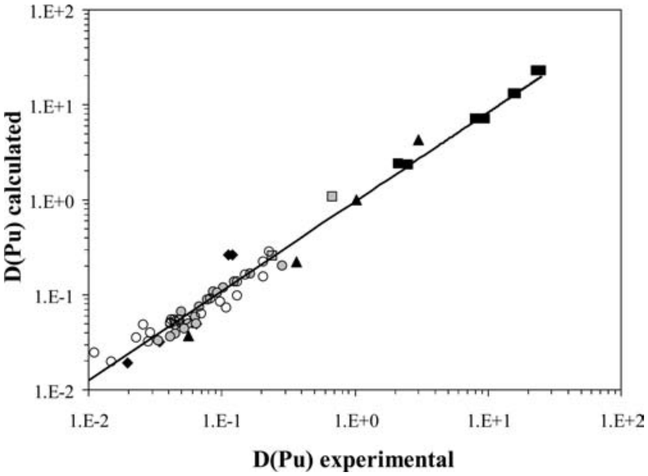

Figure 3. Plot of experimental versus calculated data for the Pu(IV) distribution ratio determined using eq 9 and extraction constant of $K_1 = 1.06\cdot10^5$ for $Pu(NO_3)_4(TBP)_2$, $K_2 = 2.12\cdot10^4$ for $Pu(NO_3)_4(TBP)(TBP\cdot HNO_3)$ from ref 11, and $K_3 = 6.95\cdot10^2$ for $Pu(AHA)(NO_3)_3(TBP)_2$ and $K_4 = 35.2$ for $Pu(AHA)_2(NO_3)_2(TBP)_2$. The line represents the linear regression between experimental and calculated data of distribution ratios ($R^2 = 0.985$). ■, no HAHA and (1 to 4) $\mathrm{mol\cdot L^{-1}}$ HNO_3; ◆, 0.4 $\mathrm{mol\cdot L^{-1}}$ HAHA and (0.1 to 2) $\mathrm{mol\cdot L^{-1}}$ HNO_3; ▲, 0.5 $\mathrm{mol\cdot L^{-1}}$ HNO_3, 0.4 $\mathrm{mol\cdot L^{-1}}$ HAHA, and (0.48 to 3.41) $\mathrm{mol\cdot L^{-1}}$ $LiNO_3$; gray ■, 1.0 $\mathrm{mol\cdot L^{-1}}$ HNO_3, 0.4 $\mathrm{mol\cdot L^{-1}}$ HAHA, and (0.98 to 1.95) $\mathrm{mol\cdot L^{-1}}$ $LiNO_3$; gray ●, 1.0 $\mathrm{mol\cdot L^{-1}}$ HNO_3 and ($1.11\cdot10^{-4}$ to 0.833) $\mathrm{mol\cdot L^{-1}}$ HAHA; ○, (0.1 to 2) $\mathrm{mol\cdot L^{-1}}$ HNO_3 and (0.025 to 2) $\mathrm{mol\cdot L^{-1}}$ HAHA, ref 6.

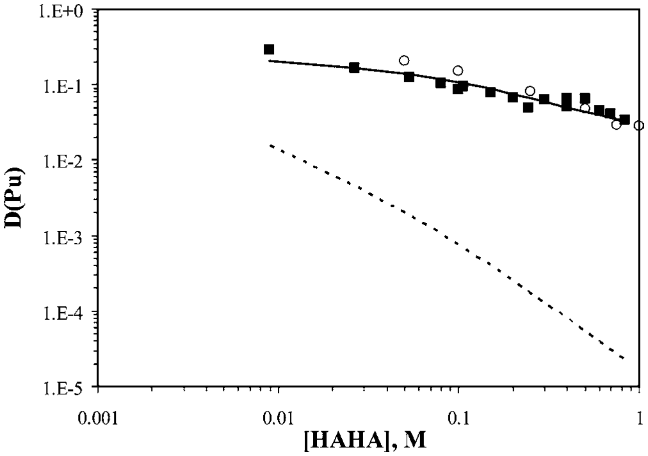

Figure 4. Comparison of the experimental distribution ratios measured for 1.0 $\mathrm{mol\cdot L^{-1}}$ HNO_3 and various concentrations of HAHA (symbols, ■, this work; ○, ref 6) and the calculated distribution ratios, obtained excluding (broken line) and including (solid line) the coextraction of two Pu−AHA complexes.

Table 1. Extraction Constants of Pu(IV) Species for the Extraction System Containing H^+, NO_3^-, HAHA, and 0.30 Volume Fraction TBP

organic Pu(IV) species	extraction constant[a]	extraction constant[b]
$Pu(NO_3)_4(TBP)_2$	$1.06\cdot10^5 \pm 1.1\cdot10^4$[c]	$51.1\ \mathrm{mol\cdot L^{-1}}$[c]
$Pu(NO_3)_4(TBP)(TBP\cdot HNO_3)$	$2.12\cdot10^4 \pm 5\cdot10^3$[c]	$45.2\ \mathrm{mol\cdot L^{-1}}$[c]
$Pu(AHA)(NO_3)_3(TBP)_2$	695 ± 42	$0.75\ \mathrm{mol\cdot L^{-1}}$
$Pu(AHA)_2(NO_3)_2(TBP)_2$	35.2 ± 21	$0.068\ \mathrm{mol\cdot L^{-1}}$

[a] Calculated using activity coefficients for Pu^{4+}. [b] Calculated by neglecting activity coefficients for Pu^{4+}. [c] Ref 11.

experimental distribution ratios of Pu from 1 $\mathrm{mol\cdot L^{-1}}$ HNO_3 and various HAHA concentrations together with the calculated distribution ratios using the extraction constants[11] K_1 for $Pu(NO_3)_4(TBP)_2$ and K_2 for $Pu(NO_3)_4(TBP)(TBP\cdot HNO_3)$ species when the extraction of Pu species containing HAHA was excluded (broken line) and with the values calculated using eq 9 (solid line). It is evident that the model assuming only non-AHA plutonium species in the organic phase provides an unsatisfactory fit, and the necessity of including the ternary Pu(IV)-nitrato-acetohydroxamate species among the extractable species increases with increasing the initial HAHA concentration.

It is helpful to present the extraction constants for Pu species containing HAHA also when neglecting the importance of activity coefficients of the Pu^{4+} ion. This should be used for comparison purposes as previously reported[11] for the extraction constants K_1 for $Pu(NO_3)_4(TBP)_2$ and K_2 for $Pu(NO_3)_4(TBP)(TBP\cdot HNO_3)$ species when neglecting the activity coefficients for Pu^{4+}. When using the values $K_1 = 51.1\ \mathrm{mol\cdot L^{-1}}$ and $K_2 = 45.2\ \mathrm{mol\cdot L^{-1}}$ from ref 11 and optimizing the values of K_3 and K_4 using the Microsoft Excel Solver plug-in, the best fit ($R^2 = 0.982$) between experimental and calculated data was attained for extraction constants $K_3 = 0.75\ \mathrm{mol\cdot L^{-1}}$ for $Pu(AHA)(NO_3)_3(TBP)_2$ and $K_4 = 0.068\ \mathrm{mol\cdot L^{-1}}$ for $Pu(AHA)_2(NO_3)_2(TBP)_2$. The extraction constants for all Pu species included in this model are summarized in Table 1.

Conclusions

A thermodynamic model describing the distribution of tetravalent plutonium between aqueous solutions of nitric acid, lithium nitrate, and HAHA and 0.30 volume fraction TBP in *n*-dodecane is presented.

Experimental data of distribution ratios with a trace concentration of $^{239}Pu(IV)$ for the system containing 0.30 volume fraction TBP in *n*-dodecane and a variety of concentrations of HNO_3, $LiNO_3$, and HAHA were collected and compared with data reported in the literature. The speciation of Pu in conditions related to the TBP/HNO_3/HAHA extraction process can significantly affect its further behavior. In the presence of HAHA, the extracted species is primarily $Pu(AHA)(NO_3)_3(TBP)_2$. However, increasing the concentration of HAHA, the contribution of the $Pu(AHA)_2(NO_3)_2(TBP)_2$ species to the total distribution ratio of Pu becomes a factor. The presence of $Pu(NO_3)_4(TBP)_2$ and $Pu(NO_3)_4(TBP)(TBP\cdot HNO_3)$ species under the conditions when HAHA was present was negligible. The thermodynamic extraction constants $K_3 = 695 \pm 42$ for mono- and $K_4 = 35.2 \pm 21$ for diacetohydroxamate species, obtained by fitting procedures available in the Microsoft Excel Solver plug-in, provided a very good fit ($R^2 = 0.985$) between experimentally obtained and calculated data of distribution ratios for Pu(IV) in the presence of HAHA.

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