Inorganic Chemistry
Article

DOI: 10.1021/ic901081j

Redox Reactions of Pu(IV) and Pu(III) in the Presence of Acetohydroxamic Acid in HNO$_3$ Solutions

Peter Tkac,[†,⊥] **Martin Precek,**[‡] **and Alena Paulenova***[,§]

[†]*Radiation Center,* [‡]*Department of Chemistry, and* [§]*Department of Nuclear Engineering and Radiation Health Physics, Oregon State University, Corvallis, Oregon 97331.* [⊥]*Current address: Argonne National Laboratory, Chemical Technology Division, Argonne, Illinois 60439.*

Received June 4, 2009

The reduction of Pu(IV) in the presence of acetohydroxamic acid (HAHA) was monitored by vis-NIR spectroscopy. All experiments were performed under low HAHA/Pu(IV) ratios, where only the Pu(IV)-monoacetohydroxamate complex and Pu uncomplexed with HAHA were present in relevant concentrations. Time dependent concentrations of all absorbing species were resolved using molar extinction coefficients for Pu(IV), Pu(III), and the Pu(AHA)$^{3+}$ complex by deconvolution of spectra. From fitting of the experimental data by rate equations integrated by a numeric method three reactions were proposed to describe a mechanism responsible for the reduction and oxidation of plutonium in the presence of HAHA and HNO$_3$. Decomposition of Pu(AHA)$^{3+}$ follows a second order reaction mechanism with respect to its own concentration and leads to the formation of Pu(III). At low HAHA concentrations, a two-electron reduction of uncomplexed Pu(IV) with HAHA also occurs. Formed Pu(III) is unstable and slowly reoxidizes back to Pu(IV), which, at the point when all HAHA is decomposed, can be catalyzed by the presence of nitrous acid.

Introduction

The PUREX (Plutonium and Uranium Recovery by EXtraction) based extraction process is used worldwide to recover uranium and plutonium from dissolved spent nuclear fuel using the tri-*n*-butyl phosphate/nitric acid extraction system. To successfully predict the behavior of Pu in this extraction system, the speciation of Pu in nitric acid solutions must be carefully evaluated. It is well-known that the chemistry of plutonium is quite complicated, since several oxidation states can co-exist in aqueous solution. However, at higher nitric acid concentrations, Pu(IV) is quite stable and several Pu(IV) nitrates complexes can be formed: the mono-, di-, tetra-, and hexa-nitrate (Pu(NO$_3$)$^{3+}$, Pu(NO$_3$)$_2^{2+}$, Pu(NO$_3$)$_4$, Pu(NO$_3$)$_6^{2-}$). At concentrations of HNO$_3$ < 4 M, only the formation of mono- and dinitrate Pu(IV) are significant. Even at relatively low pH, hydrolysis, polymerization, and disproportionation reactions of Pu(IV) can occur. The addition of acetohydroxamic acid to a modified PUREX process has been proposed to optimize the stripping of plutonium from the tri-*n*-butyl phosphate (TBP) extraction product.[1] Acetohydroxamic acid (HAHA) acts as a scrubbing agent by forming non-extractable complex species of Np(IV) and Pu(IV) and reducing Np(VI) to Np(V). The reduction capability of acetohydroxamic acid has been recently demonstrated also toward pertechnetate (TcO$_4^-$), which is an important fission product and long-lived radionuclide present in (reprocessed) solutions of spent nuclear fuel. Reduction of pertechnetate occurs only under acidic conditions with relatively high HAHA concentrations and is quite slow. The resulting low-valency *trans*-aquonitrosyl-(diacetohydroxamic)-technetium(II) complex ([Tc(NO)(AHA)$_2$H$_2$O]$^+$) is highly soluble in water, extremely hydrophilic, and is not extracted by TBP.[2]

In addition to the reduction and complexation ability of HAHA, it is also noteworthy to mention that under acidic conditions HAHA is unstable and undergoes hydrolysis.[3,4] The acidic hydrolysis of HAHA is an irreversible destructive process resulting with formation of acetic acid and hydroxylamine as degradation products. The latter is also capable

---

*To whom correspondence should be addressed. E-mail: alena.paulenova@oregonstate.edu.

[1] Vandegrift, G. F.; Regalbuto, M. C.; Aase, S. B.; Arafat, H. A.; Bakel, A. J.; Bowers, D. L.; Byrnes, J. P.; Clark, M. A.; Emery, J. W.; Falkenberg, J. R.; Gelis, A. V.; Hafenrichter, L. D.; Leonard, R. A.; Pereira, C.; Quigley, K. J.; Tsai, Y.; Vander Pol, M. H.; Laidler, J. J. Lab-Scale Demonstration of the UREX+ Process. In *Proceedings of Waste Management WM'04 Conference*, Tucson, AZ, Feb 29−March 4, 2004; WM-4323, Waste Management Conference, Tucson, AZ, 2004.

[2] Gong, C. M. S.; Lukens, W. W.; Poineau, F.; Czerwinski, K. R. *Inorg. Chem.* **2008**, *47*, 6674–6680.

[3] Alyapyshev, M.; Paulenova, A.; Cleveland, M. A.; Bruso, J. E.; Tkac, P. Hydrolysis of Acetohydroxamic Acid under UREX+ Conditions. In *Proceedings of GLOBAL 2007: Advanced Nuclear Fuel Cycles and Systems*, Boise, ID, Sept 9−13, 2007; pp 1861−1864; American Nuclear Society, Omnipress, 2007.

[4] Andrieux, F. P. L.; Boxal, C.; May, I.; Taylor, R. J. *J. Solution Chem.* **2008**, *37*, 215–232.

of reducing Pu(IV) to Pu(III). Several papers relevant to the extraction and complexation of Pu in the presence of hydroxamic acids, HNO_3, and additional nitrate were recently published.[5−15] Although the reduction of Pu(IV) in the presence of hydroxamic acids has been known for about 10 years, only a few papers[10,14,15] related to the reduction of Pu(IV) with hydroxamic acids have been published. The complexity of the reduction of Pu(IV) by hydroxamic acids was the main reason for a limited number of publications. Recently, Carrott et al.[15] studied the oxidation−reduction reactions of Pu(IV) with formohydroxamic (FHA) and acetohydroxamic acids under various nitric acid concentrations and temperatures by cyclic voltammetry and spectrophotometry. It was observed that the reduction of Pu(IV) is consistent with a mechanism in which the Pu(IV) ions remain fully complexed with hydroxamate ligands while the free hydroxamic acid in solution undergoes hydrolysis until, at some point near a 1:1 Pu(IV)/hydroxamic acid ratio, some free Pu^{4+} is released from the complex and the reduction of Pu(IV) with HAHA is initiated.[15] At lower ratios of Pu/HAHA, they observed that the reduction is characterized by a variable induction period, during which no Pu(III) is formed. The authors[15] suggested that the reductant is hydroxamic acid rather than hydroxylamine, as the addition of up to 1.0 M hydroxylamine did not affect significantly the reduction of Pu(IV) in the presence of hydroxamic acid. It was also observed that in the presence of HAHA, the redox potential of Pu(IV)/Pu(III) shifts. However, even though hydroxylamine (hydrolysis product of HAHA) should thermodynamically reduce Pu(IV)-AHA complexes, the negligible effect of hydroxylamine on the reduction of Pu(IV) in the presence of HAHA was explained by kinetic hindrance, possibly because of steric constraints.[15]

To date, the products of the oxidation of hydroxamic acids (RCONHOH, R = CH_3 for acetohydroxamic acid) are relatively unclear and various products have been proposed. Previous data[16−20] indicate that the oxidation of simple hydroxamic acids causes the formation of various radicals. In acidic solutions we may expect that the $R\text{-}CO\text{-}NH\text{-}O^\bullet$ radical forms, whereas in alkali solution a free radical of the type $R\text{-}CO\text{-}N\text{-}O^\bullet$ is more probable to exist. Intermediate products of the oxidation of hydroxamic acids can vary with conditions and R-substituents. Boyland and Nery[18] postulated the occurrence of a series of homolyses, which might give both acyl and alkyl free radicals together with nitroxyl (HN = O). Formation of acyl radical can be described as the following:

$$\mathrm{RCONHOH} \rightarrow \mathrm{RCONH{-}O^\bullet} \rightarrow \mathrm{RCO^\bullet} + \mathrm{HN{=}O} \qquad (1)$$

$RCO^\bullet$ radical can then react with hydroxamic acid:

$$\mathrm{RCO^\bullet} + \mathrm{R{-}CO{-}NHOH} \xrightarrow{-H^\bullet} \mathrm{R{-}CO{-}NH{-}O{-}CO{-}R} \qquad (2)$$

As illustrated in the work of Glennon et al.,[21] hydroxamic acids can also act as a two-electron reductant. At a positive potential, they undergo an irreversible electrochemical oxidation process, as described by eq 3:

$$\mathrm{RCONHOH} + 2\mathrm{H_2O} \rightarrow \mathrm{RCOOH} + \mathrm{H_3NO_2} + 2\mathrm{H^+} + 2e^- \qquad (3)$$

forming the intermediate product, azinic acid, which slowly converts to nitroxyl and hyponitrous acid.[21] If an excess of HAHA is present, the hydrolysis leads to the formation of hydroxylamine that can later be oxidized and form the aminoxyl radical $NH_2O^\bullet$, which is a weak acid and deprotonates to $HNO^{-\bullet}$.[20]

This paper reports experimental data on the reduction of Pu(IV) by acetohydroxamic acid in the presence of 1 M HNO_3. Data were obtained by deconvolution of Pu absorption spectra and analyzed by application of numeric methods. Experimental results suggest a complicated mechanism with several reactions responsible for the reduction and oxidation of plutonium in the presence of HAHA and HNO_3. Focus was made to describe the mechanism of the key reactions.

Experimental Section

Caution! *Pu-242 is an alpha emitting radioactive isotope. Working with radioactive isotope 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 purification. All solutions were prepared with deionized water with a resistivity ≥18 MΩ·cm. Pu-242 was obtained from Argonne National Laboratory in chloride form. Plutonium chloride was dissolved in the reagent grade (67 Vol. %) HNO_3, evaporated to dryness and redissolved in 4 M 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. Purity of the tetravalent oxidation state of Pu was confirmed by absorption spectroscopy and also by using the extraction with

---

(5) Taylor, R. J.; May, I.; Wallwork, A. L.; Denniss, I. S.; Hill, N. J.; Galkin, B. Y.; Zilberman, B. Y. *J. Alloys Compd.* **1998**, *271−273*, 534–537.

(6) May, I.; Taylor, R. J.; Dennis, I. S.; Wallwork, A. L. *Czech. J. Phys.* **1999**, *49*/*S1*, 597–601.

(7) Karraker, D. G.; Rudisil, T. S.; Thompson, M. C. In *Studies of the Effect of Acetohydroxamic Acid on Distribution of Plutonium and Neptunium by 30 Vol % Tributyl Phosphate*, WSRC-TR-2001−00509; Westinghouse Savannah River Company: Aiken, SC, 2001.

(8) Carrott, M. J.; Fox, O. D.; Jones, C. J.; Mason, C.; Taylor, R. J.; Sinkov, S. I.; Choppin, G. R. *Solv. Extr. Ion Exch.* **2007**, *25*, 723–745.

(9) Birkett, J. E.; Carrott, M. J.; Fox, O. D.; Jones, C. J.; Maher, C. J.; Roube, C. V.; Taylor, R. J.; Woodhead, D. A. *J. Nucl. Sci. Technol.* **2007**, *44*, 337–343.

(10) Taylor, R. J.; May, I. *Czech. J. Phys.* **1999**, *49*/*S1*, 617–621.

(11) Tkac, P.; Paulenova, A. *Sep. Sci. Technol.* **2008**, *43*, 2670–2683.

(12) Paulenova, A.; Tkac, P.; Matteson, B. S. Speciation of Plutonium and Other Metals under UREX Process Conditions. In *Proceedings of GLOBAL 2007: Advanced Nuclear Fuel Cycles and Systems*, Boise, ID, September 9−13, 2007; pp 723−727; American Nuclear Society, Omnipress, 2007.

(13) Tkac, P; Paulenova, A.; Vandegrift, G. F.; Krebs, J. F. *J. Radioanal. Nucl. Chem.* **2009**, *280*, 339–342.

(14) Butler, R. J.; Sinkov, S.; Renshaw, J. C.; Collison, D.; Livens, F. R.; Taylor, R. J.; Choppin, G. R. Reactions of Plutonium with Acetohydroxamic Acid in Aqueous Solution: First Results, In *Proceedings of Atalante 2000*, Avignon, France, Oct 24−26, 2000; P2−09; Atalante, Avignon, France, 2000.

(15) Carrott, M. J.; Fox, O. D.; LeGurun, G.; Jones, C. J.; Mason, C.; Taylor, R. J.; Andrieux, F. P. L.; Boxal, C. *Radiochim. Acta* **2008**, *96*, 333–343.

(16) Gutch, C. J. W.; Waters, W. A. *J. Chem. Soc.* **1965**, 751–755.

(17) Ramsbottom, J. V.; Waters, N. A. *J. Chem. Soc. B* **1966**, 132–134.

(18) Boyland, E.; Nery, R. *J. Chem. Soc. C* **1966**, 354–358.

(19) Ramsbottom, J. V.; Waters, N. A. *J. Chem. Soc. B* **1967**, 180–184.

(20) Lind, J.; Mereneyi, G. *J. Phys. Chem. A* **2006**, *110*, 192–197.

(21) Glennon, J. D.; Woulfe, M. R.; Senior, A. T.; NiChoileain, N. *Anal. Chem.* **1989**, *61*, 1474–1478.

0.5 M thenoyl trifluoroacetone[22] (TTA) in xylene from 1 M nitric acid, and it was found to be >99.5%. The concentration of the stock solution of Pu(IV) in 4 M HNO_3 was 0.031 M, and its oxidation state purity was periodically confirmed by absorption spectroscopy. To prevent the formation of Pu colloids, all solutions of Pu(IV) were prepared by acid dissolution with the concentration of at least 0.5 M HNO_3. A sample solution of Pu(III) was prepared by reducing a known concentration of Pu(IV) solution in 1 M HNO_3 by electrolysis,[23] and if necessary stabilized by hydroxylamine. It was found that the presence of hydroxylamine does not have an effect on absorption spectrum of Pu(III). It was experimentally verified that the disproportionation reaction of Pu(IV) is significantly suppressed by the presence of a high concentration of HNO_3 (1 M), and the stability of tetravalent oxidation state of Pu(IV) in 1 M HNO_3 over several weeks was confirmed by absorption spectroscopy.

vis-NIR Spectroscopy. All vis-NIR spectrophotometric experiments were performed with Pu-242 using an OLIS RSM 1000 spectrophotometer and a 1 cm glass microcuvette against the blank solution that was always identical with the measured sample except the component of interest. Scanning of absorption spectra was performed using 400 lines/mm gratings blazed at 500 nm, 0.120 mm wide intermediate and exit slits, and a 400 nm cutoff filter. The instrument was calibrated using holmium oxide filter. To maintain the constant temperature of solution during the experiment at (22 ± 0.1 °C), an external water bath (Julabo CF31 Cryo-Compact Circulator) was used to control the desired temperature by an external probe connected to the cuvette holder.

Reduction Experiment. The stock solution of HAHA was prepared in water on weekly basis, and its stability toward acidic hydrolysis was confirmed experimentally. Solutions of Pu(IV) in nitric acid were prepared in a cuvette to the desired concentration and let stand for 5 min to reach the specific temperature (22 °C). Then, a freshly prepared solution of HAHA in water was added, mixed, and the cuvette was sealed with a cap. The volume of the HAHA solution added was insignificant compared to the volume of the Pu solution in the cuvette and did not affect the temperature of the solution. Upon the addition of acetohydroxamic acid to the aqueous solutions of Pu(IV) in HNO_3, a red-brown complex of $Pu(AHA)^{3+}$ was formed immediately (AHA stands for acetohydroxamate anion of HAHA). The spectra were recorded under aerobic conditions from 30 s after the addition of HAHA for up to 1500 min in 2.5 min intervals, in the range of 400−700 nm with a spectral resolution of 0.75 nm. The initial concentration of Pu and HAHA was varied in the range of 1.5×10^{-3}−3.0×10^{-3} M and 8.33×10^{-4}−3.3×10^{-3} M, respectively. The ionic strength (I) was fixed at 1 M using 1 M HNO_3, and the presence of Pu was considered to have negligible effect on ionic strength.

Measurement of Redox Potential. Simultaneous measurements of the change in redox potential of the system (Eh) and absorption spectra after the addition of HAHA to Pu(IV) in the nitric acid were performed in a 1 cm quartz cuvette. The redox potential was measured by an EC Epsilon electrochemical workstation potentiostat from Bioanalytical Systems Inc. using a 0.5 mm Pt wire working electrode and a silver/silver chloride (SSC) reference electrode with 3 M NaCl filling solution. The electrodes were immersed approximately 5 mm in 2.5 mL of the reacting solution in the cuvette to prevent any interference with the optical path of spectrophotometer.

Molar Absorptivity. When several absorbing species are present simultaneously in the solution, a simple evaluation of the particular absorption bands only at peak maxima or several wavelengths usually leads to erroneous results. This is especially true when the molar extinction coefficients of the absorbing species are very different. Since the molar extinction coefficients of the $Pu(AHA)^{3+}$ complex and other Pu species differ significantly, a better approach to simultaneously determine the concentrations of several absorbing species is a deconvolution of the spectra within a wide spectral range by applying known molar extinction coefficients. Thus, for every spectrum analyzed, the concentrations of all Pu absorbing species were found by applying Lambert−Beer's law at 400 different wavelengths:

$$A_{(\lambda)} = [Pu(AHA)^{3+}]\cdot\varepsilon_{Pu(AHA)^{3+}}\cdot d + [Pu(IV)]\cdot\varepsilon_{Pu(IV)}\cdot d + [Pu(III)]\cdot\varepsilon_{Pu(III)}\cdot d \qquad (4)$$

where $A_{(\lambda)}$ is the absorbance at selected wavelength (λ), ε is the molar extinction coefficient at selected wavelength (λ), [X] is the concentration of particular absorbing species X, and d is the path length of the light through the sample, which was constant and equal to 1.0 cm. Optimal values with minimum differences between the calculated and experimentally observed concentrations were resolved using the Microsoft Excel Solver plug-in.

Fitting the Kinetic Data. The model was based upon a numeric integration of a general set of differential equations:

$$\frac{d[A_i]}{dt} = \sum_{m=1}^{m=M}\left(c_{im}\cdot k_m\cdot\prod_{j=1}^{j=n}[A_j]^{\alpha_{mj}}\right) \qquad (5)$$

using the Runge−Kutta fourth order method (RK4).[24] The model calculated the concentrations of reacting species as a function of time. For a given set of c_{im} and α_{mj} (usually integers or half-integer numbers selected manually) the optimized variables were the rate constants k_m of each assumed reaction m. A mathematical solution was searched as a set of differential equations (eq 5), where each reaction was expected to be proportional to concentrations of reactants present in the system, each raised to a certain power. The calculated concentrations of absorbing Pu species were compared to their experimentally established concentrations. Optimal values of the rate constants k_m were then acquired by using a fitting procedure by the least-squares method performed by the Microsoft Excel Solver plug-in. To explain the behavior of all Pu species in the system, several reaction mechanisms were investigated to describe the oxidation−reduction processes involved. The procedure how the experimental data were fitted by the RK4 model is provided in the Supporting Information.

Results and Discussion

Speciation of Pu in Solution. The addition of HAHA to the aqueous solution containing Pu(IV) in nitric acid leads to the formation of a red-brown colored solution with high extinction coefficients in the range of 400−600 nm because of the formation of the $Pu(AHA)^{3+}$ complex:

$$Pu^{4+} + HAHA \Leftrightarrow Pu(AHA)^{3+} + H^+ \qquad (6)$$

Depending on the initial concentrations of all components, the formation of mono-, di, and triacetohydroxamate Pu(IV) complexes should be considered to be present in the aqueous solutions containing acetohydroxamic acid. Therefore, the study of the reductive properties of HAHA toward Pu(IV) is complicated by

---

[22] Nitsche, H.; Lee, S. C.; Gatti, R. C. *J. Radioanal. Nucl. Chem.* **1988**, *124*, 171–185.

[23] Cohen, D. *J. Inorg. Nucl. Chem.* **1961**, *18*, 207–210.

[24] Kaw, A. K. In *An Interactive E-book for Illustrating Runge-Kutta 4th Order Method of Solving Ordinary Differential Equations*; Holistic Numerical Methods Institute, College of Engineering, University of South Florida: Tampa, FL, May 4, 2006; http://numericalmethods.eng.usf.edu/ebooks/runge4th_08ode_ebook.pdf.

the presence of several complexes between Pu(IV) and AHA. To keep the evaluation of Pu absorption spectra as simple as possible, we kept the concentration of HAHA low compared to the initial concentrations of Pu(IV) to avoid the formation of Pu(IV)-diacetohydroxamate and Pu(IV)-triacetohydroxamate complexes. Therefore, the experiments were performed under the conditions non-applicable to pseudo first order reaction kinetics with the high excess of either metal or ligand. For analysis of Pu spectra in the presence of HAHA and HNO_3, several species must be considered to be present simultaneously in the solution. As a result of the reduction of Pu(IV) by HAHA, Pu(III) species must also be included. To create a speciation diagram of Pu in 1 M HNO_3 and various concentrations of HAHA, the stability constants for Pu(III) and Pu(IV) complexes with hydroxo, nitrate, and HAHA must be applied. The most reliable data for the hydrolysis of Pu(IV) were obtained by solvent extraction with a trace concentration of Pu by Metivier and Guillaumont[25] and recalculated to zero ionic strength by the specific ion interaction theory (SIT) approach[26] to obtain $K^0_{H1} = 0.6$ and $K^0_{H2} = 0.6$. The reason for selection of these constant is discussed elsewhere.[27,28] The stability constants for the first two Pu(IV)-nitrate complexes measured for different ionic strengths, and calculated for zero ionic strength by applying the SIT approach, were reported[29] earlier by Berg et al. Their values of log $\beta^0_1 = 2.12$ for $Pu(NO_3)^{3+}$ and log $\beta^0_2 = 3.66$ for $Pu(NO_3)_2^{2+}$ complexes[29] were applied in this work, and log $\beta_1 = 0.66$ for $Pu(NO_3)^{3+}$ and log $\beta_2 = 1.17$ were the stability constants calculated for 1.0 M ionic strength by the SIT approach. 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.[8] Pu(III) forms much weaker complexes with AHA, with the stability constants of log $\beta_1 = 5.77$, log $\beta_2 = 11.66$, log $\beta_3 = 14.84$, and log $\beta_4 = 15.85$ for $Pu(AHA)^{2+}$, $Pu(AHA)_2^{+}$, $Pu(AHA)_3$, and $Pu(AHA)_4^{-}$ determined by Sinkov and Choppin.[30] For the interaction of trivalent plutonium with nitric acid, the stability constants for Pu(III) nitrates species[31] log $\beta_1 = 0.771$, log $\beta_2 = 1.155$, and log $\beta_3 = 1.158$, and hydrolysis constant[32] log $K_{H1} = -5.54$ were used. The speciation diagram calculated for the mixture of 2×10^{-3} M Pu(IV) and 1×10^{-3} M Pu(III) in 1 M HNO_3 and concentration of HAHA in the range of $5 \times 10^{-4}-4 \times 10^{-3}$ M is shown in Figure 1.

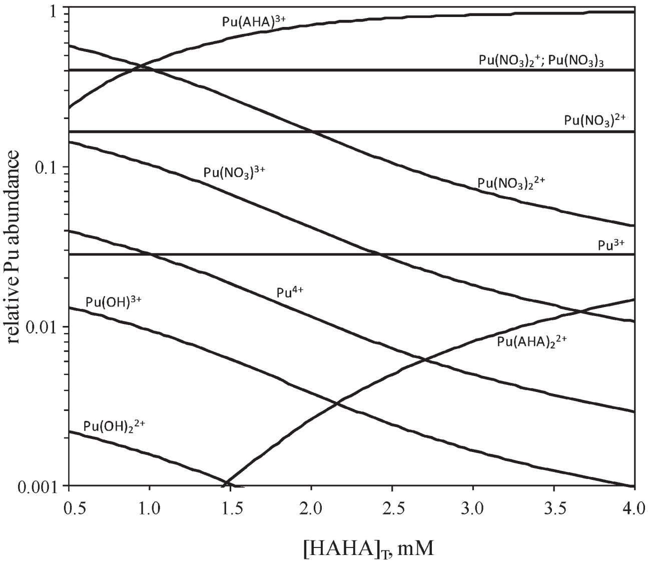

Figure 1. Speciation diagram of Pu(IV) and Pu(III) in 1 M HNO_3 containing various concentration of HAHA and 2×10^{-3} M Pu(IV) and 1×10^{-3} M Pu(III).

The presence of ternary and/or quaternary Pu(IV) complexes such as $Pu(NO_3)_x(AHA)_y(OH)_z^{(4-x-y-z)}$ can be neglected, since the hydrolysis of Pu(IV) in 1 M HNO_3 is negligible (Figure 1), mixed Pu(IV) acetohydroxamate-nitrate species were not identified by Carrott et al.[15] who used absorption spectroscopy for the determination of stability constants for Pu(IV)-acetohydroxamate complexes in the presence of 0.38 M nitrate. Since Pu(III) forms weaker complexes with AHA, their formation in the studied concentration range of HAHA and HNO_3 was not observed. Also, hydrolyzed Pu(III) species are not formed in 1 M HNO_3, and only the Pu^{3+} and Pu(III)-nitrate complexes are present in solution, and are unaffected by HAHA (Figure 1); hence, all Pu(III) species can be considered $Pu(III)_{free}$ (uncomplexed with AHA). Monoacetohydroxamate and nitrate Pu(IV) complexes are the main species present in the HAHA concentration range studied. As reported by Walther et al.,[33] there is no observable effect of plutonium hydrolysis on the absorption spectra of mononuclear mono- and dihydroxo complexes of Pu(IV), which means that hydrolyzed Pu(IV) cannot be distinguished by vis-NIR spectroscopy from the Pu^{4+} ion in the aqueous solution. The speciation of Pu(IV) in the presence of HAHA can be easily divided to Pu(IV) complexed, and uncomplexed with AHA ($Pu(IV)_{free}$), because the relative distribution of $Pu(IV)_{free}$ species, Pu^{4+}, $Pu(OH)^{3+}$, $Pu(OH)_2^{2+}$, $Pu(NO_3)^{3+}$, and $Pu(NO_3)_2^{2+}$, remains constant with changing HAHA concentration and changes only with nitric acid concentration.

Therefore, $Pu(IV)_{free}$ species contribute with the same proportion to the absorption spectrum of Pu(IV) in 1 M HNO_3. Their concentration decreases proportionally with HAHA, while their spectrum remains unaffected by changing HAHA concentration. The same approach was applied to speciation of Pu(III). Thus, we can consider only three Pu absorbing species: $Pu(AHA)^{3+}$ com-

---

(25) Metivier, H.; Guillaumont, R. *Radiochem. Radioanal. Lett.* **1972**, *10*, 27–35.

(26) Guillaumont, R.; Fanghanel, T.; Fuger, J.; Grenthe, I.; Neck, N.; Palmer, D. A.; Rand, M. H. *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*; Chemical Thermodynamics Series 5; Elsevier: Amsterdam, 2003.

(27) Knopp, R.; Neck, V.; Kim, J. I. *Radiochim. Acta* **1999**, *86*, 101–108.

(28) Tkac, P.; Paulenova, A.; Vandegrift, G. F.; Krebs, J. F. *J. Chem. Eng. Data* **2009**, *54*, 1967–1974.

(29) Berg, J. M.; Veirs, D. K.; Vaughn, R. B.; Cisneros, M. A.; Smith, C. A. *J. Radioanal. Nucl. Chem.* **1998**, *235*, 25–29.

(30) Sinkov, S. I.; Choppin, G. R. *J. Nucl. Sci. Technol.* **2002**, *Suppl. 3*, 359–362.

(31) Shevchenko, V. B.; Timoshev, V. G.; Volkova, A. A. *Atomic Energy* **1959**, *6*, 293–296.

(32) Nair, G. M.; Chander, K.; Joshi, J. K. *Radiochim. Acta* **1982**, *30*, 37–40.

(33) Walther, C.; Cho, H. R.; Marquardt, C. M.; Neck, V.; Seibert, A.; Yun, J. I.; Fanghanel, Th. *Radiochim. Acta* **2007**, *95*, 7–16.

plex, Pu(IV)$_{free}$ and Pu(III)$_{free}$, which includes all Pu(III) and Pu(IV) species uncomplexed with AHA (Figure 1). The total concentration of Pu(IV) in the system with low Pu/HAHA ratio containing 1 M HNO_3 can be expressed as follows:

$$\begin{aligned}[\mathrm{Pu(IV)}]_{\mathrm{T}} &= [\mathrm{Pu(IV)}_{\mathrm{free}}] + [\mathrm{Pu(AHA)}^{3+}] \\ &= [\mathrm{Pu}^{4+}] + [\mathrm{Pu(OH)}^{3+}] + [\mathrm{Pu(OH)}_2^{2+}] \\ &+ [\mathrm{Pu(NO_3)}^{3+}] + [\mathrm{Pu(NO_3)}_2^{2+}] + [\mathrm{Pu(AHA)}^{3+}] \end{aligned} \quad (7)$$

and by applying the hydrolysis and stability constants for Pu-nitrates and -acetohydroxamate:

$$\begin{aligned}[\mathrm{Pu(IV)}]_{\mathrm{T}} &= [\mathrm{Pu}^{4+}] + \left(1 + \frac{K_{\mathrm{H1}}}{[\mathrm{H}^+]} + \frac{K_{\mathrm{H2}}}{[\mathrm{H}^+]^2}\right. \\ &\left. + \beta_{1\mathrm{N}}[\mathrm{NO}_3^-] + \beta_{2\mathrm{N}}[\mathrm{NO}_3^-]^2 + \beta_1[\mathrm{AHA}]_{\mathrm{f}}\right) \end{aligned} \quad (8)$$

where [AHA]$_f$ is the concentration of free AHA, dissociated and uncomplexed with Pu(IV), KH is the hydrolysis constant, and β is the stability constant of a particular complex (β_{1N} and β_{2N} represent the stability constants of the Pu(IV) complex with one and two nitrates, respectively). Similarly, the total concentration of all forms of HAHA, [HAHA]$_T$, can be written as

$$[\mathrm{HAHA}]_{\mathrm{T}} = [\mathrm{HAHA}] + [\mathrm{AHA}] + [\mathrm{Pu(AHA)}^{3+}] \quad (9)$$

where [HAHA] and [AHA] represents the concentration of acetohydroxamic acid and its dissociated form, respectively. Consequently, by a rearrangement of eqs 8 and 9 the concentration of HAHA can be expressed as follows:

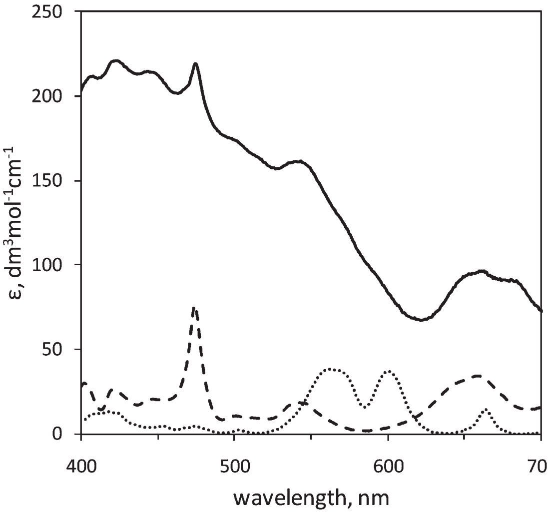

Figure 2. Molar extinction coefficients (ε) of Pu(IV)-monoacetohydroxamate complex (solid line); Pu(IV) representing Pu^{4+}, $(Pu(NO_3))^{3+}$, and $Pu(NO_3)_2{}^{2+}$ species (dashed line) and Pu(III) (dotted line) in 1.0 M HNO_3 at 22 °C.

connection with the determination of the extinction coefficients for the $Pu(AHA)^{3+}$ complex. Even in the region of ~600 nm, where the Pu(III) has the highest and Pu-$(AHA)^{3+}$ complex the lowest absorption, the contribution of Pu(III) to the total absorbance is less than 2%, and the absorbance of $Pu(AHA)^{3+}$ complex dominates. At the other wavelengths the contribution of Pu(III) is even lower. The molar extinction coefficients (ε) of the three major Pu absorbing species are illustrated in Figure 2 (HAHA does not have any absorption spectrum in this region). The absorption spectra of plutonium in the presence of HAHA are dominated by the intense bands of Pu(IV)-monoacetohydroxamate complex.

$$[\mathrm{HAHA}] = \frac{[\mathrm{H}^+][\mathrm{Pu(AHA)}^{3+}]\left(1 + \frac{K_{\mathrm{H1}}}{[\mathrm{H}^+]} + \frac{K_{\mathrm{H2}}}{[\mathrm{H}^+]^2} + \beta_{1\mathrm{N}}[\mathrm{NO}_3^-] + \beta_{2\mathrm{N}}[\mathrm{NO}_3^-]^2 + \beta_1[\mathrm{AHA}]\right)}{K_{\mathrm{a}}([\mathrm{Pu(IV)}]_{\mathrm{T}}\beta_1 - [\mathrm{Pu(AHA)}^{3+}]\beta_1)} \quad (10)$$

Determination of Molar Extinction Coefficients for the Pu-Monoacetohydroxamate Complex. The extinction coefficients for plutonium(IV)-monoacetohydroxamate complex were resolved from the experimental data obtained by absorption spectroscopy using chemical equilibrium modeling software FITEQL 4.0,[34] as described earlier.[11] The concentrations of all Pu(IV) species were determined by applying stability constants for Pu(IV)-hydroxo, -nitrates, and acetohydroxamate complexes. The extinction coefficients for a whole spectrum of Pu-$(AHA)^{3+}$ in the range of 400−700 nm were obtained by subtracting the spectra of Pu(IV)$_{free}$ from the original spectra of solution mixture obtained immediately upon the addition of HAHA to the solution of Pu(IV) in 1.0 M HNO_3. The presence of Pu(III) within the first minute after mixing Pu(IV) and HAHA can be neglected in

Deconvolution of the Absorption Spectra. Upon the addition of HAHA to the solution containing Pu(IV) in nitric acid, the absorption spectra of Pu changes significantly because of the strong absorption of the Pu-$(AHA)^{3+}$ complex that forms immediately. Then, as the reaction proceeds, the spectra change continuously over time because of the reduction of Pu(IV) and the formation of Pu(III). To monitor this complex system, more than 400 spectra were taken for every experiment with various initial concentrations of Pu(IV) and HAHA. From these data, several spectra were selected and used to investigate the concentration profiles of three major absorbing Pu species: $Pu(AHA)^{3+}$, Pu(IV)$_{free}$, and Pu(III)$_{free}$. Calculations were performed according to eq 4 simultaneously at 400 different wavelengths, which significantly improves the accuracy of the concentration profile determined. Figure 3 shows a comparison of the experimental spectra (dotted line) and the spectra resolved by the optimization procedure (solid line) for the concentrations of all Pu species at different times, and initial composition of 1.85×10^{-3} M Pu(IV) and 1.67×10^{-3} M HAHA. As

---

[34] Herbelin, A. L.; Westall, J. C. (1999) In *FITEQL 4.0: A Computer Program for Determination of Chemical Equilibrium Constants from Experimental Data*, Report 99−01; Department of Chemistry, Oregon State University: Corvallis, OR, U.S.A., 1999.

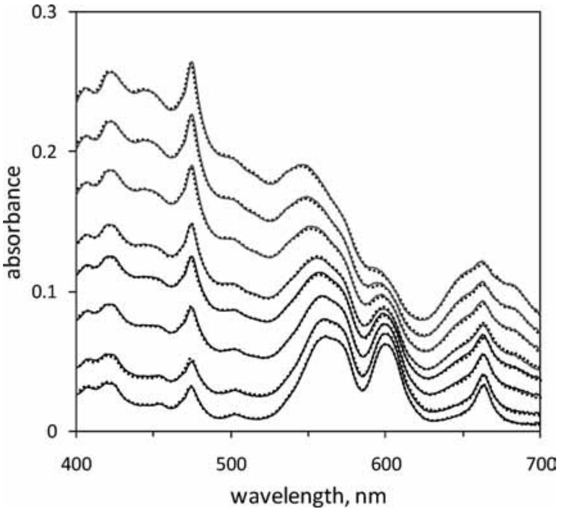

Figure 3. Set of experimental (dotted line) and calculated spectra (solid line) for mixture of Pu species in 1.0 M HNO_3 as the reduction of Pu(IV) complexed with AHA progress at different times (from the top to the bottom: 0.2, 0.5, 1, 2, 3, 6, 15, and 24 h after mixing Pu(IV) with HAHA). $T = 22$ °C, initial concentrations: $[\mathrm{Pu(IV)}] = 1.85 \times 10^{-3}$ M, $[\mathrm{HAHA}] = 1.67 \times 10^{-3}$ M. $[\mathrm{Pu(IV)}]_T/[\mathrm{HAHA}] = 1.11$.

Table 1. Concentration Profiles of Pu Absorbing Species at Different Times Calculated Using an Optimization Procedure for Spectra in Figure 3, and Associated Error Represented by GOF[a]

time, h	$[\mathrm{Pu(AHA)}^{3+}]$ M	$[\mathrm{Pu(IV)}_{\mathrm{free}}]$ M	$[\mathrm{Pu(III)}_{\mathrm{free}}]$ M	GOF
0.2	1.10×10^{-3}	2.65×10^{-4}	4.80×10^{-4}	5.08×10^{-4}
0.5	9.35×10^{-4}	2.45×10^{-4}	6.70×10^{-4}	5.26×10^{-4}
1	7.71×10^{-4}	2.28×10^{-4}	8.50×10^{-4}	5.16×10^{-4}
2	5.90×10^{-4}	2.09×10^{-4}	1.05×10^{-3}	4.18×10^{-4}
3	4.81×10^{-4}	2.01×10^{-4}	1.17×10^{-3}	2.97×10^{-4}
6	3.15×10^{-4}	1.79×10^{-4}	1.36×10^{-3}	1.51×10^{-4}
15	1.45×10^{-4}	1.47×10^{-4}	1.56×10^{-3}	3.81×10^{-4}
24	4.36×10^{-5}	2.07×10^{-5}	1.6×10^{-3}	1.09×10^{-4}

[a] Initial conditions are the same as described in Figure 3.

illustrated in Figure 3, a very good fit between experimental and calculated spectra was observed during the entire experiment. The optimized concentrations of all three Pu absorbing species for every spectrum in Figure 3 are listed in Table 1 together with the goodness of fit (GOF) values, calculated using eq 11:

$$\mathrm{GOF} = \sum_{k=0}^{n} (A_{\mathrm{exp}} - A_{\mathrm{calc}})^2 \tag{11}$$

where n is the number of wavelengths ($n = 400$), and A_{exp} and A_{calc} are the experimental and calculated absorbances at a particular wavelength, respectively. A perfect fit would yield GOF = 0. For comparison, if our experimental spectrum is entirely composed of only $\mathrm{Pu(III)}_{\mathrm{free}}$, but in the fitting procedure we wrongly assign the composition of Pu(IV)/Pu(III) = 1:1, it causes an increase of GOF to 0.157, which is about 1000× higher value than what we usually obtained for a good fit. Thus, the optimization procedure used for deconvolution of absorption spectra allows to determine the concentration profiles of $\mathrm{Pu(AHA)}^{3+}$ complex, $\mathrm{Pu(IV)}_{\mathrm{free}}$, and $\mathrm{Pu(III)}_{\mathrm{free}}$ very precisely at any time.

It should be noted that an excellent fit between experimental and calculated spectra was obtained for all experimental conditions used in this study. However, for some spectra, especially for those with high initial Pu/HAHA ratio a correction for the baseline was necessary at longer times (±0.004 absorbance units). This is most likely due to the possible formation of gaseous products, which could accumulate in the cuvette during the experiment, or partially due to a baseline drift over long period of time.

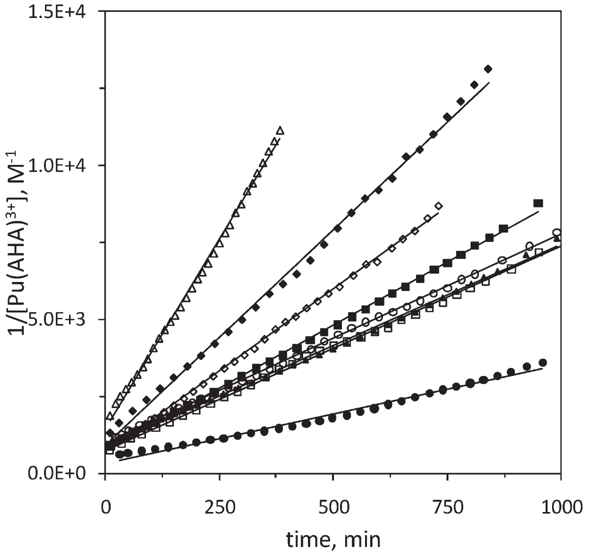

Figure 4. Plot of $1/[\mathrm{Pu(AHA)}^{3+}]$ versus time for various initial concentrations of Pu(IV) and HAHA. Initial conditions were $T = 22$ °C, $[\mathrm{HNO_3}] = 1.0$ M, and initial concentrations in mM for Pu and HAHA, respectively: (△) 1.84, 0.833; (♦) 1.81, 1.17; (◇) 3.0, 1.67; (■) 2.56, 1.67; (▲) 1.85, 1.67; (□) 2.72, 1.8; (○) 1.50, 1.67; (●) 2.65, 3.30.

Identification of Redox Reactions. Solving the set of several differential equations by the RK4 model was simplified, as the instantaneous concentration of HAHA was not calculated by the RK4 model. The main reason was that the concentration of uncomplexed AHA is governed mainly by the very fast complexation kinetics of AHA with Pu(IV). The limitations of the size of the RK4 model did not allow the introduction of this kinetics in the modeling system. From the equilibrium reaction (eq 6), it is obvious that when the concentration of acetohydroxamic acid changes in the system, for example, by hydrolysis/decomposition reaction of HAHA, or by oxidation, the concentration of $\mathrm{Pu(AHA)}^{3+}$ complex changes accordingly. Therefore, the concentration of HAHA for every time step was calculated based on the complexation equilibrium between $[\mathrm{Pu(IV)}]_T$ and $[\mathrm{Pu(AHA)}^{3+}]$ (eq 10).

By plotting the concentration profiles for experiments with several different initial concentrations of the Pu(IV) and HAHA, we have found that the decrease of the Pu-AHA concentration over time follows a second order reaction with respect to its own concentration for all experimental trials performed. This can be clearly seen in Figure 4, where the plots of $1/[\mathrm{Pu(AHA)}^{3+}]$ versus time give the straight lines for various initial concentrations of Pu(IV) and HAHA confirming the second order reaction with respect to $[\mathrm{Pu(AHA)}^{3+}]$:

$$-\frac{\mathrm{d}[\mathrm{Pu(AHA)}^{3+}]}{\mathrm{d}t} = k_1'[\mathrm{Pu(AHA)}^{3+}]^2 \tag{12}$$

Analysis of the absorption spectra indicates that decomposition of the $\mathrm{Pu(AHA)}^{3+}$ complex leads to the direct formation of Pu(III), possibly by an intramolecular electron transfer. This is, however, in discrepancy with the mechanism proposed by Carrott et al.[15] who suggested a consecutive reaction, where the $Pu(AHA)^{3+}$ complex first decomposes to Pu(IV), and then it is reduced by an available HAHA. Under the conditions investigated in this work, we have observed a relatively fast production of Pu(III) upon the addition of HAHA. The increase of Pu(III) concentration was directly linked with a decrease of the concentration of the $Pu(AHA)^{3+}$ complex. For all experiments performed, a mechanism that considers a decomposition of the $Pu(AHA)^{3+}$ complex to Pu(IV) followed by the reduction with AHA released from the complex did not provide a satisfactory fit of the experimental data. The different observation can be explained by a quite different reaction mechanism at higher concentrations of HAHA where also Pu(IV)-di- and triacetohydroxamate complexes are present.

Nevertheless, the reduction of the $Pu(IV)_{free}$ by acetohydroxamic acid also occurs:

$$-\frac{d[Pu(IV)]}{dt} = k_2'[Pu(IV)][AHA] \qquad (13)$$

Apparently, the reduction of $Pu(IV)_{free}$ by HAHA (eq 13) strongly depends on initial conditions. This reaction significantly contributes to the reduction of total Pu(IV), and this occurs mainly under the conditions with a higher concentration ratio Pu/HAHA, when a significant amount of $Pu(IV)_{free}$ is present in the system. Concentration profiles (symbols) of $Pu(AHA)^{3+}$, $Pu(IV)_{free}$, $Pu(III)_{free}$, and HAHA over time for various initial concentrations of Pu(IV) and HAHA (Figure 5) determined from the spectra deconvolution clearly demonstrate that HAHA is capable of reducing greater than an equivalent amount of Pu(IV). This is especially evident for the experiments where the Pu/HAHA ratio was more than one (Figure 5a−f). However, as shown in Figure 5, a maximum concentration of Pu(III) never reaches twice the initial concentration of HAHA, which would explain the two-electron reduction. Factors like decomposition of HAHA by acidic hydrolysis that lowers the concentration of HAHA available for reduction of Pu(IV), and/or reoxidation of Pu(III) back to Pu(IV), can play a certain role; however, the main reason is that the decomposition of the $Pu(AHA)^{3+}$ complex is the major reaction controlling production of Pu(III) concentration, which, as discussed later, is a one-electron reduction process. Clearly, under the conditions when the initial concentration of HAHA was higher than Pu, but the formation of Pu(IV)-diacetohydroxamate complex could be still neglected (Figure 5 g, h), the concentration change of $Pu(IV)_{free}$ is minimal, and thus it does not play an important role in formation of Pu(III).

It is interesting to take a closer look at the relationship of the formation of Pu(III) and the decrease of total HAHA concentration, as determined from the experimental data (the numerical values of changes in the concentrations of $Pu(AHA)^{3+}$, $Pu(IV)_{free}$, $Pu(III)_{free}$, and HAHA for all experiments are listed in the Supporting Information). At the beginning of the reaction (after ~10 min), when the Pu/HAHA ratio is high, the analysis of the concentration changes of Pu(III) and HAHA shows that more than one Pu(III) is produced for every HAHA decomposed. On the other hand, when the ratio of Pu/HAHA is near or lower than one, about one or less than one atom of Pu(III) is formed per one HAHA destroyed. This could be explained as followed: when the initial concentration of HAHA is lower than that of Pu, the reduction of Pu(IV) by HAHA (eq 13) occurs as a two-electron reduction process, which explains the higher concentration of Pu(III) formed compared to the initial HAHA concentration. At higher HAHA concentrations, where $Pu(AHA)^{3+}$ species dominates, a one-electron reduction occurs. This is evident from Figure 5h, where during the first 400 min after mixing Pu and HAHA, the production of Pu(III) is solely governed by the decomposition of $Pu(AHA)^{3+}$ complex; therefore, one atom of Pu(III) is formed per one molecule of $Pu(AHA)^{3+}$ decomposed. A similar dependence on the ratio of metal and reductant was previously observed for the reduction of Pu(IV) by hydroxylamine.[35] When the ratio of Pu(IV)]/NH_3OH^+ > 1, the following reaction of 2-electron reduction is significant:

$$2NH_3OH^+ + 4Pu^{4+} \rightarrow 4Pu^{3+} + N_2O + H_2O + 6H^+ \qquad (14)$$

but when the ratio of Pu(IV)/NH_3OH^+ < 1, the reaction of 1-electron reduction predominates:

$$2NH_3OH^+ + 2Pu^{4+} \rightarrow 2Pu^{3+} + N_2 + 2H_2O + 4H^+ \qquad (15)$$

Also data reported by Carrott et al.[15] show that more than one-electron reduction of HAHA toward Pu(IV) occurs, especially at Pu/HAHA ratios 2:1 and 3.5:1. Moreover, they observed that at some point Pu(III) can be reoxidized back to Pu(IV), which is most probably catalyzed by nitrous acid (HNO_2), which accumulates in the HNO_3 solutions. The absence of the reoxidation of Pu(III) in the presence of HAHA was explained by the scavenging properties of HAHA toward HNO_2.

Previously, it was observed by Olsson[36] that as the pH in the solution of Pu(III) is increased, the formation of Pu(IV) is evident even under non-oxic conditions when a mixture of hydrogen (4%) and argon was bubbled through the solution. In our work, under oxic conditions, it was observed that Pu(III), freshly prepared by electrolysis without addition of hydroxylamine, was unstable in solutions of 1 M HNO_3, and slowly oxidized to Pu(IV). Instability of Pu(III) solutions is well-known, and can be explained by several reactions, for example, photochemically by UV light[37] or by oxidation with oxygen[38] or nitrate.[39,40] Under our experimental conditions, reoxidation by UV light can be neglected because we used a 400 nm high pass filter. It is very likely that oxidation of

---

(35) Barney, G. S. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1677–1681.

(36) Olsson, M. *Radiochim. Acta* **2006**, *94*, 575–578.

(37) Shilov, V. P.; Yusov, A. B. *Radiochem.* **2001**, *43*, 364–370.

(38) Cleveland, J. M. *The Chemistry of Plutonium*; Gordon and Breach, Science Publishers, Inc.: New York, 1970; p. 49.

(39) Lee, M. H.; Park, Y. J.; Kim, W. H. *J. Radioanal. Nucl. Chem.* **2007**, *273*, 375–382.

(40) Koltunov, V. S.; Zhuravleva, G. I.; Marchenko, V. I.; Dvoeglazov, K. N.; Savilova, O. A.; Koltunov, G. V.; Taylor, R. J.; Bankhead, M. *Radiochim. Acta* **2007**, *95*, 559–567.

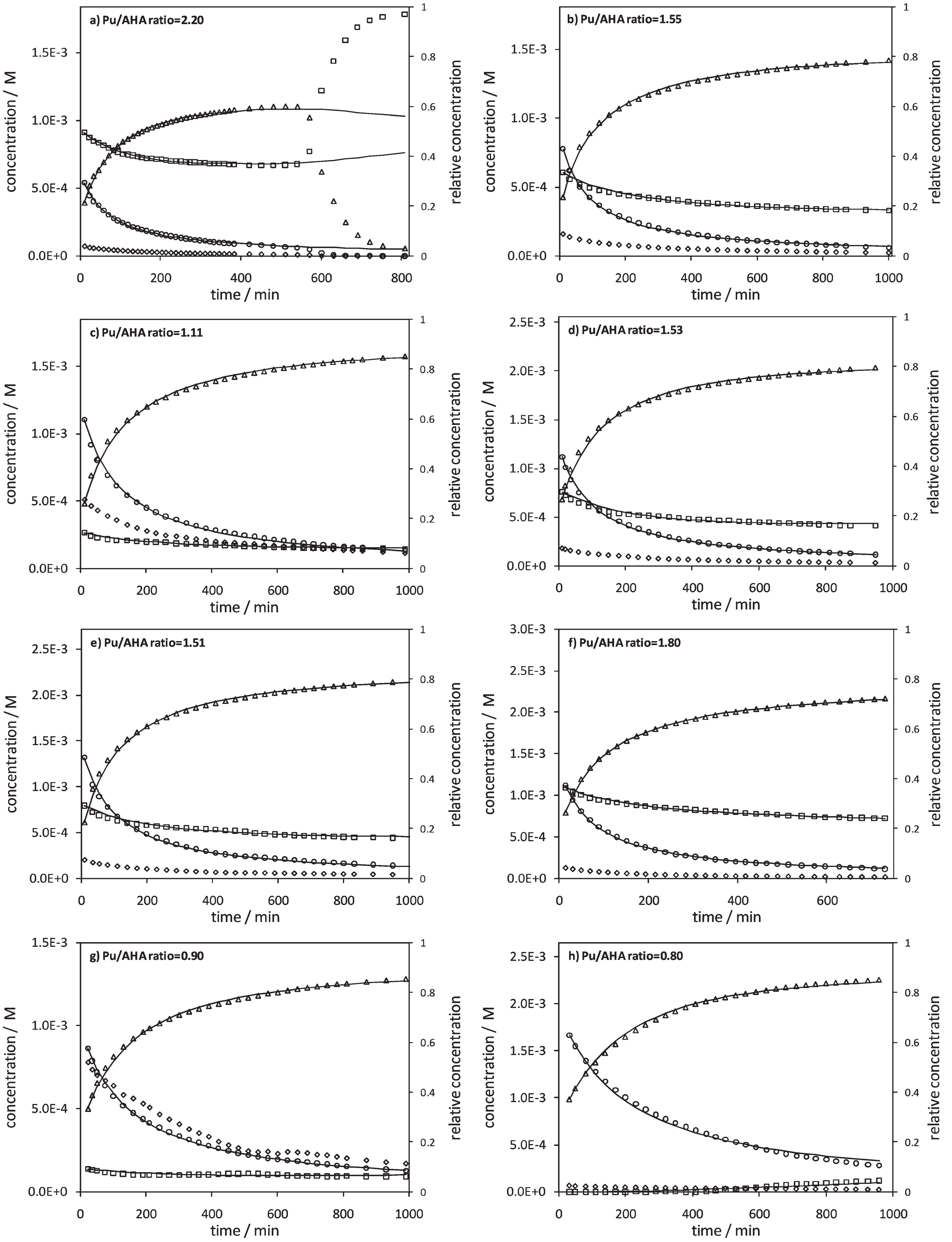

Figure 5. Experimental (symbols) vs calculated (line) data for concentration profiles of (○) $Pu(AHA)^{3+}$ complex, (□) Pu(IV), (△) Pu(III) and (◇) HAHA. Initial conditions were $T = 22$ °C, $[HNO_3] = 1.0$ M; and concentrations in mM for initial Pu and HAHA, respectively. (a) 1.84, 0.833; (b) 1.81, 1.17; (c) 1.85, 1.67; (d) 2.56, 1.67; (e) 2.72, 1.80; (f) 3.0, 1.67; (g) 1.5, 1.67; (h) 2.65, 3.30. Relative concentration on the side *y*-axis is the ratio of the actual concentration of the particular species ($Pu(AHA)^{3+}$, $Pu(IV)_{free}$, $Pu(III)_{free}$, and HAHA) to the total concentration of plutonium in the system.

Pu(III) is driven mainly by its instability in nitric acid under oxic conditions:

$$\frac{\mathrm{d}[\mathrm{Pu(IV)}]}{\mathrm{d}t} = k_3'[\mathrm{Pu(III)}] \qquad (16)$$

Lee et al.[39] have observed the instability of Pu(III) and its oxidation to Pu(IV) with an increase of acidity from 1 to 6 M HNO_3. Therefore, the slow reoxidation of Pu(III) to Pu(IV) (eq 16) was assigned to oxidation properties of nitric acid, which was constant under all experimental conditions and equal to 1 M. With the system of three differential kinetic equations (eqs 12, 13, 16) we were able to consistently describe the time dependence of the concentrations of the plutonium species after ~10 min of mixing Pu(IV) and HAHA for all experiments. The data obtained by calculation using RK4 method (lines in Figure 5) show that the suggested model of three kinetic reactions can explain the reaction mechanism very well. Our experimental results show that partial reoxidation of Pu(III) (eq 16) occurs also in the presence of HAHA. Full recovery of Pu(IV) occurs at higher Pu/HAHA ratio when all HAHA disappears from the system. This is very clearly demonstrated in Figure 5a.

When the concentration of HAHA drops to a minimum, the fast reoxidation of Pu(III) appears to be a predominant process. From this point, calculated data (line) in Figure 5a differ significantly from those obtained experimentally (symbols), since the reoxidation of Pu(III) by nitrous acid was not measured and hence, not included in the calculations. This would be difficult to model as the concentration profile of HNO_2 needs to be first determined as well as the correct kinetic reaction responsible for the production of nitrous acid. When the reoxidation of Pu(III) by HNO_2 appears, it leads to a complete recovery of Pu(IV), which was stable for several weeks. However, the complete reoxidation of Pu(III) back to Pu(IV) was not observed in every experiment. Under some conditions, when the initial concentration of HAHA was lower than Pu(IV), the complete reoxidation of Pu(III) was not observed even in the time scale of 3 weeks. This suggests that the oxidation of Pu(III) is a more complex process and various catalytic/inhibiting reactions might be responsible for this behavior, especially those that regulate the concentration of HNO_2. At Pu/HAHA = 0.8 (Figure 5h) where the $\mathrm{Pu(AHA)}^{3+}$ complex dominates, the production of $\mathrm{Pu(IV)}_{\mathrm{free}}$ due to the oxidation of Pu(III) is evident after ~400 min and confirms that under the conditions when the initial presence of $\mathrm{Pu(IV)}_{\mathrm{free}}$ is minimal, the process described by eq 12 plays a key role in the formation of Pu(III).

From the experimental data, it can be concluded that depending on HAHA concentration, HAHA can act either as a two-electron reductant when unbound with Pu(IV) or as a one-electron reductant with intramolecular electron transfer in Pu-monoacetohydroxamate complex. In both cases, during the course of the reaction the balance of Pu(III) over HAHA decreases because of the reoxidation of Pu(III) back to Pu(IV). Also, the experiments performed with simultaneous measurement of Eh and Pu absorption spectra confirmed that addition of HAHA into the system containing Pu(IV) in 1 M HNO_3 results in a drop in the redox potential. When all HAHA was consumed and the fast reoxidation to Pu(IV) initiated, the redox potential was observed to increase. Nevertheless, the concentration ratios of $\mathrm{Pu(III)}_{\mathrm{free}}$ and $\mathrm{Pu(IV)}_{\mathrm{free}}$ that were determined by spectral deconvolution suggest that the redox potential measured by the platinum electrode could not be explained only on the basis of the Nernstian behavior of Pu ions (Supporting Information, Figure S1). The redox potential measurement therefore did not contribute to a greater understanding of the analyzed reaction system.

The main goal of this study was to describe the kinetics of redox reactions of Pu in the presence of HAHA and HNO_3. Nonetheless, a successful description of kinetic behavior identified in the later stage (more than 10 min) was not compatible with the observation within the first 10 min after mixing Pu and HAHA. In the early stage of the reaction, it is most likely that some additional processes, which are faster than the studied processes, affect the progress of the reaction with the reagents. These processes are difficult to identify. After the addition of HAHA to the solution containing Pu(IV), a relatively fast reduction of Pu(IV) occurs, which is later followed by the mechanism described by eqs 12, 13, and 16. The processes involved at the beginning might be controlled by intermediate oxidation degradation products[16−21] of HAHA (see Introduction), such as aminoxyl radical $H_2NO^\bullet$, which is also a good reductant.[20] Then, as the reaction proceeds, accumulation of some HAHA oxidation products probably suppresses the reaction of intermediates, and redox reaction of Pu is controlled mainly by HAHA and HNO_2. To identify the reactants responsible for the first stage of the reduction, a quite different approach and different techniques applicable mainly to the early stage of the reaction will be required. However, the scope of this paper was the overall description of redox kinetics with identification of the key reactions governing the main part of Pu(III) production.

Thus, Figure 5 does not show the data at the very beginning of the reaction, when HAHA was added to the solution of Pu(IV) in 1.0 M HNO_3. Experimental data suggest that several catalysts/inhibitors can affect the reactions described by eqs 12, 13, and 16, and therefore, the evaluation of kinetic parameters is difficult. Under the conditions when the concentration of $\mathrm{Pu(IV)}_{\mathrm{free}}$ is low (low Pu/HAHA ratio), the concentration of Pu(III) in the system is controlled primarily by the second order reaction of decomposition of the $\mathrm{Pu(AHA)}^{3+}$ complex and slow reoxidation of Pu(III).

Conclusions

After the addition of HAHA to a solution containing Pu(IV) in nitric acid, the formation of the $\mathrm{Pu(AHA)}^{3+}$ complex occurs. Then, the complex of $\mathrm{Pu(AHA)}^{3+}$ decomposes and Pu(III) is formed. The experimental data obtained by absorption spectroscopy suggest that several reactions are responsible for this oxidation−reduction mechanism. $\mathrm{Pu(AHA)}^{3+}$ complex decomposes to Pu(III) by a second order reaction with respect to its own concentration, and it is a major reaction contributing to the production of Pu(III).

A two-electron reduction of uncomplexed Pu(IV) with HAHA occurs mainly at high Pu/HAHA ratio. The third reaction is the reoxidation of Pu(III) in the presence of nitric acid. At some point, when all HAHA disappears from the system, Pu(III) can be reoxidized completely back to Pu(IV), which is probably catalyzed by nitrous acid. However, since several catalysts/inhibitors are expected to control these reactions, the kinetic parameters will be difficult to obtain.

Acknowledgment. This work was supported by the U.S. DOE University Program U-NERI 07-14829.

Supporting Information Available: Data obtained by simultaneous measurement of redox potential and absorption spectra after the addition of HAHA into Pu(IV) solution in 1 M HNO_3. Tables for numerical values of concentration profiles of Pu(AHA)$^{3+}$, Pu(IV)$_{free}$, Pu(III)$_{free}$, and HAHA for all experiments shown in Figure 5. This material is available free of charge via the Internet at http://pubs.acs.org.