Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Matteson, Brent S. , Tkac, Peter and Paulenova, Alena(2010) 'Complexation Chemistry of Zirconium(IV), Uranium(VI), and Iron(III) with Acetohydroxamic Acid', Separation Science and Technology, 45: 12, 1733 — 1742

To link to this Article: DOI: 10.1080/01496395.2010.493829

URL: http://dx.doi.org/10.1080/01496395.2010.493829

Separation Science and Technology, 45: 1733–1742, 2010
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.493829

Complexation Chemistry of Zirconium(IV), Uranium(VI), and Iron(III) with Acetohydroxamic Acid

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The complexation of zirconium(IV), uranium(VI), and iron(III) with acetohydroxamic acid (AHA) has been analyzed spectrophotometrically in various ionic strengths at 25°C. Arsenazo III (AAIII) was used as an indicator for unbound zirconium. The SQUAD computational program was employed to evaluate the stability constants. Conditional stability constants of four zirconium complexes $Zr(AAIII)^{3+}$, $Zr(AAIII)_2^{2+}$, $Zr(AHA)^{3+}$, and $Zr(AHA)_2^{2+}$ were determined in $1\,mol \cdot L^{-1}$ $HClO_4$ as $\log \beta' = 5.09$, 10.29, 12.78, and 23.13, respectively. Conditional stability constants of $UO_2(AHA)^+$, $Fe(AHA)^{2+}$, $Fe(AHA)_2^+$, and $Fe(AHA)_3$, in $0.1\,mol \cdot L^{-1}$ HNO_3 were calculated as $\log\beta'_1 = 8.32$, 11.00, 20.93, and 28.75, respectively.

Keywords arsenazo III; complexation; hydroxamic acid; iron; SQUAD; uranium; zirconium

INTRODUCTION

Used nuclear fuel (UNF) has been reprocessed for decades in countries such as France, Russia, Japan, and the United Kingdom in order to separate actinoids from fission products and other elements. The PUREX process is the most widely used method, which extracts uranium and plutonium using tri-n-butyl phosphate (TBP) diluted in kerosene from UNF dissolved in nitric acid. Recent attention has been given to advanced reprocessing schemes in order to increase proliferation resistance, create a sustainable energy source by recovering uranium resources from UNF, and minimize the amount of radioactive waste that would be required for long-term geologic storage. To meet these criteria, the UREX+ process has been developed by the Advanced Fuel Cycle Initiative (1). Acetohydroxamic acid (AHA) has been proposed for use in UREX to effectively separate neptunium and plutonium from uranium. Hydroxamic acids are salt-free compounds with the general formula RC(=O)NHOH (2) and are much weaker organic acids than carboxylic acids (RC(=O)OH), yet are structurally related. Dissociation constants for acetic acid and AHA at $I = 1\,mol \cdot L^{-1}$ and 25°C are $pK_a = 4.58$ and 9.07, respectively (3). AHA is a di-oxygen donor with a high affinity for hard cations. In acidic solutions, the deprotonated species (AHA^-) forms stable complexes as five-member chelate rings (4).

Zirconium is an important metal in the nuclear industry, as it is used for fuel cladding because of its low neutron cross section and its alloys are resistant to corrosion. Zirconium is also a fission product and produced in significant amounts in UNF (5). During UNF dissolution zirconium can co-precipitate with molybdenum and plutonium (6), but can also exist as both the extractable Zr^{4+} and $Zr(OH)^{3+}$ ions and inextractable $Zr_3(OH)_4^{8+}$ species during reprocessing. In addition, a synergistic effect occurs with technetium, as complexation occurs between Zr^{4+} and TcO_4^- ions and the co-extraction of the two metals is enhanced (7). Also, uncomplexed zirconium can be extracted as strongly as the actinoids (8). Therefore, controlling the flow of Zr in separation streams is crucial to achieve effective separation during advanced reprocessing of UNF.

Zirconium exists in a greater quantity in UNF than neptunium (5) and the reactivity of Zr with AHA must be considered in advanced reprocessing schemes if AHA were to be effectively used as a reductant/complexant for Np. Despite the importance of Zr and similarities with tetravalent actinoids, the complexation of Zr(IV) with AHA has not been studied to date. Therefore, we provide an initial study of the complexation of Zr^{4+} with AHA. In this paper we report the conditional stability constants of $Zr(AAIII)^{3+}$, $Zr(AAIII)_2^{2+}$, $Zr(AHA)^{3+}$, and $Zr(AHA)_2^{2+}$ calculated with SQUAD (Stability Quotients from Absorbance Data) (9) using experimentally determined spectrophotometric absorption data.

Uranium is the most abundant element in UNF and its recovery is of major interest for reprocessing. Previous

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Received 26 October 2009; accepted 8 April 2010.

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studies show that AHA forms complexes with uranyl (10,11) yet AHA has little effect on the extraction of uranium by TBP (12), whereas AHA can strip Pu back into the aqueous phase (13). Thus, the use of AHA for advanced reprocessing of UNF is very promising. However, only a limited number of $UO_2(AHA)^+$ studies that determined the stability constants of $UO_2(AHA)^+$ have been published (10,14,15). Therefore, we provide additional data of the complexation of uranyl with AHA using spectrophotometric analysis. Conditional stability constants of $UO_2(AHA)^+$ in 0.1 and $1.0\,mol \cdot L^{-1}$ NO_3^- and ClO_4^- in pH 1.0 and 25°C are determined by the SQUAD program.

With the aim to confirm the validity of our approach and for comparison with previously publish data, the complexation of AHA with iron(III) was also studied. Acetohydroxamic acid forms strong complexes with iron(III) which can be monitored by observing the intense color of the complex formation. Conditional stability constants of $Fe(AHA)^{2+}$, $Fe(AHA)_2^+$, and $Fe(AHA)_3$ in $0.1\,mol \cdot L^{-1}$ NO_3^- and pH 1.0 at 25°C are reported and compared with previously reported values (16,17).

EXPERIMENTAL

Materials

All reagents used were of analytical grade and used without further purification.

Thenoyltrifluroracetone (TTA, 99%, Acros Organics) was kept in darkness at 4°C and dissolved in xylene (Mallinckrodt, Inc.) immediately prior to any extraction experiments.

Arsenazo III, (AAIII, 2,7-Bis(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid, VWR Scientific Co.) was dissolved in water. A stock concentration of $6.0 \times 10^{-3}\,mol \cdot L^{-1}$ AAIII was determined by spectrophotometric titrations using a uranyl nitrate standard (Inorganic Ventures, Inc.).

Acetohydroxamic Acid (AHA, Toronto Research Chemicals) was kept at −18°C, dissolved in water when needed, and was the final component added in order to minimize hydrolytic degradation in acidic solutions.

Iron Nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Alfa Aesar) was dissolved in $0.5\,mol \cdot L^{-1}$ nitric acid.

Uranyl Nitrate ($UO_2(NO_3)_2$, Mallinckrodt, Inc.) was dissolved in either $1\,mol \cdot L^{-1}$ nitric acid or $1\,mol \cdot L^{-1}$ perchloric acid, depending on the nature of the subsequent experiments.

Zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$, Fisher Scientific Co.) was dissolved in $10\,mol \cdot L^{-1}$ perchloric acid.

Ionic strength (I) of solutions was adjusted using stock solutions of either nitric acid and lithium nitrate or perchloric acid and sodium perchlorate, prepared from HNO_3 (70%, Fisher Scientific Co.), $LiNO_3$ (Alfa Aesar), $HClO_4$ (70%, Mallinckrodt Baker, Inc.), and $NaClO_4 \cdot H_2O$ (EMD Chemicals, Inc.). The acid concentration was determined by a pH-metric titration with standardized sodium hydroxide (Mettler-Toledo DL58 Titrator). Distilled, deionized water (Barnstead, $18\,M\Omega \cdot cm$ resistivity) was used for all experiments.

Sample Preparation and Transfer of Solutions

Required volumes of stock solutions (except for AHA) were brought to 25°C in a temperature controlled water bath. Solutions were made in small plastic vials with pipettes calibrated to assure accurate transfer of preheated solutions. A small volume of AHA was added last, which did not affect the solution temperature. Each vial contained a total solution volume of 2 mL. Vials were placed in a temperature controlled mixer for 3 minutes at 1000 rpm. Vials for the iron and uranium experiments were taken immediately after mixing for spectroscopic analysis. Solutions of the Zr/AAIII/AHA experiments were returned to the water bath for 20 minutes to assure complete complexation.

UV-Vis Spectroscopy

All optical experiments were performed using an Ocean Optics QE65000 spectrometer and an Ocean Optics DH-2000-BAL light source. The prepared samples were transferred to 1-cm quartz cuvettes and placed in a temperature controlled cuvette holder.

Identification of Zr(IV) Species

To determine the species of zirconium in our experiments, TTA dissolved in xylene was used as an extractant of zirconium. $5.0 \times 10^{-5}\,mol \cdot L^{-1}$ Zr(IV) in $1\,mol \cdot L^{-1}$ $HClO_4$ was extracted by various concentrations of TTA at 25°C, and the concentration of zirconium not extracted by TTA was determined by monitoring the Zr(AAIII) complex using absorption spectroscopy. A slope of 3.7 was determined for the linear regression for the plot of the log(D) versus the log([TTA]), where D is the ratio of the concentration of zirconium in the TTA phase to the concentration of zirconium in the aqueous phase. The slope indicates that in the acidic solutions of our experiments zirconium exists primarily as the Zr^{4+} ion, and not as zirconyl ZrO^{2+} (18,19).

Computation of Stability Constants

Absorption spectra from a given set of experiments were introduced into a modified version of SQUAD (Stability Quotients from Absorbance Data), a program designed to calculate stability constants from absorbance data using a nonlinear least-squares approach (9). SQUAD simultaneously processes numerous spectra and refines several stability constants from a set of experiments of a metal-ligand solution. Absorption spectra data were converted to [8D10.4] Fortran format using a simple Java program. The absorption spectra were incorporated into the SQUAD input files as a refined parameter, which were then used to determine the stability constant of the metal complex upon convergence of the program. The values for pK_a of AHA at 25°C (3), $pK_a = 9.33$ at $I = 0.1\,mol.L^{-1}$; 9.07 at $I = 2.0\,mol.L^{-1}$; and 9.02 at $I = 2.0\,mol.L^{-1}$, were added to each appropriate input file. The baseline from each experiment was also included to each input file.

SQUAD calculates a number of statistical parameters, including the standard deviation of the absorbance data, s_{DATA}, and the standard deviation of each refined stability constant, s_{CONST}. SQUAD s_{DATA} values determined were all ≤ 0.01 and all s_{CONST} were considerably less than 1% of the calculated stability constant. These values are indicative of a good fit and suggest that the correct model had been found by SQUAD (9). The uncertainty of the calculated stability constants include error associated with the experiments themselves and were calculated using Eq. (1) (20).

$$s_{\log\beta} = \sqrt{s^2_{CONST} + \sum_i s^2_i} \tag{1}$$

where $s_{\log\beta}$ is the uncertainty of a given stability constant and s_i is an estimation of the error associated with the experiments (e.g., pH, ionic strength, reagent concentration, and AHA hydrolytic degradation). Calculated $s_{\log\beta}$ values are listed with their associated stability constants in Tables 1, 2, and 5.

RESULTS AND DISCUSSION

Fe(III) Acetohydroxamate Complexes

Iron(III) can form up to three mononuclear complexes with AHA^-, as described by Eq. (2). In order to obtain absorbance spectra useful for the determination of stability constants in SQUAD, distinct concentration ratio ranges of Fe(III) and AHA were determined from the Hyperquad Simulation and Speciation (HySS) program (21) and previous literature (16,17). Critically assessed equilibrium data indicated that the formation of $Fe(OH)^{2+}$ only becomes significant above pH 2.17 (17,22,23). Therefore, the hydrolysis of Fe(III) was not of consideration in HySS, as the pH of all solutions was 1 and the concentration of the ferric ion was low. The concentration ranges used are listed in Table 1 and their corresponding spectra are shown in Fig. 1. Peak maxima shift from 503 nm for the mono complex, 465 nm for the bis complex, and 425 nm for the tris complex. Spectral points for all concentration ratios in the wavelength range of 350–700 nm were inputted into the SQUAD program and stability constants for the mono, bis, and tris complexes (Eq. (3)) were determined simultaneously upon convergence of the program.

$$Fe^{3+} + nAHA^- \leftrightarrow Fe(AHA)_n^{3-n} \tag{2}$$

$$\beta'_n = \frac{[Fe(AHA)_n^{3-n}]}{[Fe^{3+}][AHA^-]^n} \tag{3}$$

Conditional stability constants of the $Fe(AHA)^{2+}$, $Fe(AHA)_2^+$, and $Fe(AHA)_3$ complexes were determined in $0.1\,mol \cdot L^{-1}$ HNO_3, $0.1\,mol \cdot L^{-1}$ NO_3^-, and 25°C as $\log\beta'_n = 11.00 \pm 0.03$, 20.93 ± 0.01, and 28.75 ± 0.01

TABLE 1

The conditional stability constants, and molar extinction coefficients for $Fe(AHA)_n^{3-n}$ experiments at $0.1\,mol \cdot L^{-1}$ HNO_3, $I = 0.1\,mol \cdot L^{-1}$ NO_3^-, and 25°C

[Fe(III)] ($mol \cdot L^{-1}$)	$[AHA]_{init}$ ($mol \cdot L^{-1}$)	Fe(III):AHA	Species of interest
1.00×10^{-2}	1.00×10^{-5}–1.00×10^{-3}	1000:1–50:1	$Fe(AHA)^{2+}$
5.00×10^{-4}	1.00×10^{-3}–1.75×10^{-2}	1:2–1:35	$Fe(AHA)^{2+}$ & $Fe(AHA)_2^+$
5.00×10^{-4}	8.00×10^{-2}–7.5×10^{-1}	1:160–1:1,500	$Fe(AHA)_2^+$ & $Fe(AHA)_3$
7.50×10^{5}	1.2×10^{0}	1:16,000	$Fe(AHA)_3$

Complex	$\log\beta'_n$ (this paper)	$\log\beta'_n$ (ref. (17))	ε $Fe(AHA)_n^{3-n}$ ($mol^{-1} \cdot L \cdot cm^{-1}$) (this paper)	ε $Fe(AHA)_n^{3-n}$ ($mol^{-1} \cdot L \cdot cm^{-1}$) (ref. (17))	ε $Fe(AHA)_n^{3-n}$ ($mol^{-1} \cdot L \cdot cm^{-1}$) (ref. (16))
$Fe(AHA)^{2+}$	11.00 ± 0.03	10.94	$1.073 \times 10^3 \pm 40$ at 503 nm	1.01×10^3 at 510 nm	1.13×10^3 at 501 nm
$Fe(AHA)_2^+$	20.93 ± 0.01	20.68	$1.960 \times 10^3 \pm 60$ at 465 nm	1.65×10^3 at 465 nm	1.98×10^3 at 465 nm
$Fe(AHA)_3$	28.75 ± 0.01	28.26	$2.005 \times 10^3 \pm 80$ at 425 nm	3.63×10^3 at 420 nm	2.41×10^3 at 426 nm

Note: Conditional stability constants for Andrieux el al. (17) at 25°C for $0 \leq pH \leq 1.00$ and $NO_3^- \approx 0.1\,mol \cdot L^{-1}$ were calculated from their published data for comparative purposes using 9.33 (3) as the pK_a for AHA at $I = 0.1\,mol \cdot L^{-1}$.

TABLE 2
The conditional stability constants, and molar extinction coefficients for $UO_2(AHA)^+$ experiments at 25°C

$[UO_2^{2+}]$ $(mol \cdot L^{-1})$	[AHA] $(mol \cdot L^{-1})$	U(VI):AHA
6.25×10^{-2}	2.00×10^{-2}–9.00×10^{-2}	0.32:1–1.44:1
5.00×10^{-3}–6.25×10^{-2}	5.00×10^{-2}	10:1–0.80:1

Acidity $(mol \cdot L^{-1})$	I $(mol \cdot L^{-1})$	$\log \beta'_1$	ε $UO_2(AHA)^+$ at 411 nm $(mol^{-1} \cdot L \cdot cm^{-1})$
0.1 HNO_4	0.1 NO_3^-	8.32 ± 0.02	58.0 ± 0.7
0.1 HNO_4	1.0 NO_3^-	8.05 ± 0.09	50.3 ± 1.1
0.1 $HClO_4$	0.1 ClO_4^-	8.19 ± 0.06	69.1 ± 0.7
0.1 $HClO_4$	1.0 ClO_4^-	8.07 ± 0.05	60.0 ± 1.0
HNO_3	0.1 NO_3^-	8.22 ± 0.03	Ref. (10)

Note: Koide et al. (10) determined $UO_2(AHA)^+$ stability constant using potentiometric titration at 25°C.

respectively. The values are listed in Table 1 and are comparable with Andrieux et al. (17) ($\log \beta_n = 10.94$, 20.68, and 28.26 at 25°C for $0 \leq pH \leq 1.00$ and $NO_3^- \approx 0.1\,mol \cdot L^{-1}$, calculated from their published data using 9.33 (3) as the pK_a for AHA at $I = 0.1\,mol \cdot L^{-1}$). Our values are also in agreement with other published data (3,24). Molar extinction coefficients were also determined by SQUAD and listed in Table 1. These values agree fairly well with previously published values (16).

U(VI)-Acetohydroxamate Complex

The uranyl cation begins to hydrolyzes in aqueous solutions above pH 2 (25), so the hydrolysis of uranyl was not of concern for this study, as the pH of all solutions was kept at 1. The concentration ranges of uranyl and AHA are listed in Table 2 and their corresponding spectra are shown in Fig. 2. Neither a bathochromic shift nor isosbestic points were observed, but a significant change in spectra occurred as the absorbance ratio of the three peak maxima at 400, 411, and 422 nm changed as the ratio of U(VI):AHA changed. A total of four sets of experiments were performed: $0.1\,mol \cdot L^{-1}$ HNO_3 in ionic strengths of 0.1 and $1.0\,mol \cdot L^{-1}$ NO_3^- and $0.1\,mol \cdot L^{-1}$ $HClO_4$ in ionic strengths of 0.1 and $1.0\,mol \cdot L^{-1}$ ClO_4^-. Spectral points for all concentration ratios for a given set of experiments in the wavelength range of 350–600 nm were inputted into SQUAD and the conditional stability constant (Eq. (5)) was determined upon convergence of the program. Uranyl nitrate stability constants (26) were also included in the

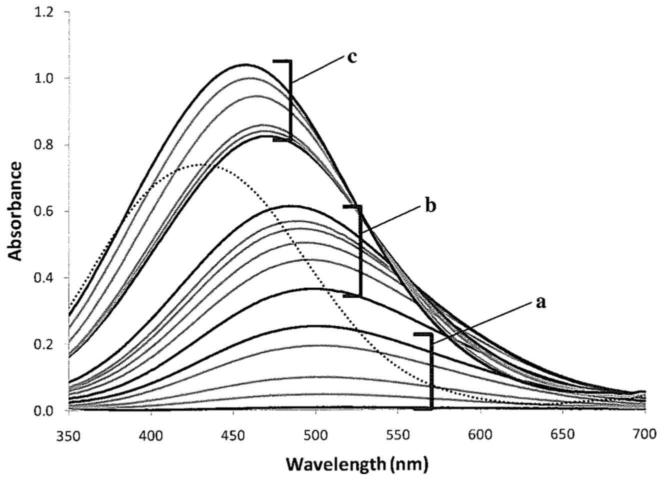

FIG. 1. Absorbance spectra of the $Fe(AHA)_n^{3-n}$ complexation system in $0.1\,mol \cdot L^{-1}$ HNO_3, $I = 0.1\,mol \cdot L^{-1}$ NO_3^-, and T = 25°C. Concentration ratio regions of Fe(III):AHA are a) 1000:1–50:1, b) 1:2–1:35, and c) 1:1,000–1:1,500. The dashed line is spectrum of a Fe(III):AHA ratio of 1:16,000.

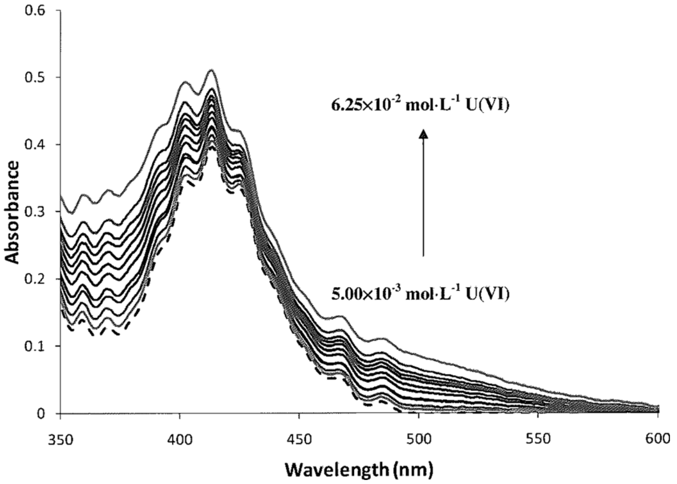

FIG. 2. Absorbance spectra of the $UO_2(AHA)^+$ complexation system in $0.1\,mol \cdot L^{-1}$ HNO_3, $I = 1.0\,mol \cdot L^{-1}$ NO_3^-, $6.25 \times 10^{-2}\,mol \cdot L^{-1}$ AHA, and T = 25°C. The dashed line is the spectrum of $5.00 \times 10^{-2}\,mol \cdot L^{-1}$ uranyl nitrate in the absence of AHA.

input files.

$$UO_2^{2+} + AHA^- \leftrightarrow UO_2(AHA)^+ \quad (4)$$

$$\beta_1' = \frac{[UO_2(AHA)^+]}{[UO_2^{2+}][AHA^-]} \quad (5)$$

Conditional stability constants of the $UO_2(AHA)^+$ complex and molar extinction coefficients of the 411 nm absorption peak for the four sets of experiments are provided in Table 2. Our results are in good agreement with Koide et al. (10) who calculated $\log\beta_1$ as 8.22 ± 0.03 in $I = 0.1\,mol \cdot L^{-1}$ at 25°C by potentiometric titrations. Koide et al. (10) also determined $\log\beta_2$ as 15.30 ± 0.07.

Zr(IV)-Acetohydroxamate Complexes

Little has been investigated of the complexation of hydroxamic acids with Zr(IV). The complexation of Zr(IV) with benzohydroxamic acid (BHA) was studied, with stability constants calculated as $\log\beta_1$ for $Zr(BHA)^{3+}$ as 12.43 and $\log\beta_2$ for $Zr(BHA)_2^{2+}$ as 24.08 (27). The limited published material of Zr(IV) with hydroxamic acids is in part due to the tendency of Zr(IV) to form hydrolyzed and polymerized species in aqueous solutions. This could lead to inconsistent results when determining stability constants of unhydrolyzed Zr(IV)-hydroxamate species. Therefore, the hydrolysis and polymerization of zirconium were considered throughout this study.

Hydrolysis of Acetohydroxamic Acid and its Complexes

Preliminary experiments showed that the ligand-exchange reaction of Zr(AAIII) with AHA is relatively slow and needed 20 minutes to achieve the complete exchange of the AAIII ligand for AHA (Fig. 3). The significant difference of absorbance of the Zr(AAIII) complex in 1 and $2\,mol \cdot L^{-1}$ ClO_4^- shown in Fig. 3 is due to the change in concentration of the ionic media itself (28,29). AHA undergoes hydrolytic degradation under acidic conditions, forming acetic acid and hydroxylamine (Eq. (6)) (30).

$$CH_3C(=O)NHOH + H_2O + H^+ \rightarrow CH_3COOH + NH_3OH^+ \quad (6)$$

We found no study of the hydrolytic degradation of AHA in such a low acid concentration as $1\,mol \cdot L^{-1}$ perchloric acid and varying ionic strengths published to date. For comparison, previous nitric acid studies (31,32) determined that the half life of AHA in $1\,mol \cdot L^{-1}$ decreases as the $[NO_3^-]$ increases. On the other hand, Carrott et al. (33) did not find any appreciable difference in the degradation of AHA in $1\,mol \cdot L^{-1}$ HNO_3 and $I = 1 - 6.99\,mol \cdot L^{-1}$ $NaNO_3$ during the experiment. Nonetheless, in this study the half life of the AHA hydrolytic degradation in $1\,mol \cdot L^{-1}$ $HClO_4$ with $I = 2\,mol \cdot L^{-1}$ ClO_4^- at 25°C was estimated as 415 minutes using Alyapyshev's $1.5\,mol \cdot L^{-1}$ $HNO_3/LiNO_3$ data (31). This corresponds to an AHA degradation of 3.3%. The half-life of AHA in $1\,mol \cdot L^{-1}$ $HClO_4$, without any additional ClO_4^-, was calculated as 513 minutes at 25°C using the $t_{1/2}$ data previously reported (31) for the hydrolytic degradation of AHA at perchloric acid concentrations of $\geq 1.5\,mol \cdot L^{-1}$ and extrapolating back to $1\,mol \cdot L^{-1}$ $HClO_4$. This corresponds to approximately 2.7% of AHA degradation after 20 minutes of contact time.

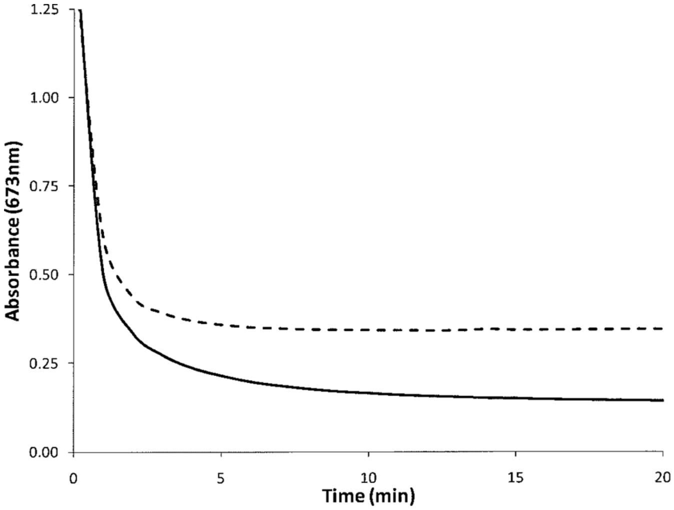

FIG. 3. Absorbance of the Zr/AAIII 673 nm peak as a function of time. Time zero is just prior to addition of AHA. $[Zr^{4+}]_{tot} = 5.0 \times 10^{-5}\,mol \cdot L^{-1}$, $[AAIII] = 1.25 \times 10^{-4}\,mol \cdot L^{-1}$, $[AHA] = 0.113\,mol \cdot L^{-1}$, $[HClO_4] = 1\,mol \cdot L^{-1}$ Solid line: $I = 1.0\,mol \cdot L^{-1}$ ClO_4^-. Dashed line: $I = 2.0\,mol \cdot L^{-1}$ ClO_4^-.

Initial AHA concentrations ($[AHA]_{init}$) were corrected for the 20 minutes of total contact time with the perchloric acid. The reaction was assumed to be first order with respect to both [AHA] and $[H^+]$ and is independent of the AHA concentration. Both the initially prepared $[AHA]_{init}$, which assumes no AHA degradation, and the corrected concentrations $[AHA]_{corr}$, were entered into separate SQUAD input files. SQUAD results indicate that no significant differences exist between the stability constants of $Zr(AHA)^{3+}$ and $Zr(AHA)_2^{2+}$ complexes for the $[AHA]_{init}$ and $[AHA]_{corr}$, as the stability constant obtained for $[AHA]_{corr}$ was within the uncertainty of the stability constant calculated for the $[AHA]_{init}$. The inconsequential differences between the two sets of stability constants could be due to the formation of the Zr(AHA) complex itself, as previous Np(IV)-AHA complexation studies by Andrieux et al. (34) confirmed the previous suggestion (31) that the formation of the chelation ring protects against the acid-catalyzed hydrolysis of AHA. However, further investigation of the complexation of Zr^{4+} with AHA is needed to confirm this postulation.

Hydrolysis of Zr^{4+} in Aqueous Solutions

Zr^{4+} can also form hydrolyzed monomeric and polymeric species in acidic solutions. Previous studies (25,35) postulated that trimeric ($Zr_3(OH)_4^{8+}$ or $Zr_3(OH)_5^{7+}$) and tetrameric ($Zr_4(OH)_8^{8+}$) species begin to form at approximately $5.0 \times 10^{-4}\,mol \cdot L^{-1}$ zirconium solutions in $1\,mol \cdot L^{-1}$ perchloric acid. More recently, Ekberg et al. (36) determined that the monomeric hydrolyzed species $Zr(OH)^{3+}$, $Zr(OH)_2^{2+}$, $Zr(OH)_3^{+}$, and $Zr(OH)_4$ and polymeric species $Zr_2(OH)_6^{2+}$, $Zr_3(OH)_4^{8+}$, and $Zr_4(OH)_8^{8+}$ exist in acidic solutions, and the solubility of Zr^{4+} in solution is highly dependent on acid strength and metal concentration.

The speciation distribution for $5.0 \times 10^{-5}\,mol \cdot L^{-1}$ Zr^{4+} in $1\,mol \cdot L^{-1}$ $HClO_4/NaClO_4$ at 25°C was created by inputting the Zr hydrolysis stability constants determined by Ekberg et al. (36) (Table 3) into the HySS program. At $pH = 0.0$ and $(Zr^{4+})_{total} = 5.0 \times 10^{-5}\,mol \cdot L^{-1}$, both the unhydrolyzed Zr^{4+} and $Zr(OH)^{3+}$ hydrolyzed species exist in solution (Fig. 4), whereas polymeric species dominate at $pH > 1$ and higher metal concentrations ($[Zr^{4+}]_{total} = 10^{-3}\,mol \cdot L^{-1}$). Similar results were also determined by Davydov et al. (37). To calculate the abundance of polymeric hydrolyzed species that form at higher ionic strengths, zirconium stability constants (36) were adjusted by the Specific Ion Interaction Theory (38). The corrected zirconium stability constants at $2\,mol \cdot L^{-1}$ ClO_4^- were inputted into the HySS program. It was determined that the relative abundance of hydrolyzed species increased with increasing ionic strength. However, at an ionic strength of $2\,mol \cdot L^{-1}$ ClO_4^-, pH 0.0, and at the highest $[Zr^{4+}]$ used in our experiments of $7.00 \times 10^{-5}\,mol \cdot L^{-1}$, the greatest abundance of any polymeric species, $Zr_3(OH)_4^{8+}$, was only 1.2×10^{-2}%. The other polymeric species formed in minute amounts under these solution conditions, as $Zr(OH)^{3+}$ was the only monomeric hydrolyzed species that formed with any significance. However, as shown in Figs. 4 and 5, the modeling program HySS confirmed that when a strong complexing ligand, such as AAIII or AHA, are added to the aqueous solution, all zirconium hydrolyzed species concentrations become insignificant because the hydroxyl groups on zirconium are replaced with covalently bound organic ligands.

TABLE 3
Hydrolysis constants of Zr^{4+} in $I = 1\,mol \cdot L^{-1}$ ClO_4^- at 25°C as reported by Ekberg et al. (36) using potentiometry and solvent extraction

Species	Log K_H (25°C)
$Zr(OH)^{3+}$	-0.87 ± 0.05
$Zr(OH)_2^{2+}$	-2.1 ± 0.2
$Zr(OH)_3^{+}$	-4.0 ± 0.3
$Zr(OH)_4$	-6.7 ± 0.3
$Zr_2(OH)_6^{2+}$	-2.42 ± 0.13
$Zr_3(OH)_4^{8+}$	4.1 ± 0.5
$Zr_4(OH)_8^{8+}$	5.2 ± 0.2

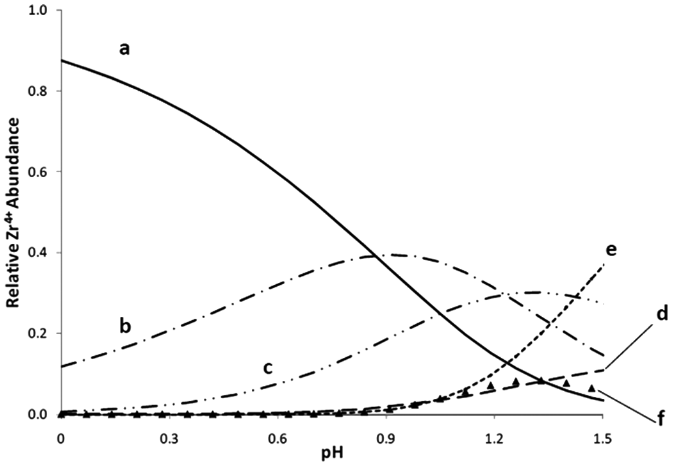

FIG. 4. The speciation distribution diagram of Zr^{4+} in pH 0–1.5 $HClO_4$ and 25°C. $[Zr^{4+}]_{total} = 5.0 \times 10^{-5}\,mol \cdot L^{-1}$. (a) Zr^{4+}, (b) $Zr(OH)^{3+}$, (c) $Zr(OH)_2^{2+}$, (d) $Zr(OH)_3^{+}$, (e) $Zr_2(OH)_6^{2+}$, and (f) $Zr_4(OH)_8^{8+}$. Other possible Zr^{4+}-species such as $Zr(OH)_4$ and $Zr_3(OH)_4^{8+}$ have relative molar fractions ≤0.015 under these conditions and are not shown for clarity.

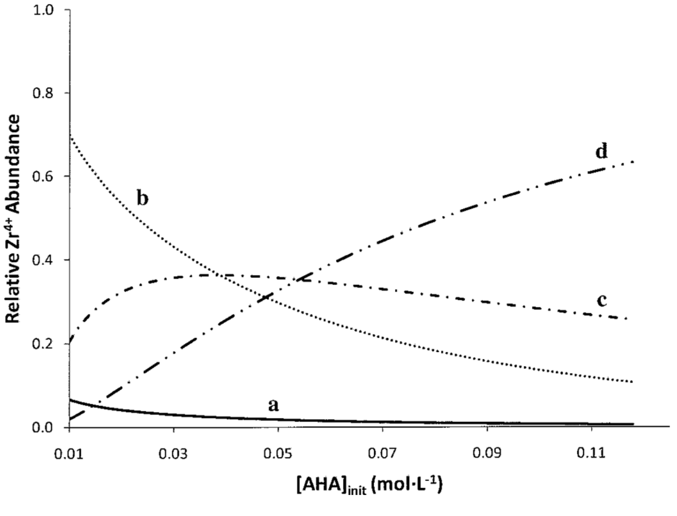

FIG. 5. The speciation distribution diagram of Zr^{4+} in aqueous solutions of AHA: $[Zr^{4+}]_{total} = 5.0 \times 10^{-5}\,mol \cdot L^{-1}$, $[AAIII]_i = 1.25 \times 10^{-4}\,mol \cdot L^{-1}$, and $[AHA]_{init} = 0.005–0.113\,mol \cdot L^{-1}$ in $1\,mol \cdot L^{-1}$ $HClO_4$, $1\,mol \cdot L^{-1}$ ClO_4^-, and 25°C. (a) $Zr(AAIII)^{3+}$: (b) $Zr(AAIII)_2^{2+}$: (c) $Zr(AHA)^{3+}$: (d) $Zr(AHA)_2^{2+}$. Zr_{free} abundance was ≤1% for the studied AHA concentration range.

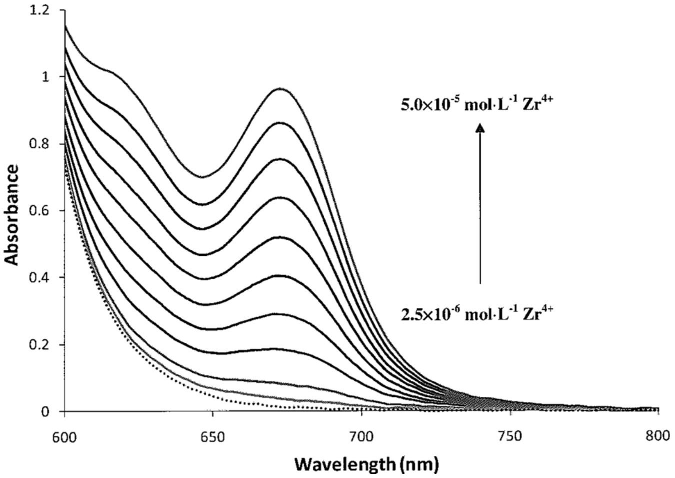

FIG. 6. Optical absorbance spectra of Zr^{4+}/AAIII in 1 mol · L^{-1} $HClO_4$, 1 mol · L^{-1} ClO_4^-, and 25°C. [AAIII] = 1.25×10^{-4} mol · L^{-1}. $[Zr^{4+}]_{total}$ = 2.5×10^{-6}–5.0×10^{-5} mol · L^{-1} except for dotted line, where $[Zr^{4+}]_{total}$ = 0.0 mol · L^{-1}.

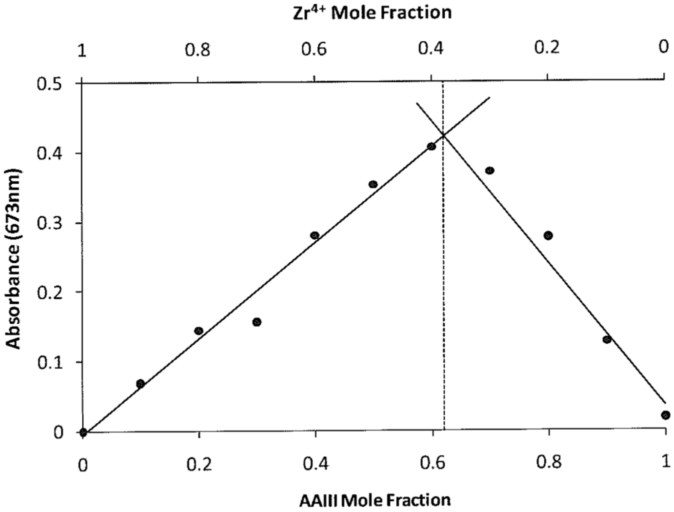

FIG. 7. Job's method experiment of Zr^{4+} and AAIII with a total concentration of 5.0×10^{-5} mol · L^{-1}. The AAIII mole fraction was determined as 0.62.

Complexation of Zr with Arsenazo III

AAIII is a brightly colored chelate anion used as an indicator to detect metals and their complexes that are spectroscopically silent. It is widely used for analytical spectroscopy of zirconium (28,39) actinoids (40,41), and rare earth elements (42). Zr^{4+} and its complexes with AHA lack an absorbance peak in the visible spectral range but zirconium will form complexes with AAIII (Eq. (7)) yielding an absorption peak that can be measured by monitoring changes in the 650–700 nm region with a maximum at 673 nm, (Fig. 6).

$$Zr^{4+} + mAAIII- \leftrightarrow Zr(AAIII)_m^{4-m} \quad (7)$$

The absorbance of free AAIII (520–540 nm) at the absorbance maxima of the Zr(AAIII) complex is negligible, as shown by the dotted line in Fig. 6. Previous studies (43) show that the composition of the complex depends on the ratio of AAIII and Zr^{4+} in solution, with a 1:1 Zr:AAIII ratio when Zr^{4+} is in excess and a 1:2 Zr:AAIII ratio when AAIII is in excess. In order to determine the Zr:AAIII ratio of our experiments, a Job's method experiment was performed with the sum of the $[Zr^{4+}]_{init}$ and [AAIII] concentrations equal to 5.0×10^{-5} mol · L^{-1} at 25°C and 1 mol · L^{-1} $HClO_4$. At this total concentration, a maximum absorbance at the 673 nm peak occurred at a ratio of 0.62 (Fig. 7). A ratio of 0.50 would indicate that a 1:1 complexation ratio of Zr:AAIII, whereas a 0.66 ratio would indicate a 1:2 Zr:AAIII complexation ratio. Therefore, with a ratio of 0.62 our data indicates that both 1:1 and 1:2 Zr:AAIII ratios are present, but with the 1:2 complex in a greater relative abundance. Experiments were performed where the $[Zr^{4+}]_{init}$ and [AAIII] varied, as listed in Table 4. Absorption spectral data for all experiments were inputted into SQUAD, along with the pK_as of AAIII (3), to simultaneously determine the molar extinction coefficients for the $Zr(AAIII)^{3+}$ and $Zr(AAIII)_2^{2+}$ complexes at 673 nm. Results are provided in Table 5. It is important to note that the molar extinction coefficients reported in this paper for 1 and 2 mol · L^{-1} perchloric acid are significantly smaller than the molar coefficients for Zr-AAIII complexes originally determined by Savvin for a 9 mol · L^{-1} solution of HCl (29). However, Muk and Radosavljevic (44) determined that the absorbance of the Zr(AAIII) complex in 1 mol · L^{-1} $HClO_4$ is approximately 6 times less than the absorbance in 6 mol · L^{-1} $HClO_4$ for Zr^{4+} and AAIII concentrations similar to our experiments. Therefore, we attribute the lower molar extinction coefficients to the lower acid concentration used in our experiments.

Complexation of Zr with AHA

Zr(AHA) complexes and their conditional stability constants are described by Eqs. (8) and (9).

$$Zr(AAIII)_m^{4-m} + nAHA^- \leftrightarrow Zr(AHA)_n^{4-n} + mAAIII^- \quad (8)$$

$$\beta'_n = \frac{[Zr(AHA)_n^{4-n}]}{[Zr(AAIII)_m^{4-m}][AHA^-]^n} \quad (9)$$

$Zr(AHA)_n^{4-n}$ complexes do not absorb light in the visible region. However, the addition of AHA to a Zr(AAIII) solution decreases the $Zr(AAIII)^{3+}$ complex by forming $Zr(AHA)_n^{4-n}$ species. AAIII is replaced by AHA^- because acetohydroxamic acid forms much stronger complexes with

TABLE 4
Reagent concentrations ranges for Zr^{4+}/AAIII/AHA experiments

$[Zr^{4+}]$ ($mol \cdot L^{-1}$)	[AAIII] ($mol \cdot L^{-1}$)	[AHA] ($mol \cdot L^{-1}$)
2.50×10^{-6}–5.00×10^{-5}	1.25×10^{-4}	0
5.00×10^{-5}	1.00×10^{-5}–1.25×10^{-4}	0
0	1.00×10^{-5}–1.25×10^{-4}	0
5.00×10^{-5}	1.25×10^{-4}	5.00×10^{-3}–1.13×10^{-1}
1.00×10^{-5}–7.00×10^{-5}	1.25×10^{-4}	4.00×10^{-2}

Zr^{4+} than AAIII, as indicated by the large difference in their conditional stability constants. The absorbance of the $Zr(AAIII)^{3+}$ complex in the 650–700 nm spectral range decreased with increasing [AHA], (Fig. 8). Thus, the complexation of AHA with Zr^{4+} can be observed by monitoring the changes of absorption of $Zr(AAIII)^{3+}$. Reagent concentrations ranges for the Zr^{4+}/AAIII/AHA experiments are provided in Table 4.

The conditional stability constants of $Zr(AAIII)_m^{4-m}$ and $Zr(AHA)_n^{4-n}$ for m and n = 1 and 2 were calculated using SQUAD under the assumption that no Zr polymerized species existed in solution, which was based on the HySS results described above. Speciation distribution diagrams indicate that only Zr^{4+}, $Zr(AAIII)^{3+}$, $Zr(AAIII)_2^{2+}$, $Zr(AHA)^{3+}$, and $Zr(AHA)_2^{2+}$ species were present, even when all hydrolyzed species were considered in HySS (Fig. 5). See Table 5 for calculated conditional stability constants for $Zr(AHA)^{3+}$, and $Zr(AHA)_2^{2+}$ in $1\,mol \cdot L^{-1}$ $HClO_4$, I = 1 and $2\,mol \cdot L^{-1}$ ClO_4^-, and 25°C. No Zr hydrolyzed species existed in any solution containing either AAIII or AHA this study, as the $[Zr^{4+}]$ was low (on the order of $10^{-5}\,mol \cdot L^{-1}$) and the acidity was high ($1\,mol \cdot L^{-1}$). This finding agrees with Zielen and Connick (35), who also found that in the perchloric acid range of 1 to $2\,mol \cdot L^{-1}$ the principal zirconium species at low zirconium concentrations is the unhydrolyzed monomer, Zr^{4+}. Also, under all solution conditions, the concentrations of AAIII and AHA^- were high compared to the negligible amount of hydroxide ions present in solution needed to form zirconium hydrolyzed species. Therefore, hydrolyzed zirconium species did not form and interfere with the Zr(AAIII) and Zr(AHA) compiexation because of the initial reagent concentrations chosen for all experiments.

Overall, it was confirmed that zirconium forms strong complexes with AHA, which have stability constants nearly as large as for tetravalent plutonium-AHA complexes ($\log \beta = 14.2 \pm 0.2$ and 24.1 ± 0.2 for $Pu(AHA)^{3+}$ and $Pu(AHA)_2^{2+}$, respectively (15). Both plutonium and zirconium-AHA complexes are much stronger than uranyl-AHA complexes, as evident by the significant differences in their stability constants. With the formation of particularly strong hydrophilic complexes of $Pu(AHA)_n^{4-n}$, acetohydroxamic acid significantly decreases the distribution of plutonium between the aqueous and TBP phases (32,45–47). The same is also true for zirconium, as AHA decreases the distribution of Zr^{4+} by TBP (48) by forming strong $Zr(AHA)_n^{4-n}$ complexes. On the contrary, uranyl-AHA complexes are much weaker than both the plutonium and zirconium-AHA complexes, since their stability constants differ by at least four orders of magnitude. The significant differences of the stability constants are in part due to their effective cationic charges. Tetravalent Pu has a charge of 4+, whereas UO_2^{2+} has an effective charge of +3.2, with uranium being partially shielded by the two oxygen atoms (49). This causes plutonium to be a stronger Lewis acid, allowing for the formation of stronger complexes with organic and inorganic ligands. Since the $UO_2(AHA)^+$ complex is much weaker, acetohydroxamic acid has little effect on the stripping of

TABLE 5
The conditional stability constants of $Zr(AAIII)^{3+}$, $Zr(AAIII)_2^{2+}$, $Zr(AHA)^{3+}$, and $Zr(AHA)_2^{2+}$ and molar extinction coefficients of Zr(AAIII) species in $1\,mol \cdot L^{-1}$ $HClO_4$, I = 1–2 $mol \cdot L^{-1}$ ClO_4^-, and 25°C

Species	$\log \beta'$ $1.0\,mol \cdot L^{-1}$ ClO_4^-	ε $Zr(AAIII)_m^{4-m}$ ($mol \cdot L^{-1} \cdot cm^{-1}$) at 673 nm	$\log \beta'$ $2.0\,mol \cdot L^{-1}$ ClO_4^-	ε $Zr(AAIII)_m^{4-m}$ ($mol^{-1} \cdot L \cdot cm^{-1}$) at 673 nm
$Zr(AHA)^{3+}$	5.09 ± 0.07	$2.96 \times 10^4 \pm 1.29 \times 10^3$	5.27 ± 0.08	$2.77 \times 10^4 \pm 9.26 \times 10^2$
$Zr(AAIII)_2^{2+}$	10.29 ± 0.09	$2.05 \times 10^4 \pm 3.17 \times 10^3$	10.34 ± 0.09	$2.08 \times 10^4 \pm 2.94 \times 10^2$
$Zr(AAIII)^{3+}$	12.77 ± 0.02	–	12.82 ± 0.09	–
$Zr(AHA)_2^{2+}$	23.13 ± 0.03	–	23.61 ± 0.06	–

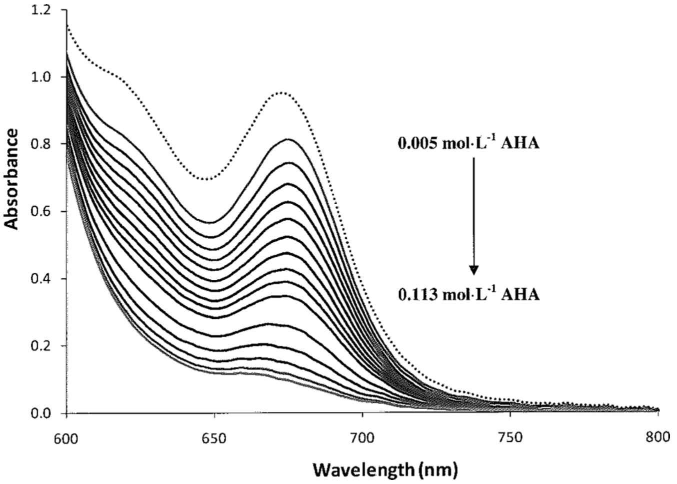

FIG. 8. Optical absorbance spectra of Zr^{4+}/AAIII/AHA system in $1\,mol\cdot L^{-1}$ $HClO_4$, $1\,mol\cdot L^{-1}$ ClO_4^-, and 25°C. $[Zr^{4+}]_{total} = 5.0 \times 10^{-5}$ $mol \cdot L^{-1}$ and $[AAIII] = 1.25 \times 10^{-4}\,mol \cdot L^{-1}$. $[AHA] = 0.005–0.113\,mol \cdot L^{-1}$ except for dashed line, where $[AHA] = 0.0\,mol \cdot L^{-1}$.

uranyl nitrate under UREX process conditions (11). Therefore, the utilization of AHA in the UREX process results in a greater retention of plutonium and zirconium in the aqueous phase and effective separation from uranium.

CONCLUSION

The conditional stability constants of the mono- and di-acetohydroxamate complexes of zirconium have been determined by spectrophotometric analysis in $1\,mol \cdot L^{-1}$ $HClO_4$ aqueous solutions at various ionic strengths and 25°C. Zr^{4+} and AAIII form 1:1 and 1:2 complexes and neither monomeric nor polymeric hydrolyzed Zr^{4+} species formed under experimental conditions. Conditional stability constants for $UO_2(AHA)^+$, $Fe(AHA)^{2+}$, $Fe(AHA)_2^+$, $Fe(AHA)_3$, $Zr(AAIII)^{3+}$, $Zr(AAIII)_2^{2+}$, $Zr(AHA)^{3+}$, and $Zr(AHA)_2^{2+}$ were determined at 25°C. It has been shown that zirconium-AHA complexes are much stronger than uranyl-AHA complexes, with their stability constants differing by six orders of magnitude. Therefore, AHA is a promising complexant to separate zirconium from uranium in the UREX process.

ACKNOWLEDGEMENTS

We express our gratitude to Lin Kong for his work of the uranium spectroscopy experiments. We thank Peter Sprunger for creating a Java program to align the SQUAD input files. This research was performed under the financial support of the Office of Civilian Radioactive Waste Management Graduate Fellowship Program administered by Oak Ridge Institute for Science and Education and USDOE NERI Program, Award 054657.

REFERENCES

1. Kelly, J.; Savage, C. (2005) Advanced Fuel Cycle Initiative Program Plan, in afci.sandia.gov/downloads/2005_AFCI_Program_Plan.pdf.
2. Chatterjee, B. (1978) Donor properties of hydroxamic Acids. *Coord. Chem. Rev.*, 26: 281.
3. Martell, A.E.; Smith, R.M. (1995) NIST Critically Selected Stability Constants of Metal Complexes, in NIST Standard Reference Database 46 Version 2.0.
4. Bass, V.C.; Voe, J.H. (1966) Hydroxamic acids as colorimetric reagents. *Talanta*, 13 (5): 735.
5. Bakel, A.; Gelis, A.V. (2008) Dissolution and Analysis of Nuclear Fuels and Targets, in www.cmt.anl.gov/oldweb/Science_and_Technology/Poster_Tour/Posters/Process_Chemistry_and_Engineering/Dissolution_and_Analysis-Bakel.pdf.
6. Pokhitonov, Y.; Aleksandruk, V.; Bibichev, B.; Novikov, G.; Riazantsev, V.; Saprykin, V. (2002) Composition of insoluble residues generated during spent fuel dissolution. *Waste Management*. Tucson, AZ.
7. Garraway, J.; Wilson, P.D. (1985) Coextraction of pertechnetate and zirconium by tri-n-butyl phosphate. *J. Less Common Metals*, 106: 183.
8. Brewer, K.N.; Herbst, R.S.; Todd, T.A.; Christian, J.D. (1998) Zirconium extraction into octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide and tributyl phosphate. *Solvent Extr. Ion Exch.*, 16 (4): 1047.
9. Leggett, D.J. (1985) *Commutational Methods for the Determination of Formation Constants*; Plenum Press: New York.
10. Koide, Y.; Uchino, M.; Shosenji, H.; Yamada, K. (1989) Studies of collectors. X. Complexing ability of amino hydroxamic acid ligands with dioxouranium(VI) in aqueous solution. *Bull. Chem. Soc. Japan*, 62 (11): 3714.
11. Tkac, P.; Matteson, B.; Bruso, J.; Paulenova, A. (2008) Complexation of uranium(VI) with acetohydroxamic acid. *J. Radioanal. Nucl. Chem.*, 277 (1): 31.
12. Taylor, R.J.; May, I.; Wallwork, A.L.; Denniss, I.S.; Hill, N.J.; Galkin, B.Ya.; Zilberman, B.Ya.; Federov, Yu.S. (1998) The applications of formo- and aceto-hydroxamic acid in nuclear fuel reprocessing. *J. Alloys Compd.*, 271–273: 534.
13. Govindan, P.; Sukumar, S.; Subba Rao, R.V. (2008) Partitioning of uranium and plutonium by acetohydroxamic acid. *Desalination*, 232 (1–3): 166.
14. Sekhon, B.S.; Kaur, N. (1995) Complex formation equilibria of aceptohydroxamic acid with H^+ and UO_2^{2+} ion in aqueous organic mixtures. *J. Indian Chem Soc.*, 72: 545.
15. Carrott, M.J.; Fox, O.D.; Maher, C.J.; Mason, C.; Taylor, R.J. (2007) Solvent extraction behavior of plutonium(IV) ions in the presence of simple hydroxamic acids. *Solvent Extr. Ion Exch.*, 25: 723.
16. Birus, M.; Bradic, Z.; Kujundzic, N.; Pribanic, M.; Wilkins, P.; Wilkins, R. (1985) Stopped-flow and rapid-scan spectral examination of the iron(III)-acetohydroxamic acid system. *Inorg. Chem.*, 24: 3980.
17. Andrieux, F.P.L.; Boxall, C.; Taylor, R.J. (2008) Acetohydroxamatoiron(III) complexes: Thermodynamics of formation and temperature dependent speciation. *J. Solution Chem.*, 37: 1511.
18. Connick, R.E.; McVey, W.H. (1949) The aqueous chemistry of zirconium. *J. Am. Chem. Soc.*, 71: 3182.
19. Schultz, B.G.; Larsen, E.M. (1950) The fractional reparation of zirconium and halfnium by extraction with trifluoroacetylacetone. *J. Am. Chem. Soc.*, 72: 3610.
20. Ekberg, C.; Albinsson, Y.; Comarmond, M.J.; Brown, P.L. (2000) Studies on the complexation behavior of thorium(IV). 1. Hydrolysis equilibria. *J. Solution Chem.*, 29 (1): 63.
21. Gans, P.; Sabatini, A.; Vacca, A. (2006) Hyperquad2006: Equilibrium constants from Potentiometric and/or Absorbance Data, in http://www.hyperquad.co.uk/hq2000.htm.
22. Cornell, R.M.; Schwertmann, U. (1996) *The Iron Oxides*; Wiley-VCH: New York.

23. Bard, A.J.; Parsons, R.; Jordan, J. (1985) *Standard Potentials in Aqueous Solution*; Marcel Dekker, Inc.: New York.
24. Renshaw, J.C.; Robson, G.D.; Trinci, A.P.J.; Wiebe, M.G.; Livens, F.R.; Collison, D.; Taylor, R.J. (2002) Fungal siderophores: Structures, functions and applications. *Mycol. Res.*, 106 (10): 1123.
25. Baes, C.F.; Mesmer, R.E. (1986) *The Hydrolysis of Cations*, 2nd Ed.; Kreiger: New York.
26. Fuger, J.; Konings, R.J.M.; Lemire, R.J.; Muller, A.B.; Nguyen-Trung Cregu, C.; Wanner, H. (2004) *Chemical Thermodynamics of Uranium*; Nuclear Energy Agency, OECD: Paris, France.
27. Baroncelli, F.; Grossi, G. (1965) The complexing power of hydroxamic acids and its effect on the behaviour of organic extractants in the reprocessing of irradiated fuels. *J. Inorg. Nucl. Chem.*, 27 (5): 1085.
28. Buděšinský, B. (1964) Spektralphotometrische studie der reaktion von zirkonium(IV) mit arsenazo III: Über die unterscheidung der mehrkernigkeit der complexe 1:1 Z. *Anal. Chem.*, 206 (6): 401.
29. Savvin, S.B. (1961) Analytical use of arsenazo III: Determination of thorium, zirconium, uranium and rare earth elements. *Talanta*, 8: 673.
30. Ghosh, K.K. (1997) Kinetic and mechanistic aspects of acid-catalysed hydrolysis of hydroxamic acids. *Indian J. Chem. Sect. B.*, 36: 1089.
31. Alyapyshev, M.; Paulenova, A.; Cleveland, M.A.; Bruso, J.E.; Tkac, P. (2007) Hydrolysis of Acetohydroxamic Acid under UREX + Conditions, in Global 2007. Boise, Idaho, 1861.
32. Karraker, D.G.; Rudisill, T.S.; Thompson, M.C. (2001) Studies of the Effect of Acetohydroxamic Acid on Distribution of Plutonium and Neptunium by 30 Vol% Tributyl Phosphate. WSRC-TR-2001-00509.
33. Carrott, M.J.; Fox, O.D.; LeGurun, G.; Jones, C.J.; Mason, C.; Taylor, R.J.; Andrieux, F.P.L.; Boxall, C. (2008) Oxidation-reduction reactions of simple hydroxamic acids and plutonium(IV) tons in nitric acid. *Radiochim. Acta*, 96: 333.
34. Andrieux, F.P.L.; Boxall, C.; May, I.; Taylor, R.J. (2008) The hydrolysis of hydroxamic acid complexants in the presence of non-oxidizing metal ions 2: Neptunium(IV) ions. *J. Solution Chem.*, 37: 215.
35. Zielen, A.J.; Connick, R.E. (1956) The hydrolytic polymerization of zirconium in perchloric acid solutions. *J. Am. Chem. Soc.*, 78 (22): 5785.
36. Ekberg, C.; Kallvenius, G.; Albinsson, Y.; Brown, P.L. (2004) Studies of the hydrolytic behavior of zirconium(IV). *J. Solution Chem.*, 33 (1): 47.
37. Davydov, Y.P.; Davydov, D.Y.; Zemskova, L.M. (2006) Speciation of Zr(IV) radionuclides in solutions. *Radiochemistry*, 48 (4): 358.
38. Pettit, D. (2002) *Ionic Strength Corrections Using Specific Interaction Theory, Version 1.2*; Academic Software: Otley Yorks, UK.
39. Mel'chakova, N.V.; Stanislavskaya, M.N.; Peshkova, V.M. (1964) Spectrophotometric titration of zirconium with a solution of arsenazo III. *J. Anal. Chem.*, 19: 650. Translation of Zh. Anal. Khim., 19(6): 701.
40. Kus, S.; Obarski, N.; Marczenko, Z. (1992) Determination of thorium, uranium and zirconium with arsenazo III using third-order derivative spectrophotometry. *Anal. Sci.*, 8 (2): 213.
41. Grigor'eva, M.G.; Nikitina, S.A.; Pevtsova, E.V.; Pen'kin, M.V.; Stepanov, A.V. (2003) Precision spectrometric determination of Th and Pu in solutions with arsenazo III using internal standardization. *Radiochemistry*, 45 (4): 388.
42. Surin, I.G.; Spitsyn, P.K.; Barkovskii, V.F. (1979) Study of reactions between rare earth elements and arsenazo III over a pH range of 0.5–4.0. *Zh. Anal. Khim.*, 34 (6): 1103.
43. Muk, A.A.; Savvin, S.B. (1971) Complex rormation of zirconium and thorium ions with arsenazo III in perchloric acid solutions. *Zh. Anal. Khim.*, 26 (1): 98.
44. Muk, A.A.; Radosavljevic, R. Formation of metal complexes with the arsenazo I and arsenazo III reagents as functions of the medium acidity. *Croat. Chem. Acta.*, 39: 1.
45. Tkac, P., Paulenova, A. (2008) The effect of acetohydroxamic acid on extraction and speciation of plutonium. *Sep. Sci. Technol.*, 43 (9): 2670.
46. Tkac, P.; Paulenova, A., Vandegrift, G.F.; Krebs, J.F. (2009) Distribution and identification of plutonium(IV) species in tri-n-butyl phosphate/HNO_3 extraction system containing acetohydroxamic acid. *J. Radioanal. Nucl. Chem.*, 280 (2): 339.
47. Tkac, P.; Paulenova, A.; Vandegrift, G.F.; Krebs, J.F. (2010) Modeling of Pu(IV) extraction by tri-n-butyl phosphate from acidic nitrate media containing acetohydroxamic acid. *J. Chem. Eng. Data*, (accepted) ACS ASAP: DOI: 10.1021/je100162y.
48. Tkac, P.; Matteson, B.; Bruso, J.; Lobach, S.; Paulenova, A. (2006) Extraction of Tetravalent Metals by TBP: Effect of Nitrate and Acetohydroxamic Acid. MARC VII Conference Proceedings, Hawaii.
49. Choppin, G.; Rydberg, J.; Liljenzin, J.O. (1995) *Radiochemistry and Nuclear Chemistry*, 2nd Ed.; Butterworth-Heinemann, Ltd.: Oxford.