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The Effect of Acetohydroxamic Acid on Extraction and Speciation of Plutonium

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Abstract: The effect of acetohydroxamic acid (AHA) on speciation of transuranic elements has been investigated in the extraction and spectrophotometric experiments relevant to UREX extraction process. The distribution ratios decreased with increased concentration of added AHA rapidly, and a considerable ability of AHA to form complexes with plutonium even under strong acidic conditions was confirmed. Using FITEQL 4.0, a computer modeling program for equilibrium experimental data, the speciation distribution of tetravalent plutonium was determined. Acetohydroxamate species of Pu(IV) identified in Vis-NIR spectra of the extraction organic phase confirms formation of extractable neutral solvates of ternary acetohydroxamate-nitrate complexes of plutonium with tributyl phosphate (TBP).

Keywords: Acetohydroxamic acid, actinides, complexation, extraction, plutonium, speciation, TBP, UREX

INTRODUCTION

Separation of actinides from fission products and other elements present in spent nuclear fuel, based on solved extraction process using tri-*n*-butyl phosphate diluted in kerosene has been investigated extensively for several decades (1). The focus of research programs on the advanced spent nuclear fuel treatment is optimization of separation of uranium from plutonium, neptunium and other minor actinides and fission products. To meet these criteria, the UREX + suite process has been developed at Argonne National Laboratory and other national laboratories under the Advanced Fuel Cycle Initiative and the Global Nuclear Energy

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Partnership (2). Several salt-free reagents have been tested for UREX + process to optimize the separation of plutonium and neptunium from uranium. Effective stripping ligands should meet required criteria such as strong complexation of tetravalent actinides in nitric acid matrix, low extractability, formation of no precipitates, gaseous or volatile products, chemical and radiolytic stability, low material corrosion activity, and commercial availability. One of these proposed reagent is acetohydroxamic acid (AHA), that does not affect extraction of uranium (3,4), but significantly reduce the extraction of Pu and Np to the organic phase by either rapid reduction of hexavalent Pu (5) and Np (6–8) to non-extractable pentavalent oxidation state or by formation of strong complexes of AHA with tetravalent Pu and Np, which are also non-extractable. In solutions containing relatively high concentration of HNO_3 (relevant to UREX process), the hydroxamic acid can hydrolyze to the parent carboxylic acid and hydroxylamine (9–13) Therefore, depending on conditions in aqueous solution complexation of Pu(IV) and Np(IV) with AHA can lead to the formation of mono-, di- and tri-acetohydroxamate species. Stability constants of acetohydroxamic acids with Pu(IV) ($\beta_1 = 14.2 \pm 0.2$, $\beta_2 = 24.1 \pm 0.2$, $\beta_3 = 32.2 \pm 0.2$) and Np(IV) ($\beta_1 = 12.83 \pm 0.04$, $\beta_2 = 22.96 \pm 0.07$, $\beta_3 = 30.06 \pm 0.11$) determined by Sinkov and co-workers (14) confirm strong complexation of Pu and Np with AHA. However, the complexation and separation yields depend also on such factors as kinetics and thermodynamics of the chemical reactions, solvation of species in both the organic and aqueous phases, and structure of complexes formed in both phases. Although some experimental data for distribution ratio of U(VI), Pu(IV) and Np(IV) in the presence of hydroxamic acid relevant to UREX process conditions are already available (3,4,14–16) determination of plutonium species in the presence of acetohydroxamic acid and their extraction by TBP is still of great interest. Such experimental data from distribution experiments and identification of plutonium species present under various conditions in both aqueous and organic phase can considerably help predict behavior of plutonium in the extraction process relevant to the proposed flow sheet.

EXPERIMENTAL

Materials and Methods

Pu-239 and Pu-242 isotopes were obtained from Argonne National Laboratory and purified as described below. All other reagents used in this work were of analytical reagent grade purity and used without further purification.

Original stock solution of Pu arrived as a mixture of hexavalent and tetravalent oxidation states; therefore, Pu was reduced by addition of acidified hydrogen peroxide, and then, Pu(III) was re-oxidized to Pu(IV) by a cautious addition of crystals of solid $NaNO_2$. Impurities of Am-241 (for Pu-239) were removed by anion exchange chromatography using a small column filled with the resin Dowex 1x-4, conditioned with 7 M HNO_3. Plutonium, dissolved in concentrated HNO_3, was placed on the top of the resin bed, and Am washed out with several column volumes of 7 M HNO_3. Finally, Pu(IV) was eluted with 0.36 M HCl. Purity of the tetravalent oxidation states of Pu was confirmed by absorption spectroscopy and using the extraction scheme with thenoyl trifluoroacetone (TTA) in xylene from 1 M nitric acid and it was found to be $>99.5\%$.

Solvent Extraction

A solution of 30% TBP (1.1 M) in *n*-dodecane was used as an organic phase for all extraction experiments. Before extraction, TBP was pre-equilibrated with the aqueous phase containing various concentrations of HNO_3, as used in the extraction experiment. Samples were rigorously agitated (VORTEX) in plastic extraction vials at the 1:1 organic/aqueous volume phase ratio for 4 minutes. After agitation, aqueous and organic phase were separated by centrifugation and aliquots from both phases were taken for measurements. The reported distribution ratios are average values from at least two extractions. Activity of Pu-239 in the organic and aqueous phase was determined using a liquid scintillation counter (Backman) and using Ultima Gold scintillation cocktail.

Spectrometry

All Vis-NIR spectrophotometric experiments were performed with Pu-242 (2.26×10^{-3} M) using an Ocean Optics QE65000 spectrophotometer and 1 cm quartz cuvettes against the blank solution that was always identical with the measured sample except the component of interest.

RESULTS AND DISCUSSION

Extraction and Speciation of Pu in the Presence of AHA

A steep reduction of extraction yields of tetravalent plutonium (Pu-239) from 1 M HNO_3 by 30% TBP in *n*-dodecane upon addition of acetohydroxamic acid is displayed in Fig. 1. Already a very small concentration

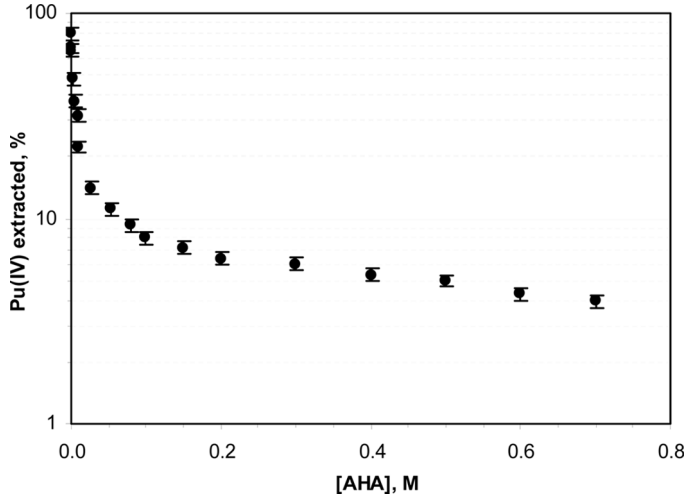

Figure 1. Dependence of extraction yield of Pu(IV) by 30% TBP from 1 M HNO_3 on concentration of AHA.

of acetohydroxamic acid reduces the extraction yield of Pu dramatically due to the formation of a strong Pu-acetohydroxamate complex in aqueous solution. At concentration of AHA >0.1 M, extraction yield of Pu decreases only slightly and even at very high concentration of AHA (0.1–0.8 M), still reasonable amount of Pu is extracted to the organic phase. These species of Pu extracted to organic phase are expected to be ternary complexes of $Pu(AHA)_x(NO_3)_{4-x}$ solvated with TBP. Extraction of metal-acetohydroxamate solvates to organic phase have been observed also for U(VI) (17) and Mo(VI) (18) by 30% TBP in the presence of AHA.

The speciation of Pu(IV) (Pu-242, 2.26×10^{-3} M) in 1 M nitric acid and various concentration of acetohydroxamic acid (2.5×10^{-4}M – 0.8 M AHA) were investigated by Vis-NIR spectroscopy. To study the speciation of Pu with acetohydroxamic acid under acidic conditions (HNO_3) also hydrolytic degradation of AHA and reduction of Pu(IV) to Pu(III) by AHA should be considered. As it has been found from our preliminary data, reduction of Pu(IV) to Pu(III) by AHA is very slow (several hours are needed for complete reduction). Therefore, in a short time period (2–3minutes), instability of Pu(IV)-acetohydroxamate complexes and hydrolysis of AHA in acidic conditions affects complexation between Pu(IV) and AHA just slightly. However, all Vis-NIR spectra of Pu in the presence of AHA and HNO_3 were taken under the shortest operation time to minimize changes of conditions due to hydrolytic and redox reactions.

Addition of acetohydroxamic acid to aqueous solution of Pu(IV) in nitric acid lead to significant change of absorption spectra in Vis-NIR region. These changes are due to the formation of Pu-acetohydroxamate complexes. In general, complexation of Pu(IV) in HNO_3 by acetohydroxamic acid can be written as:

$$\mathrm{Pu(IV)} + x\mathrm{HL} + n\mathrm{H^+} + y\mathrm{NO_3^-} = [\mathrm{Pu(L)}_x(\mathrm{NO_3^-})_y]^{(4-x-y)+} + (n+x)\mathrm{H^+} \quad (1)$$

where HL denotes protonated (non-dissociated) acetohydroxamic acid. For a conditions where Pu(IV) and HNO_3 concentration are constant, we can assume that the absorbance variations are attributed to the variation in the Pu(IV) distribution among $[\mathrm{Pu(IV)}]_{\mathrm{free}}$ (non-compexed with AHA), Pu(IV)-mono-, di-, and tri-acetohydroxamate species. The mass balance for total Pu concentration $[\mathrm{Pu(IV)}]_{\mathrm{tot}}$ in aqueous solution is written:

$$[\mathrm{Pu(IV)}]_{\mathrm{tot}} = [\mathrm{Pu(IV)}]_{\mathrm{free}} + [\mathrm{Pu(IV)L_1}] + [\mathrm{Pu(IV)L_2}] + [\mathrm{Pu(IV)L_3}] \quad (2)$$

Because all Pu(IV) species on the right side of equation (2) contribute to absorption spectra, the absorbance of plutonium solution at a given wavelength, when concentrations of HNO_3 and Pu(IV) are constant and concentration of AHA are changed, can be expressed as:

$$\begin{aligned} \mathrm{A}_{(ij)} = {} & \varepsilon_{\mathrm{Pu(free)}(i)} \cdot [\mathrm{Pu}]_{\mathrm{free}(j)} + \varepsilon_{\mathrm{Pu(L_1)}(i)} \cdot [\mathrm{PuL_1}]_{(j)} \\ & + \varepsilon_{\mathrm{Pu(L_2)}(i)} \cdot [\mathrm{PuL_2}]_{(j)} + \varepsilon_{\mathrm{Pu(L_3)}(i)} \cdot [\mathrm{PuL_3}]_{(j)} \end{aligned} \quad (3)$$

where $\mathrm{A}_{(ij)}$ is absorbance of system at the wavelength i and concentration of ligand j, ε is extinction coefficient for particular absorbing species in solution.

Plutonium(IV)-acetohydroxamate species were resolved from the experimental data obtained by absorption spectroscopy using the chemical equilibrium modeling software FITEQL 4.0 (19). FITEQL 4.0 involves the iterative application of a specified chemical equilibrium model to a set of equilibrium complexation data. Since FITEQL is a nonlinear optimization program, initial estimates for the values of the adjustable parameters are needed. Through calculation of the sum of squares of residuals between the experimental complexation data and predictions made with initial estimates, values of extinction coefficients (ε) for Pu-AHA, Pu-AHA_2 and Pu-AHA_3 complexes at $\lambda = 423$ nm were determined for the complexation reactions specified (1). The experimental values

of Pu concentration (2.26×10^{-3} M), hydrogen ion concentration (1 M HNO_3), various concentrations of acetohydroxamic acid ($2.5 \times 10^{-4} - 8 \times 10^{-1}$ M) and stability constants determined (14) for Pu-AHA complexes were taken as inputs for distribution of plutonium species. Using the chemical equilibrium modeling it was found that formation of three Pu-acetohydroxamate species formed is possible in 1 M HNO_3 and studied range of AHA concentration (Fig. 2). Under conditions of lower AHA concentrations, mainly the non-acetohydroxamate and mono-acetohydroxamate species of Pu are formed. At 0.1 M concentration of AHA and higher, which is more relevant to UREX process conditions, the di-acetohydroxamate species of plutonium becomes predominant and also concentration of Pu-tri-acetohydroxamate species grows up. Values of log ε for Pu-AHA, Pu-AHA_2, and Pu-AHA_3 calculated by FITEQL 4.0 at 423 nm are 2.29, 2.72, and 2.80 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, respectively. Figure 3 compares experimental absorbance of Pu(IV) at $\lambda = 423$ nm with absorbance calculated from equation (3) as a function of [AHA, free]. In this case, [AHA, free] denotes the concentration of non-complexed protonated ligand, which was calculated from pKa and given concentrations of AHA, Pu and HNO_3 using FITEQL.

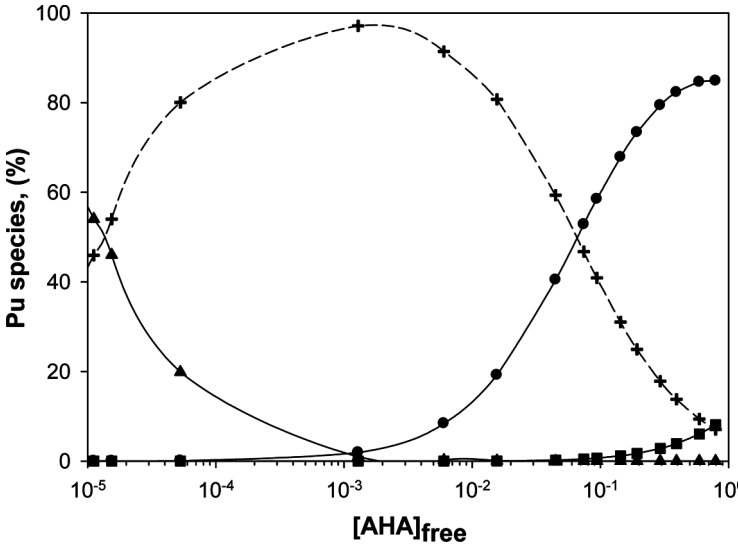

Figure 2. Speciation diagram for Pu(IV)–AHA system calculated for total [Pu(IV)] = 2.26×10^{-3} M, 1 M HNO_3 and various concentration of AHA ($[AHA]_{free}$ denotes AHA non-complexed with Pu). Pu non-complexed with AHA (▲); Pu-mono-acetohydroxamate species (+); Pu-di-acetohydroxamate species(●); Pu-tri-acetohydroxamate species (■).

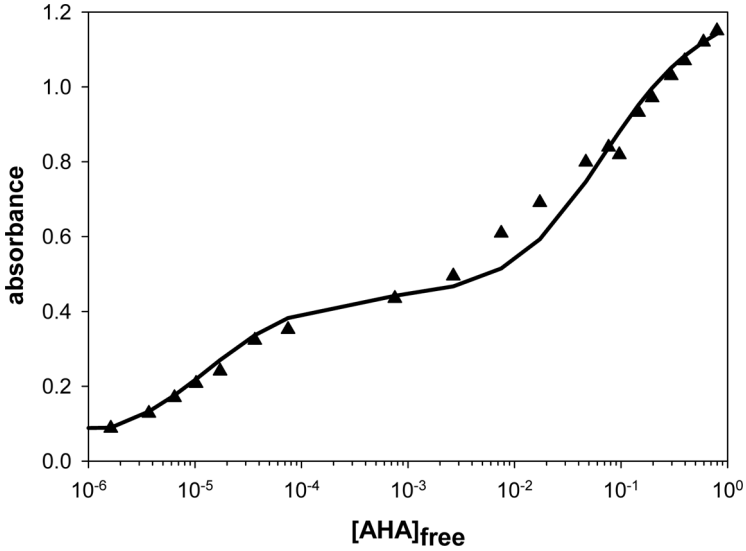

Figure 3. Experimental and calculated absorbance of aqueous solution of Pu(IV) at $\lambda = 423$ nm as a function of free concentration of AHA (non-complexed with Pu); experimental data (▲), calculated data (line).

Extinction coefficients for Pu-AHA, Pu-AHA_2 and Pu-AHA_3 species determined by FITEQL produced a very good agreement between the experimental data and calculated values of absorbance.

The effect of nitric acid concentration on speciation of plutonium in 0.4 M AHA was fitted by HYSS (Hyperquad Simulation and Speciation program) (20). From the data obtained from speciation diagram generated for 1-6 M concentration range of nitric acid, we observed that mono and di-acetohydroxamate species of plutonium are predominant in selected range of HNO_3, although the fraction of Pu non-complexed with AHA grows up with the nitric acid concentration. As we reported earlier (13), at these very high concentrations of nitric acid, a hydrolytical degradation of AHA is rapid and it will significantly affect the complexation of Pu with acetohydroxamate. The presence of Pu-acetohydroxamate species was confirmed even in a very high concentration of nitric acid by Vis-NIR spectroscopy (Fig. 4). Changes of Pu spectra due to formation of Pu-acetohydroxamate species with maximum at 423 nm can be explained by interaction of metal and bidentate bonded ligand as it was previously observed for complexation of Pu(IV) with nitrate (21). Formation of plutonium-acetohydroxamate species at very high concentration of acid confirm the very strong complexation power of AHA toward Pu(IV).

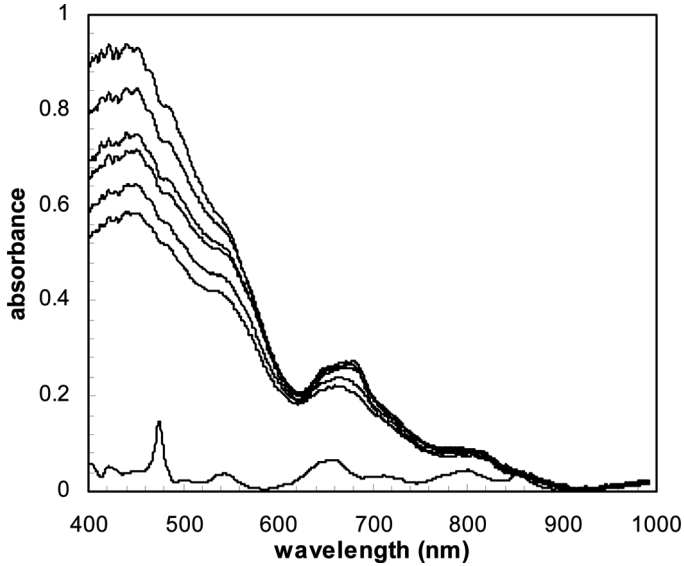

Figure 4. Absorption spectra of Pu(IV)-acetohydroxamate complexes for 1 (spectrum on the top); 2; 3; 4; 5; and 6 M HNO_3 (spectrum on the bottom) and 0.4 M initial concentration of AHA. Spectrum on very bottom belongs to Pu(IV) in 1 M HNO_3 without presence of AHA.

Speciation of Pu in TBP

All experimental data obtained from:

1. distribution experiments of plutonium in TBP/HNO_3/AHA system;
2. absorption spectroscopy and
3. modeling of distribution of Pu species in the presence of AHA suggest that some portion of Pu-acetohydroxamate species present in aqueous solution can be extracted to TBP as solvated ternary plutonium-acetohydroxamate-nitrate complexes.

It was also confirmed visually after an extraction experiment with higher Pu concentration (Pu-242), when after addition of AHA to aqueous phase containing Pu(IV) in HNO_3, color of solution turned red-brown due to formation of Pu-acetohydroxamate complexes. The same color, but with smaller intensity was also observed in the organic phase after extraction.

To determine the Pu species present in the organic phase, Vis-NIR spectroscopy was employed. Figure 5 shows the absorption spectra of Pu(IV) in TBP after extraction from aqueous solution containing 2; 4 and 6 M HNO_3 with absence and presence of 0.4 M AHA. Because addition of acetohydroxamic acid decreases distribution ratio of plutonium, low absorbance of Pu in TBP could be expected for experiments with AHA. However, the spectra of Pu(IV) in the organic phase after extraction with AHA in 2 M (Fig. 5a) and 4 M (Fig. 5b) nitric acid have higher absorbance in the range of 400–600 nm than samples without AHA. This can be explained only by the extraction of Pu-AHA species with higher extinction coefficient. Although Pu-acetohydroxamate species can be formed even in aqueous phase of 6 M nitric acid (Fig. 4), their extraction is significantly reduced and spectra of Pu in TBP for system with and without acetohydroxamic acid differs just slightly (Fig. 5c).

Influence of concentration of AHA on extraction of Pu-acetohydroxamate species to TBP from 1 M HNO_3 was also investigated. For better illustration, spectra are divided into two graphs for concentration range of $5 \times 10^{-3} - 5 \times 10^{-2}$ M AHA (Fig. 6a) and $1 \times 10^{-1} - 8 \times 10^{-1}$ M AHA (Fig. 6b). As can be seen from the speciation diagram of Pu (Fig. 2) mono- and di-acetohydroxamate species of Pu are predominant in selected range of AHA and 1 M HNO_3. Analogous to previous experiments, we have observed an increase of Pu absorbance in TBP for the range of 400–480 nm and 500–600 nm with an increase of AHA concentration (Fig. 6a). Plutonium is extracted with TBP in the form of neutral solvate adducts; therefore, when the ternary complexes $Pu(AHA)_x(NO_3)_{4-x}$ are predominant they also can be solvated and transferred into organic phase. At the lowest concentration of AHA in aqueous phase the mono-acetohydroxamate complexes of Pu are more likely to be extracted. At higher AHA concentrations, Pu-di-acetohydroxamate species with higher extinction coefficient become predominant and their extraction increases absorbance of Pu in the organic phase, even though concentration of Pu in TBP decreases with AHA.

From the graph plotted for larger concentrations of AHA (Fig. 6b) it is clear that further increase of AHA concentration in the aqueous phase up to 0.8 M actually decreases the absorbance of Pu in organic phase; however, the shape of spectra is still characteristic for Pu-acetohydroxamate complex species. This behavior can be explained by following:

1. Pu-tri-acetohydroxamate species are probably not extracted or they are extracted just slightly;
2. decrease of Pu concentration in TBP phase has higher effect on absorbance of Pu than extraction of Pu-tri-acetohydroxamate species with higher extinction coefficient.

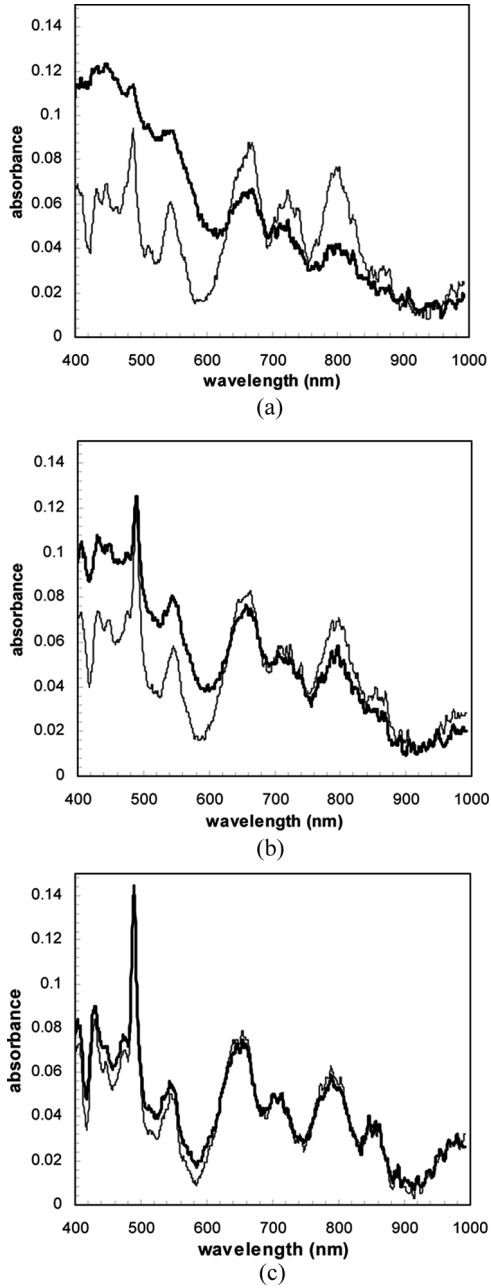

Figure 5. Absorption spectra of Pu(IV) in 30% TBP after extraction from aqueous phase containing: (a) 2 M HNO_3; (b) 4 M HNO_3; (c) 6 M HNO_3. A thicker line corresponds to system when 0.4 M AHA was present in initial aqueous solution.

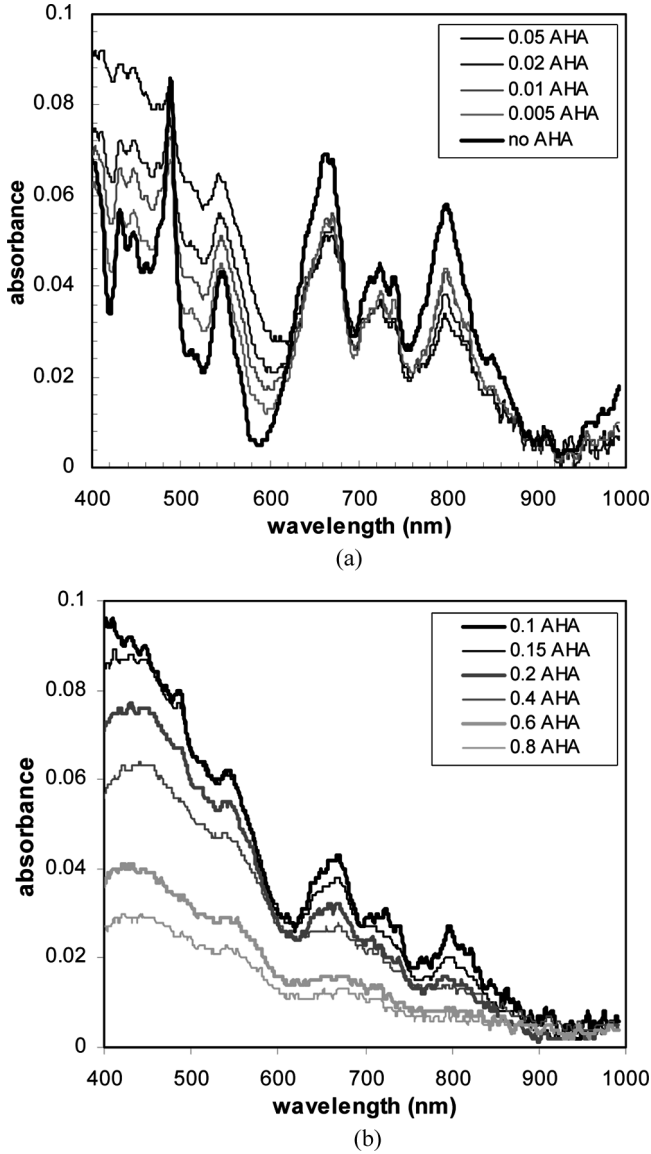

Figure 6. Absorption spectra of Pu(IV) in 30% TBP after extraction from aqueous phase containing 1 M HNO_3 and various concentration of AHA.

Concerning the fact that concentration of Pu-AHA_3 species in the aqueous solution is very low comparing to Pu-AHA_2 and Pu-AHA, their extraction and contribution to spectra of Pu in TBP is probably minimal,

and main species extracted at higher AHA concentration are most likely Pu-di-acetohydroxamate species. In addition, a slope analysis can be employed as a frequent method for analyzing the representative extraction species. Under the conditions of our experiment, the plot of log D vs. log [AHA] gives a straight line with slope of -0.5. This value does not correspond with the results concluded from spectroscopic experiments and suggests that the system is more complex; hence, the extraction of various species must be considered. Application of slope analysis for interpretation of Pu species extracted to TBP in the presence of AHA requires calculation of activity of all species in aqueous and organic solutions, including activities of free, uncomplexed Pu and TBP, and activities of water, nitrate, hydrogenium ion and AHA. Calculation of these components and modeling of extraction process are in the process.

CONCLUSION

Addition of acetohydroxamic acid to the aqueous solution containing Pu(IV) in nitric acid lead to formation of various Pu(IV)-acetohydroxamate complexes accompanied by a strong decrease of extraction yield of Pu(IV). Although AHA reduced extraction of Pu(IV) significantly, even at concentration of AHA > 0.1 M, still a significant amount of plutonium is extracted to TBP. Absorption spectra of Pu(IV) in aqueous phase containing HNO_3 and AHA were resolved using chemical equilibrium modeling software FITEQL 4.0. It was found that the formation of three Pu-acetohydroxamate species is possible in 1 M HNO_3 and studied range of AHA concentration. Pu(IV) species in organic phase extracted from HNO_3/AHA system were observed by Vis-NIR absorption spectroscopy and inferred as ternary complexes of $Pu(AHA)_x(NO_3)_{4-x}$ solvated with TBP.

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