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EDTA and Mixed-Ligand Complexes of Tetravalent and Trivalent Plutonium

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EDTA forms stable complexes with plutonium that are integral to nuclear material processing, radionuclide decontamination, and the potentially enhanced transport of environmental contamination. To characterize the aqueous $Pu^{4+/3+}$EDTA species formed under the wide range of conditions of these processes, potentiometry, spectrophotometry, and cyclic voltammetry were used to measure solution equilibria. The results reveal new EDTA and mixed-ligand complexes and provide more accurate stability constants for previously identified species. In acidic solution (pH < 4) and at 1:1 ligand to metal ratio, PuY (where Y^{4-} is the tetra-anion of EDTA) is the predominant species, with an overall formation constant of $\log \beta_{110} = 26.44$. At higher pH, the hydrolysis species, $PuY(OH)^-$ and $PuY(OH)_2{}^{2-}$, form with the corresponding overall stability constants $\log \beta_{11-1} = 21.95$ and $\log \beta_{11-2} = 15.29$. The redox potential of the complex PuY at pH = 2.3 was determined to be $E_{1/2} = 342$ mV. The correlation between redox potential, pH, and the protonation state of PuY^- was derived to estimate the redox potential of the $Pu^{4+/3+}Y$ complex as a function of pH. Under conditions of neutral pH and excess EDTA relative to Pu^{4+}, $PuY_2{}^{4-}$ forms with an overall formation constant of $\log \beta_{120} = 35.39$. In the presence of ancillary ligands, mixed-ligand complexes form, as exemplified by the citrate and carbonate complexes $PuY(citrate)^{3-}$ ($\log \beta_{1101} = 33.45$) and $PuY(carbonate)^{2-}$ ($\log \beta_{1101} = 35.51$). Cyclic voltammetry shows irreversible electrochemical behavior for these coordinatively saturated Pu^{4+} complexes: The reduction wave is shifted approximately –400 mV from the reduction wave of the complex PuY, while the oxidation wave is invariant.

Introduction

The amino tetracarboxylate EDTA, which forms stable complexes with plutonium,[1−5] was widely used in nuclear material processing and is present in appreciable amounts in mixed radioactive/hazardous chemical waste containers. There are an estimated 83 metric tons of EDTA in U.S. Department of Energy underground radioactive and mixed radioactive/hazardous chemical waste storage tanks, mostly from massive weapons production during the cold war.[6] The main concern of codisposing EDTA with radionuclides, and particularly, highly charged cations such as $^{239}Pu(IV)$ and $^{60}Co(III)$ that could persist as EDTA complexes, is its ability to enhance the solubility and transport rates of radioactive contaminants. Recent studies report increased Pu oxyhydroxide solubility and decreased Pu adsorption to soils in the presence of EDTA.[7−9]

Given the utility of EDTA and its potential to affect radionuclide environmental migration, there is a need to identify the major aqueous plutonium complexes and determine their thermodynamic stability. Tetravalent plutonium−EDTA complexes are particularly important because EDTA (denoted Y^{4-}) stabilizes Pu^{4+} over all other oxidation states.[10,11] Previously reported complexes include monometallic species of the form $PuY^{1,2,4,5}$ and $PuY(OH)_n{}^{n-}$ ($n =$

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1−3),[8] as well as bimetallic species, Pu_2H_nY.[2] A large excess of EDTA was used in most previous investigations;[1,4,8] however, species containing more than one EDTA bound to the plutonium center have not been used to interpret the experimental data. The formation of such species, as well as mixed-ligand complexes, can be anticipated by knowing that plutonium ions may accommodate up to 12 ligand donor groups in their inner coordination sphere, with eight- and ten-fold coordination being the most common.[12−15] It is equally desirable to characterize PuY equilibria in the presence of environmentally common competing ligands, like citrate and carbonate, that may form mixed-ligand complexes.

The tendency of Pu^{4+} to undergo hydrolysis is exceptional ($\log K_{PuOH} = -1.41$)[16,17] and remains high even when the cation is coordinated by high-affinity, multidentate chelators. Hydrolysis products ($PuY(OH)_n^{n-}$) form at near-neutral pH and are therefore important for accurate predictive geochemical calculations. Additionally, neither $PuY(OH)_n^{n-}$ nor other complexes have been characterized in terms of their redox behavior or absorption spectral characteristics at near-neutral pH. For these reasons, careful examination of the species formed at varying Pu/EDTA ratios and over a wide pH range (pH = 0−10) is desired. In this paper, we report the formation, corresponding equilibrium constants, and redox properties of PuY, two related hydroxo species, $PuY(OH)_1^-$ and $PuY(OH)_2^{2-}$, the bis EDTA complex, PuY_2^{4-}, and mixed-ligand complexes PuY−carbonate^{2-} and PuY−citrate^{3-}.

Experimental Section

Reagents. All solutions were prepared using argon-saturated deionized water (resistivity ≥ 18 MΩ). Sodium hydroxide used for potentiometric titrations was standardized against potassium hydrogen phthalate and contained less than 1% of dissolved carbonate as determined by Gran's method.[18] Perchloric acid titrant was prepared from reagent-grade 70% perchloric acid and standardized against a base of known concentration. Pu^{4+} stock solutions were prepared by dissolving Pu metal (approximately 93% ^{239}Pu and 6% ^{240}Pu in hydrochloric acid) and purifying the resulting Pu^{4+} solution by anion-exchange chromatography (Lewatit MP-500-CW resin).[19] The concentrations and oxidation state purities of the resulting Pu^{4+} solutions were determined using absorbance spectrophotometry.[20] Reagent-grade EDTA (ethylenediaminetetraacetic acid disodium salt hydrate, 99+%) and citric acid monohydrate were purchased from Sigma and used as received. EDTA and citric acid stock solutions used in potentiometric titrations were prepared immediately prior to the titration by dissolving measured masses of EDTA and citric acid in a measured volume of water. Sodium chloride (NaCl) and sodium bicarbonate ($NaHCO_3$) were purchased from Fisher; sodium citrate dihydrate [$HOC(COONa)(CH_2COONa)_2 \cdot 2H_2O$] was purchased from J. T. Baker.

Spectroscopic Measurements. All measurements were made in aqueous solution at 25 °C and 1.0 M ionic strength ($HClO_4$/NaCl). Spectra of all solutions were recorded using a Varian Cary 6E UV−vis−NIR spectrophotometer, which has precision of ±0.0002 absorbance units in the wavelength region used in this study. A Pyrex cell designed to contain radionuclide solutions and having a 1.0 cm path length was used for all spectrophotometric measurements. The concentration of tetravalent Pu was fixed at $[Pu^{4+}] = 0.0019$ M, as determined spectrophotometrically using an absorption coefficient $\epsilon_{470} = 56$[20] for a stock solution subsample in 1.0 M $HClO_4$. The overall stability constant, $\log \beta_{110}$, was refined from absorbance data collected at the wavelengths 440, 450, 470, 490, 500, and 510 nm as a function of $[H^+]$ (1.0 and 0.90 M) and variable EDTA concentration (0.81, 1.22, 1.62, 2.03, 2.44, 4.47 mM) using the program LETAGOP-SPEFO.[21] The EDTA deprotonation constants from Martell and Smith[22] (Table 1) were used to calculate the overall stability constant ($\log \beta_{110}$). Plutonium hydrolysis constants for the formation of $Pu(OH)^{3+}$ ($\log K_1 = -1.41$)[16,23] and $Pu(OH)_2^{2+}$ ($\log K_2 = -3.72$)[17,23] were used in the experimental design and data analysis. The cumulative or overall stability constants $\beta_{m\,ln\,l'}$ are defined as $\beta_{m\,ln\,l'} = [M_mL_lH_nL'_{l'}]/[M]^m[L]^l[H]^n[L']^{l'}$.

Potentiometric Measurements. All potentiometric equilibrium measurements were conducted on stirred solutions in a water-jacketed vessel at 25.0 ± 0.1 °C under ultrapure argon atmosphere. Titrants were dispensed using a Brinkman Metrohm 665 Dosimat autoburet. Potentiometric measurements were made using an Orion Research EA940 pH meter and an Orion ROSS combination pH electrode filled with 3 M sodium nitrate. A pK_w of 13.78 (0.10 M ionic strength $NaNO_3$, 25 °C) was used in all calculations.[22] Combination pH electrodes were calibrated by an acid−base titration in the desired electrolyte before each titration, such that hydrogen ion concentration, instead of activity, is reported and used for analyses. The titrations were performed by incremental addition (0.10 mL) of standardized sodium hydroxide (NaOH, 0.0993 M) to the complex solution maintained under argon atmosphere and constant stirring. A total of 75−90 data points were collected and analyzed for each titration curve. The titration of the Pu−EDTA−carbonate complex was performed by incremental addition of HCl (0.0985 M) to the initially basic complex solution maintained under argon atmosphere and constant stirring. Experimental data were modeled numerically using the programs SUPERQUAD[24] and BETA.[25] The deprotonation constants for EDTA, citrate, and carbonate listed in Table 1 were used to analyze potentiometric data. All values obtained from numerical analysis of potentiometric

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Table 1. Thermodynamic Constants for EDTA and Mixed-Ligand Complexes of Pu^{4+}, PuY−L (L = Y,$^{4-}$ Hydroxide, Citrate, Carbonate) Determined from Potentiometric Measurements[a]

Equilibria	Constants[b]
Plutonium Hydrolysis	
$Pu^{4+} + nH_2O \leftrightarrow Pu(OH)_n^{4-n} + nH^+$	$\log K_1 = -1.41$[16] $\log K_2 = -3.72$[17]
EDTA; Y^{4-}	
$HY^{3-} \leftrightarrow Y^{4-} + H^+$	$pK_1 = 9.52$[22]
$H_2Y^{2-} \leftrightarrow HY^{3-} + H^+$	$pK_2 = 6.13$
$H_3Y^{2-} \leftrightarrow H_2Y^{2-} + H^+$	$pK_3 = 2.69$
$H_4Y \leftrightarrow H_3Y^- + H^+$	$pK_4 = 2.0$
$H_5Y^+ \leftrightarrow H_4Y + H^+$	$pK_5 = 1.5$
$H_6Y^{2+} \leftrightarrow H_5Y^+ + H^+$	$pK_6 = 0$
Citrate; L^{3-}	
$HL^{2-} \leftrightarrow L^{2-} + H^+$	$pK_1 = 5.73$[22]
$H_2L^- \leftrightarrow HL^- + H^+$	$pK_2 = 4.3$
$H_3L \leftrightarrow H_2L^- + H^+$	$pK_3 = 3.05$
Carbonate; L^{2-}	
$HL^- \leftrightarrow L^{2-} + H^+$	$pK_1 = 9.91$[22]
$H_2L^- \leftrightarrow HL^- + H^+$	$pK_2 = 6.13$
$Y^{4-} + Pu^{4+} \leftrightarrow PuY$	$\log \beta_{110} = 26.44 \pm 0.20$[c] ($I = 1.0$ ($NaClO_4$)) 25.6 ($I = 0.1$ (not specified)) 24.2 ($I = 0.1$ (KCl))
$Y^{4-} + Pu^{4+} + OH^- \leftrightarrow PuY(OH)^- + H^+$	$\log \beta_{11-1} = 21.95 \pm 0.1$ 21.98 ± 0.86[d]
$Y^{4-} + Pu^{4+} + 2OH^- \leftrightarrow PuY(OH)_2^{2-} + H^+$	$\log \beta_{11-2} = 15.29 \pm 0.1$
$2Y^{4-} + Pu^{4+} \leftrightarrow PuY_2^{4-}$	$\log \beta_{120} = 35.39 \pm 0.15$
$2Y^{4-} + Pu^{4+} + H^+ \leftrightarrow PuY_2H^{3-}$	$\log \beta_{121} = 42.75 \pm 0.13$
$2Y^{4-} + Pu^{4+} + 3H^+ \leftrightarrow PuY_2H_3^-$	$\log \beta_{123} = 47.39 \pm 1.0$
$Y^{4-} + Pu^{4+} + CO_3^{2-} \leftrightarrow PuY{-}CO_3^{2-}$	$\log \beta_{1101} = 35.51 \pm 0.15$
$Y^{4-} + Pu^{4+} + CO_3^{2-} + H^+ \leftrightarrow PuY{-}HCO_3^-$	$\log \beta_{1111} = 40.38 \pm 0.10$
$Y^{4-} + Pu^{4+} +$ citrate$^{3-} \leftrightarrow$ PuY-citrate^{3-}	$\log \beta_{1101} = 33.46 \pm 0.30$
$Y^{4-} + Pu^{4+} +$ citrate$^{3-} + H^+ \leftrightarrow$ PuY−Hcitrate^{2-}	$\log \beta_{1111} = 38.46 \pm 0.20$

[a] $T = 25$ °C and $I = 0.1$ M $NaNO_3$ unless noted otherwise. [b] Numbers following ± represent the standard deviations of numerical model refinement. [c] Constant determined by spectrophotometry. [d] Constant determined by CV.

data using the program SUPERQUAD had χ^2 values of less than 12.60, corresponding to a 95% confidence level. The stoichiometry of the species in the model developed to best fit the data was based on the number of protons titrated. No direct structural characterization data were used to confirm the reported formulation. Attempts to isolate single crystals of individual species that would be suitable for XRD analysis have not been successful.

Cyclic Voltammetry Measurements. Solution acidity measurements for cyclic voltammetry (CV) were made using a Fisher Scientific AR 15 pH meter equipped with an Orion ROSS semimicrocombination electrode filled with a 3 M potassium chloride solution. A PAR model 273 potentiostat−galvanostat connected to a computer for automated data acquisition was used for current versus potential measurements. Cyclic voltammetry measurements were made in deionized water using a conventional three-electrode cell: A Ag/AgCl reference electrode, BAS model MF-2052 filled with 3.0 M NaCl/saturated AgCl solution, was used as a reference electrode, platinum wire as an auxiliary electrode, and a PAR G0021 glassy carbon electrode (28 mm^2 surface area) as a working electrode. The working electrode was polished using 0.5 μm alumina for 2 min and rinsed with distilled water prior to each measurement. Millimolar PuY solutions were prepared by adding the appropriate amount of Pu^{4+} from an acidic 0.2 M Pu stock solution to an EDTA solution maintained at pH 2. The solution pH was adjusted to the desired value by addition of dilute NaOH or HCl accompanied by gentle stirring and an argon purge for 10 min prior to each measurement. All measurements were made at a scan rate of 60 mV/s. $E_{1/2}$ values reported here are defined as the numerical average of the cathodic and anodic peak potentials. All electrochemical potentials are expressed relative to the normal hydrogen electrode (NHE).

Results

General Definitions. For simplicity, the deprotonated $EDTA^{4-}$ anion and the plutonium complexes are noted as Y^{4-} and PuY, respectively. Mixed-ligand complexes formed by adding hydroxide ion, EDTA, citrate, or carbonate to the complex PuY are designated as PuY−L.

Pu^{4+}EDTA Formation. Tetravalent plutonium forms highly stable and soluble complexes with EDTA and other amino carboxylate ligands.[26−28] The stoichiometry of the complexes formed strongly depends on the solution pH and the EDTA/plutonium ratio. In highly acidic media, H^+ can compete with Pu^{4+} for EDTA binding, leading to the formation of $PuYH_n^{n+}$ complexes. Acid−base potentiometric titrations could not be used to determine the stability constants of PuY or any probable $PuYH_n^{n+}$ complexes, because they are formed below the accessible pH. Instead, spectrophotometric titrations, taking advantage of the well-defined optical spectrum of Pu^{4+} in solution,[20] were used to characterize the PuY complex.

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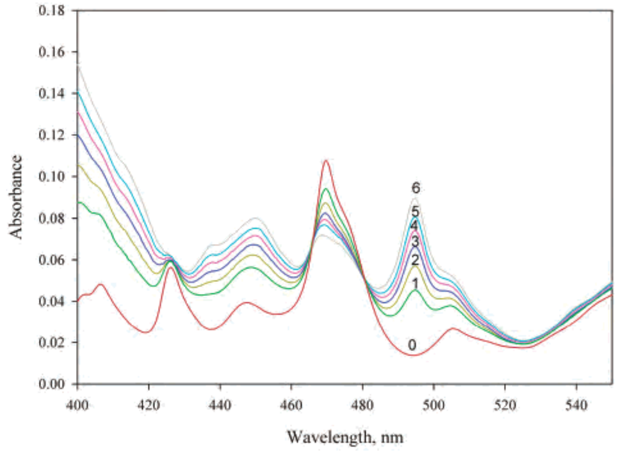

Figure 1. UV−vis absorption spectra of Pu^{4+} in 0.90 M $HClO_4$ as a function of EDTA concentration. Experimental conditions are as follows: $[Pu^{4+}] = 1.9$ mM for all spectra; EDTA concentration was increased as follows: (0) 0.0 mM, (1) 0.81 mM, (2) 1.22 mM, (3) 1.62 mM, (4) 2.03 mM, (5) 2.44 mM, (6) 4.47 mM. Ionic strength was adjusted to $I = 1.0$ M $HClO_4$/NaCl. $T = 25$ °C.

Pu^{4+} in acid (uncomplexed by EDTA) shows an absorbance maximum centered at 470 nm, consistent with previous studies (Figure 1, spectrum 0).[20] The solution color changes from rust-red to light orange upon addition of EDTA. The UV−vis absorbance spectra measured at proton concentrations of 1.0 and 0.90 M and variable Pu/EDTA ratios show a gradual decrease in the absorbance band at 470 nm, accompanied by a corresponding increase in the absorbance band of the PuY complex centered at 495 nm (Figure 1). Spectrophotometric data measured at different proton concentrations were numerically analyzed to determine the stoichiometry and the stability constant of the complex formed. Protonated $PuYH_n^{n+}$ species have been considered; however, the best fit to the data was obtained by using a single 1:1 Pu^{4+}/EDTA species (reaction 1).

$$Pu^{4+} + Y^{4-} \rightleftharpoons PuY \tag{1}$$

A plot of the absorbance at 470 nm versus the absorbance at 495 nm is linear with a slope of 0.48, consistent with the presence of two spectrally distinct species (data not shown). The stoichiometry of the complex and the solution conditions of formation agree with previously published data. The formation constant determined, $\log \beta_{110} = 26.44$, is greater than values previously reported, which range from $\log \beta_{110} = 24.2$[1,2] to $\log \beta_{110} = 25.6$.[4]

Pu^{4+}EDTA Hydrolysis. In acidic solutions (pH < 4) and equimolar Pu^{4+} and EDTA, PuY is the main species, and at higher pH, hydroxo species $PuY(OH)^-$ and $PuY(OH)_2^{2-}$ form. Potentiometric titration of 1:1 Pu^{4+}/EDTA shows three inflection points corresponding to stepwise hydrolysis. A white precipitate was observed above pH 7.5; thus, data above this pH do not correspond exclusively to solution equilibria. The first inflection point (Figure 2, curve 2) is attributed to the consumption of the protons displaced from EDTA in the complexation reaction, on the basis of the pH and previous spectrophotometric studies. At higher pH, there are two more inflection points, each occurring with a single additional equivalent of base per equivalent of plutonium. The second and third inflection points are consistent with the hydrolysis of the complex PuY, which is described by reactions 2 and 3.

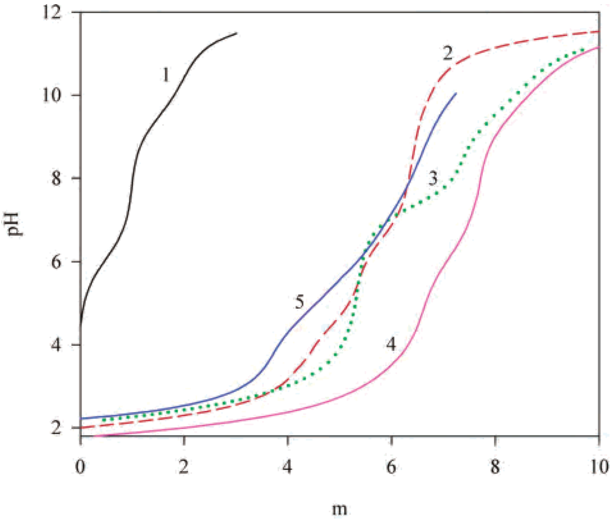

Figure 2. Potentiometric titrations of Pu−EDTA and Pu mixed-ligand solutions. All titrations were performed at $T = 25$ °C and 0.1 M (HNO_3/$NaNO_3$) ionic strength. m = moles of base added per mole of Pu^{4+}. Experimental conditions are as follows: (**1**) [EDTA] = 0.078 mM; (**2**) $[Pu^{4+}] = 0.0249$ mM, [EDTA] = 0.0253 mM; (**3**) $[Pu^{4+}] = 0.0249$ mM, [EDTA] = 0.050 mM; (**4**) $[Pu^{4+}] = 0.0249$ mM, [EDTA] = 0.025 mM, [citrate] = 0.0252 mM; (**5**) $[Pu^{4+}] = 0.0249$ mM, [EDTA] = 0.025 mM, [carbonate] = 0.0252 mM. The starting equivalents, $m = 0$, were determined by subtracting the number of equivalents of excess acid from the acidic Pu^{4+} stock solution from the total number of equivalents of base added.

$$PuY + H_2O \rightleftharpoons PuY(OH)^- + H^+ \tag{2}$$

$$PuY(OH)^- + H_2O \rightleftharpoons PuY(OH)_2^{2-} + H^+ \tag{3}$$

The hydrolyses of the metal chelate complexes are described by the equilibrium constants, K_{11-n}:

$$K_{11-n} = \frac{[PuY(OH)_n^{n-}]}{[PuY(OH)_{n-1}^{(n-1)-}][H^+]} \tag{4}$$

The potentiometric titration data were best fit using a model containing two successive hydrolysis reactions with $\log K_{11-1} = 4.49$ and $\log K_{11-2} = 6.66$, corresponding to the formation of the species, $PuY(OH)^-$ and $PuY(OH)_2^{2-}$, respectively. (Equilibrium constants expressed as overall stability constants are given in Table 1.) A third hydrolysis species, $PuY(OH)_3^{3-}$, has been previously reported[8] and is suggested by our data. The observed precipitation above pH 7.5 precludes quantitative analysis of the equilibrium.

Formation of Pu^{4+}EDTA−L (L = H_nY). The potentiometric curve obtained by titrating a solution of Pu^{4+} containing two equiv of EDTA with base (Figure 2, curve 3) shows a profile significantly different from that of curve 2, suggesting the formation of a new Pu^{4+}EDTA species. These data are consistent with optical spectrophotometric studies, which show that solutions containing 1:1 and 1:2 Pu^{4+}/EDTA have distinctly different spectra (Supporting Information Figure S1). The absorbance band observed for 1:1 Pu^{4+}/EDTA is centered at 495 nm and shifts to 504 nm when the Pu^{4+}/EDTA ratio is increased to 1:2. Unfortunately, the magnitude of the absorbance differences between the spectra for the two species is too small to accurately determine either the formation constant or the stoichiometry of the species formed.

Potentiometric titration data above pH 2 were modeled by the formation of a bis EDTA−Pu^{4+} complex and two deprotonated species $PuY_2H_3^-$ and PuY_2H^{3-} (reactions 5−7). These single and multiple proton steps correspond to the addition of one carboxylate group to the preformed PuY complex, followed by stepwise deprotonation of the remaining EDTA acetate groups. Reaction 6 can be considered the sum of two successive unresolvable deprotonations in a narrow pH range.

$$PuY + H_4Y \rightleftharpoons PuY_2H_3^{-} + H^+ \tag{5}$$

$$PuY_2H_3^{-} \rightleftharpoons PuY_2H^{3-} + 2H^+ \tag{6}$$

$$PuY_2H^{3-} \rightleftharpoons PuY_2^{4-} + H^+ \tag{7}$$

$$\beta_{12n} = \frac{[PuY_2H_n^{-4+n}][H^+]^{8-n}}{[Pu^{4+}][Y^{4-}]^2} \tag{8}$$

To determine the constants corresponding to these species, the formation constant of the PuY complex was fixed at log $\beta_{110} = 26.44$, the value determined using spectrophotometry. The overall stability constants for reactions 5−7 were calculated to be log $\beta_{123} = 47.39$, log $\beta_{121} = 42.75$, and log $\beta_{120} = 35.39$, respectively.

Formation of Pu^{4+}EDTA(L); L = Citrate, Carbonate. The ability of tetravalent Pu to accommodate as many as 12 ligand donor groups in the inner coordination sphere is illustrated by the formation of PuY_2^{4-}. In this light, chelating ligands containing O-donor groups, such as citrate or carbonate, are likely to displace coordinated solvent from the PuY complex to form PuY−$citrate^{3-}$ or PuY−$carbonate^{2-}$ mixed-ligand complexes. We monitored the formation of these two mixed-ligand complexes by potentiometry. The complexes are formed by the addition of a single equivalent of either citrate or carbonate to the PuY complex. The potentiometric titration curves measured for Pu^{4+}/EDTA/citrate (Figure 2, curve 4) and Pu^{4+}/EDTA/carbonate (Figure 2, curve 5) were analyzed to obtain constants for the formation of PuY−$(Hcitrate)^{2-}$, PuY−$(citrate)^{3-}$, PuY−$(HCO_3)^-$, and PuY−$(CO_3)^{2-}$ (reactions 9−12, Table 1)

$$PuY + H_3cit \rightleftharpoons PuY{-}Hcit^{2-} + 2H^+ \tag{9}$$

$$PuY{-}Hcit^{2-} \rightleftharpoons PuY{-}cit^{3-} + H^+ \tag{10}$$

$$PuY + H_2CO_3 \rightleftharpoons PuY{-}HCO_3^{-} + H^+ \tag{11}$$

$$PuY{-}HCO_3^{-} \rightleftharpoons PuY{-}CO_3^{2-} + H^+ \tag{12}$$

where cit represents the citrate anion.

Mixed-ligand complexes of this type have been previously reported for other tetravalent actinides but not for Pu^{4+}.[26−28]

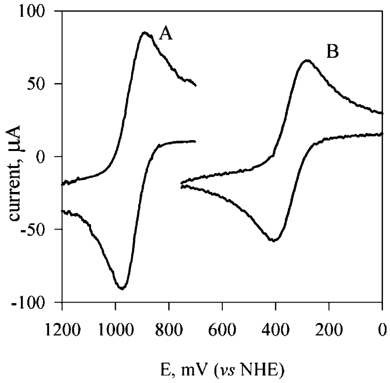

Figure 3. Cyclic voltammograms of Pu_{aq}^{4+} and Pu^{4+}EDTA complex. (A) $[Pu^{4+}] = 3.9$ mM, $[H^+] = 0.6$ M, $I = 0.6$ M ($HClO_4$/$NaClO_4$) and (B) equimolar Pu and EDTA, at pH 3.2, $[Pu^{4+}] = [EDTA] = 2.5$ mM, $I = 0.10$ M (HCl/NaCl) recorded on a glassy carbon electrode (28 mm^2 surface) at a scan rate of 60 mV/s.

Redox Chemistry of $Pu^{4+/3+}$EDTA and Hydrolysis Products $Pu^{4+/3+}$EDTA$(OH)^-$. Trivalent plutonium complexes are less stable than their tetravalent plutonium analogues, reflecting the comparatively lower affinity of EDTA for the ion. Cyclic voltammetry can be used to determine the relative stability of Pu^{3+} complexes, which are far less accessible by other techniques. Shifts in the anodic and cathodic peak potentials of $Pu^{4+/3+}$Y and the reversibility of the electrochemical process were studied as a function of pH and EDTA concentration. The cyclic voltammogram of equimolar Pu^{4+}/EDTA obtained at pH 2.3 (Figure 3) is quasireversible with a formal redox potential of $E_{1/2} = 342$ mV. On the basis of the potentiometric and spectrophotometric measurements described above, this electron-transfer process is attributed to the $Pu^{4+/3+}$Y redox couple.

At lower pH ($[H^+] = 0.60$ M), the voltammogram of Pu^{4+}/EDTA is irreversible, showing a reduction wave negatively shifted relative to the reduction wave of $Pu^{4+/3+}_{aq}$ (Figure 4A). Titration of Pu^{4+} in 0.60 M H^+ with EDTA shows a progressive decrease in the intensity of the reduction peak current of Pu^{4+} at 890 mV accompanied by an increase in the peak current at 507 mV. Because spectrophotometric data show that PuY is the only species formed under acidic conditions ($[H^+] = 1.0$ M), this wave must correspond to PuY reduction. The irreversible behavior suggests that the EDTA complex of trivalent Pu (PuY^-) is unstable at $[H^+] = 0.60$ M. Previous investigations that report the formation of two protonated PuY^- species, PuYH and $PuYH_2^+$, at $[H^+] > 0.1$ M, support this interpretation.[29]

The cyclic voltammograms of Pu^{4+}/EDTA recorded from pH 2.3 to 4.6 exhibit quasireversible behavior (Figure 4B). The anodic and cathodic peak separation increases, but the process remains quasireversible as the pH is increased. The progressive decrease in current intensity is attributed to hydrolysis, based on potentiometric titrations that show that $PuY(OH)^-$ forms in this pH range. The hydrolysis and reduction reactions of PuY that are responsible for the decrease in current intensity are described by reactions 13−15, where $[PuY]_T$ and $[PuY]_H$ are the total and the equilibrium PuY concentrations at a given pH, respectively, K_{11-1} is the acid dissociation constant of the complex PuY, and i_0

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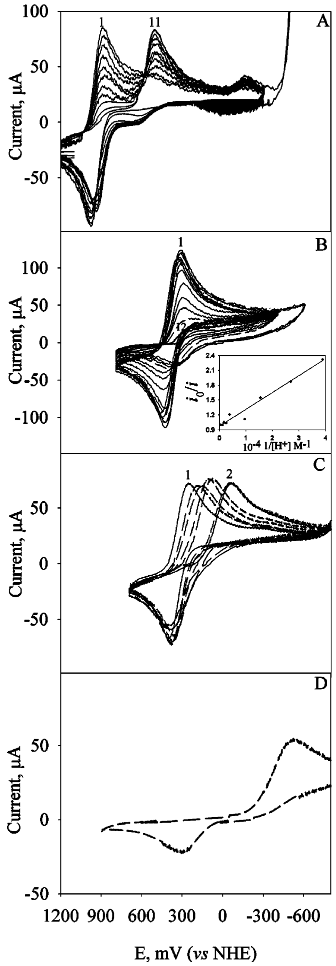

Figure 4. Cyclic voltammograms for $Pu^{4+/3+}$ complexes recorded on a glassy carbon electrode (28 mm^2 surface) at a scan rate of 60 mV/s. Experimental conditions are as follows: (**A**) Pu^{4+} as a function of EDTA concentration. $[Pu^{4+}] = 3.9$ mM; EDTA concentration was increased from 0.0 (CV 1) to 3.5 mM (CV 11) by 0.35 mM increment. $[H^+] = 0.6$ M, $I = 0.60$ M ($HClO_4/NaClO_4$). (**B**) 5.0 mM Pu^{4+}EDTA as a function of pH. The solution was prepared by mixing equimolar amounts of Pu^{4+} and EDTA at $I = 0.10$ M NaCl. Volammograms were measured at the following pHs (1−12): 2.63, 3.06, 3.26 3.43, 3.51, 3.98, 4.19, 4.43, 4.59, 4.97, 5.58, 6.42. Inset: Plot of the ratio of the initial current, i_0, and the current at a given pH, i_H, as a function of $1/[H^+]$. (**C**) Pu^{4+} in the presence of excess EDTA as a function of pH. $[Pu^{4+}] = 2.5$ mM, [EDTA] = 5.0 mM, $I = 0.1$ M NaCl, $T = 25$ °C; (1) pH 2.3, (2) pH 6.75. (**D**) $[Pu^{4+}]$ = [EDTA] = 2.50 mM, $[HCO_3] = 10.0$ mM, pH 8.2, $I = 0.10$ (HCl/NaCl).

and i_H are the initial current intensity and the current intensity at a given pH, respectively.

$$\mathrm{PuY} + \mathrm{H_2O} \rightleftharpoons \mathrm{PuY(OH)^-} + \mathrm{H^+} \qquad (13)$$

$$\mathrm{PuY} + 1e^- \rightleftharpoons \mathrm{PuY^-} \qquad (14)$$

$$\frac{[\mathrm{PuY}]_T}{[\mathrm{PuY}]_H} = 1 + K_{11-1}\frac{1}{[\mathrm{H^+}]} = \frac{i_0}{i_H} \qquad (15)$$

The plot of i_0/i_H versus $1/[H^+]$ is linear (inset in Figure 4B) and provides the value of $\log K_{11-1} = 4.46$ from the slope of this line. This hydrolysis constant agrees very well with the constant determined from potentiometric data, $\log K_{11-1} = 4.49$.

Redox Chemistry of $Pu(EDTA)_2^{4-}$. The cyclic voltammograms for PuY_2^{4-} as a function of pH (Figure 4C) show a progressive negative shift of the reduction wave and loss of reversibility with increasing pH. The negative shift of the reduction wave suggests an increase in the electron density at the Pu center resulting from an increase in the number of oxygen donor groups in the Pu coordination sphere as PuY_2^{4-} forms. The irreversible reduction is due to the dissociation or protonation of the Pu(III) complex, PuY_2^{5-}. The reoxidation peak recorded at 380 mV is at about the same potential as that of PuY^- reoxidation, suggesting that the Pu(III) complex PuY_2^{5-} undergoes fast dissociation leading to the formation of PuY^- (Eqs 16 and 17).

$$\begin{tikzcd}
\mathrm{PuY} & +\ \mathrm{H_nY^{(4-n)-}} \arrow[r, shift left] & \mathrm{PuY_2H_{n-n'}^{(4-n+n')-}} \arrow[l, shift left] \arrow[d, "1e^-"] & +\ \mathrm{n'H^+} & (16) \\
\mathrm{PuY^-} \arrow[u, "-e^-"] & +\ \mathrm{H_nY^{(4-n)-}} & \mathrm{PuY_2H_{n-n'}^{(5-n+n')-}} \arrow[l, "+n'H^+"'] & & (17)
\end{tikzcd}$$

The formal redox potential of PuY_2^{4-} could not be determined because of the irreversible behavior. Alternatively, the reduction potential can be estimated from the Nernst equation, Eq 18

$$E^{\mathrm{Pu^{4+/3+}Y_2}} = E°_{\mathrm{aq}} - 59.15 \log \frac{\beta_{\mathrm{Pu^{4+}Y_2}}}{\beta_{\mathrm{Pu^{3+}Y_2}}} - 59.15 \log(\alpha) \qquad (18)$$

$$\alpha = \frac{1 + K_1^{\mathrm{Pu^{4+}Y_2H}}[\mathrm{H^+}] + K_1^{\mathrm{Pu^{4+}Y_2H}} K_3^{\mathrm{Pu^{4+}Y_2H_3}}[\mathrm{H^+}]^3}{1 + K_1^{\mathrm{Pu^{3+}Y_2H}}[\mathrm{H^+}] + K_1^{\mathrm{Pu^{3+}Y_2H}} K_2^{\mathrm{Pu^{3+}Y_2H_2}}[\mathrm{H^+}]^2 + K_1^{\mathrm{Pu^{3+}Y_2H}} K_2^{\mathrm{Pu^{3+}Y_2H_2}} K_3^{\mathrm{Pu^{3+}Y_2H_3}}[\mathrm{H^+}]^3} \qquad (19)$$

where $E°_{aq} = 952$ is the redox potential of the $Pu^{4+/3+}$ couple in the absence of complexing agents,[30,31] and $K_n^{\mathrm{Pu^{4+/3+}H}_n}$ are the protonation constants of bis EDTA Pu^{4+} and Pu^{3+} complexes.[32,33]

At neutral pH, $\alpha = 1$ because both PuY_2^{4-} and PuY_2^{5-} are present in fully deprotonated forms. Using the values of $\log \beta_{\mathrm{Pu^{4+}Y_2}} = 35.39$ for the tetravalent *bis* Pu−EDTA complex and $\log \beta_{\mathrm{Pu^{3+}Y_2}} = 20.3$ for the Pu^{3+} complex reported in the literature,[3] the redox potential $E^{\mathrm{Pu^{4+/3+}Y_2}}$ is calculated to be 59 mV. The measured potentials indicate that EDTA generally stabilizes Pu^{4+} over Pu^{3+} and that the tetravalent complex is more stable than its trivalent analogue.

Redox Chemistry of Pu^{4+}EDTA−L. The formation of mixed-ligand complexes through the addition of an ancillary ligand to the complex PuY similarly increases the electron density around the plutonium center, as reflected by a negative shift of the redox potential. The cyclic voltammogram recorded at neutral pH for the mixed-ligand complex PuY−L (L = carbonate, Figure 4D) is similar to that obtained for the solution containing excess EDTA (Figure 4C). The reduction wave shifts to a more negative potential with loss of reversibility. The irreversibility of the redox

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Table 2. Equilibrium Constants for Trivalent and Tetravalent Actinide Complexes

Equilibrium constant quotient	M	Equilibrium constants log *K*	ref
$[MY]/[M^{4+}][Y^{4-}]$	Th^{4+}	23.2	35
	U^{4+}	25.8	36
	Np^{4+}	24.5	37
	Pu^{4+}	25.6	4
		24.2	1, 2
		26.44	this work
$[MY]/[MY(OH)^-][H^+]$	Th^{4+}	7.04	27
	U^{4+}	4.72	36
	Pu^{4+}	4.49	this work
		4.02	8
$[M_2Y_2(OH)_2{}^{2-}][H^+]^2/[MY]^2$	Th^{4+}	9.82	27
	U^{4+}	6.53	36
	Pu^{4+}	6.66	this work
		5.66	8
$[MYH^+]/[MY][H^+]$	Pu^{4+}	2.6	4
$[M^{III}Y]/[M^{III}][Y]$	Pu^{3+}	17.06	this work
		18.07	3
		17.66	
		17.57	
		16.90	
	Pr^{3+}	16.52	3, 35
	Nd^{3+}	16.77	3, 35
	Sm^{3+}	17.47	3, 35
$[M^{III}YH]/[M^{III}][Y][H^+]$	Pu^{3+}	18.65	3
$[M^{III}YH_2]/[M^{III}][Y][H^+]^2$		21.71	
$[M^{III}Y_2H_2]/[M^{III}][Y]^2[H^+]^2$	Pu^{3+}	25.46	3
$[M^{III}Y_2H_3]/[M^{III}][Y]^2[H^+]^3$	Pu^{3+}	27.07	3

process is attributed to the lower stability of the trivalent plutonium mixed-ligand complex. The larger shift in the reduction wave of PuY in the presence of excess carbonate relative to that observed for $Pu^{4+/3+}Y_2{}^{4-}$ suggests the addition of multiple carbonates to the Pu inner coordination sphere when the solution contains a large molar excess of carbonate. The stoichiometry of the complex formed is not known, but a *mono*-EDTA, *bis* carbonato species is likely on the basis of potentiometric data and structural considerations.

Discussion and Conclusions

Studies of Pu−EDTA complexation are challenging because of the extreme hydrolysis of Pu^{4+} and the inherent limits of available techniques, low solubilities of plutonium hydroxides, large number of potential species, precipitation of EDTA in strong acid solution, and uncertainties in experimental proton concentrations. To minimize these sources of systematic error and to accurately determine the formation constants for the 1:1 Pu/EDTA complex, we used experimental conditions that minimize hydrolysis and analytical uncertainties and avoid precipitation. On the basis of the hydrolysis constants $\log K_{PuOH} = -1.41$ and $\log K_{Pu(OH)_2} = -3.72$, in the absence of EDTA and, at most, 4% of the total Pu in solution would hydrolyze under these conditions. Because competing side reactions, hydrolysis, and *bis* EDTA−Pu^{4+} complex formation were avoided, the value of the formation constant for the 1:1 complex obtained in this work is larger than that of the previously published constants (Table 2).

The correlation between the redox potential of PuY, pH, and the protonation state of PuY^- can be used to verify the accuracy of the spectrophotometrically determined formation constant. The stability constant for the trivalent $Pu^{3+}Y$ complex is calculated using the Nernst equation (eq 20) and compared to the known literature values as follows:

$$\log \beta_{Pu^{3+}Y} = \log \beta_{Pu^{4+}Y} - \frac{E^0 - E^{Pu^{4+/3+}Y} + 59.15 \log(\alpha)}{59.15} \tag{20}$$

$$\alpha = \frac{1 + K_{Pu^{4+}YOH}[H^+]^- K_{Pu^{4+}YOH} K_{Pu^{4+}Y(OH)_2}[H^+]^{2-}}{(1 + K_1[H^+] + K_1K_2[H^+]^2)} \tag{21}$$

where $E° = 952$ mV is the formal potential of the $Pu^{4+/3+}$ couple,[30,31] K_1 and K_2 are the first and second protonations for the PuY^- complex, and $\log K_1 = 3.06$, $\log K_1K_2 = 5.65$,[33] and $\log K_{Pu^{4+}Y(OH)} = 4.49$ are the hydrolysis constants for the complex PuY. The redox potential measured at pH 2.3, $E_{1/2} = 342$ mV, and the value of $\log \beta_{110} = 26.44$ obtained in this work for the tetravalent Pu complex were used.

The $\log \beta_{Pu^{3+}Y} = 17.06$ value obtained from this calculation agrees well with the formation constants of EDTA complexes of Pu^{3+} and trivalent lanthanides, $\log \beta_{Pu^{3+}Y} = 16.90$, $\log \beta_{Pr^{3+}Y} = 16.52$, $\log \beta_{Nd^{3+}Y} = 16.77$, and $\log \beta_{Sm^{3+}Y} = 17.47$ previously reported.[3] Alternatively, if $\log \beta_{Pu^{4+}Y} = 25.6$[4] and $\log \beta_{Pu^{4+}Y} = 24.2$ values for the PuY complex formation are substituted into eq 20, then calculated values of $\log \beta_{Pu^{3+}Y}$ are 16.22 and 14.82, respectively, which are slightly lower than the measured values. By considering the entire $Pu^{4+/3+}$/EDTA/OH^- system and using a combination of potentiometry, spectrophotometry, and CV, we determined a higher but more accurate $\log \beta_{Pu^{4+}Y}$ value.

A plot of stability constants for EDTA complexation versus first hydrolysis for lanthanide(III) and actinide(III and IV) cations illustrates the strong correlation between these constants and the Lewis acidity of the metal ion (Supporting Information Figure S2). Among this series of metal ions, Pu^{4+} is the most acidic and has the highest $\log \beta_{110}$ value, in good agreement with reported Pu^{4+} hydrolysis constants and EDTA complexes of other f block elements. Tetravalent uranium has the most comparable hydrolysis behavior, ionic radius, and EDTA binding constant ($\log \beta_{110} = 25.8$[36]). These similarities suggest that the coordination geometry of Pu^{4+}-EDTA complexes would be similar to that shown in the crystal structure of $UYF_3{}^{3-}$,[34] where U is coordinated by three fluorides and four acetate oxygen atoms and two nitrogen atoms from EDTA.

The hydrolysis of the AnY (An = actinide) complexes follows the same trend as that established for the (free) fully aquated metal ions. Both PuY and UY undergo hydrolysis at a lower pH than ThY. We determined constants for $PuY(OH)^-$ and $PuY(OH)_2{}^{2-}$ hydroxo species using potentiometric titrations. The values reported previously[8] were determined from PuO_2 solubility experiments where EDTA is present in more than a 10-fold excess relative to Pu^{4+};

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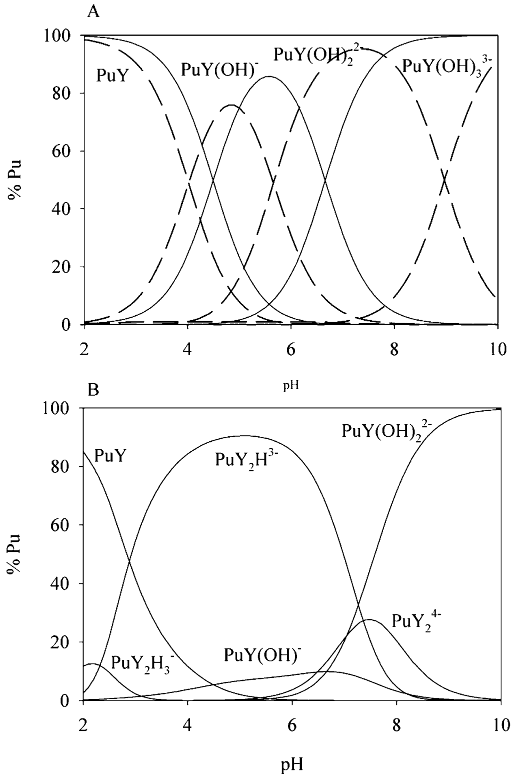

Figure 5. Pu^{4+}EDTA species distribution as a function of pH and metal-to-ligand ratios are generated using previously known stability constants (− − −) and those reported herein (−). (A, top) Distribution for equimolar EDTA and Pu^{4+}. (B, bottom) Distribution for 2 equivalents of EDTA per equivalent of Pu^{4+}.

however, $PuY_2H_n^{(4-n)-}$ complexes were not considered in the data interpretation. In effect, $PuY_2H_n^{(4-n)-}$ species form at approximately the same pH at which PuY undergoes hydrolysis, but hydrolysis is inhibited by excess EDTA. Previous Pu−EDTA spectroscopic studies assigned the shift of the absorption band from 495 to 505 nm over the pH range 1.44−4.6 to an equilibrium between PuY and $PuYH^+$. Our results show that the observed spectral changes occur only when excess EDTA is present, consistent with CV measurements of $PuY_2H_n^{(4-n)-}$ species.

The species distribution for *mono* EDTA−Pu^{4+} complexes is generated using the refined stability constants reported here, compared to the distribution based upon previously reported values, and shows that hydrolysis species $PuY(OH)_n^{n-}$ form at higher pH and that $PuY(OH)^-$ rather than $PuY(OH)_2^{2-}$ predominates at near-neutral pH (Figure 5A). The stability constant for the third hydrolysis product, $PuY(OH)_3^{3-}$, which is likely stable at pH > 8.5, could not be determined using potentiometry. When EDTA is present in excess of Pu^{4+}, the prevalent species at near-neutral pH are PuY_2H^{3-}, $PuY(OH)_2^{2-}$, and, to a lesser extent, PuY_2^{4-} (Figure 5B).

In the presence of ancillary ligands like citrate and carbonate, mixed-ligand complexes become important. For example, given equimolar concentrations of EDTA, Pu, and citrate, the solution speciation shows that, at near-neutral pH, PuY−$(Hcitrate)^{2-}$ and PuY−$(citrate)^{3-}$ represent more than 90% of the total plutonium present. Under conditions of equimolar EDTA and Pu and excess carbonate, $PuY(CO_3)^{2-}$ forms at near-neutral pH (Supporting Information Figure S3). These newly characterized species differ in molecular size, geometry, and charge from those previously considered and are expected to improve our understanding of Pu^{4+}EDTA (substrate) interactions (e.g., mineral or soil adsorption) and our forecasting of environmental contaminant transport. The complexity of Pu−EDTA aqueous speciation is a consequence of the exceptionally large coordination sphere and high charge of Pu^{4+}. Thus, similar mixed-ligand and coordinatively saturated complexes can generally be expected to form in other plutonium chelate systems.

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Supporting Information Available: Figure showing the UV−vis absorption spectra of PuY as a function of pH, plot of the stability constants for EDTA complexation versus first hydrolysis constants for lanthanide(III) and actinide(III and IV) cations, and the speciation diagram of Pu^{4+}EDTA mixed-ligand complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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