Complexation of Plutonium(IV) with *trans*-1,2-Diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic Acid (CDTA) in Acidic Solution

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Abbreviations and Symbols

ALSEP	Actinide Lanthanide Separation
CDTA	*trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid
EDTA	ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid
GANEX	Group Actinide Extraction
KHP	potassium hydrogen phthalate
PMBP	1-phenyl-3-methyl-4-benzoyl-2-pyrazolin-5-one
SIT	Specific ion Interaction Theory
TRU	transuranic
TTA	2-thenoyltrifluoroacetone
β_{mhx}	Stability constant of metal-ligand complex M:H:L
β_x^{app}	Apparent stability constant
β_{m-h0}	Hydrolysis constant
K_a	Stepwise acid dissociation constant
K_w	Autoprotolysis constant of water
K_{ex}	Extraction equilibrium constant
D_0	Distribution ratio in the absence of aqueous complexing ligand
D	Distribution ratio in the presence of aqueous complexing ligand
R	Gas constant (8.3145 $J \cdot mol^{-1} \cdot K^{-1}$)

T	Temperature (°C or K)
F	Faraday constant (96,485 C·mol^{-1})
$E°$	Standard electrode potential (V)
E	Measured electrode potential (V)
E_j	Electrode junction potential (V)
C_i	Analytical concentration (mol·L^{-1}) of species i
I, I_m	Ionic strength in molarity (mol·L^{-1}) and molality (mol·kg^{-1})
K_C, K_m	Equilibrium constant on the molar and molal scale
a_{H_2O}	Activity of water
γ_i	Activity coefficient of species i
ν_i	Stoichiometric coefficient of species i
z_i	Charge of species i
$\Delta\varepsilon$	Specific ion Interaction Theory (SIT) parameter (kg·mol^{-1})
ϑ	Conversion ratio between molarity (mol·L^{-1}) and molality (mol·kg^{-1})

Abstract

Understanding the interaction of Pu(IV) with complexing agents present in the nuclear fuel cycle is important for predicting the performance of used nuclear fuel separations. The complexation of Pu(IV) with *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid (CDTA) was studied in acidic solutions of 0.10-0.50 mol·L^{-1} $HClO_4$ with 1.00 mol·L^{-1} (Na,H)ClO_4 total ionic strength by a liquid-liquid extraction method using tracer quantities of ^{238}Pu. The acid dissociation constants of CDTA and the autoprotolysis constant of water were determined via potentiometric titrations in 0.10-2.00 mol·L^{-1} $NaClO_4$ and 25.0 ± 0.1 °C. The variation of the dissociation constants with ionic strength was modeled with the Specific ion Interaction Theory (SIT) and the associated SIT parameters were obtained. The thermodynamic dissociation constants at zero ionic strength for water and CDTA were determined from this analysis as pK_w° = 14.00 ± 0.03, pK_{a2}° = 1.52 ± 0.04, pK_{a3}° = 2.78 ± 0.05, pK_{a4}° = 4.17 ± 0.04, pK_{a5}° = 6.75 ± 0.02, and pK_{a6}° = 10.64 ± 0.04 at 25.0 ± 0.1 °C. The results of the liquid-liquid extraction experiments indicated the formation of a 1:0:1 complex, $PuCDTA^0$, and the presence of

additional protonated species, $Pu(HCDTA)^{+}$ and $Pu(H_2CDTA)^{2+}$, at these acidities. The corresponding stability constants in 1.00 $mol \cdot L^{-1}$ $(Na,H)ClO_4$ and 23 ± 1 °C were determined to be $\log_{10} \beta_{101} = 24.2 \pm 0.3$, $\log_{10} \beta_{111} = 25.4 \pm 0.2$, and $\log_{10} \beta_{121} = 25.8 \pm 0.1$.

1 Introduction

Nuclear waste management can be improved with used nuclear fuel reprocessing. Fissile U and Pu, which can represent about 97% of the mass of the used nuclear fuel, may be recovered and recycled back into the nuclear fuel cycle and used for further energy production. Additional separations allow for partitioning the remaining long-lived transuranic (TRU) elements from the relatively short-lived fission products, while TRU elements can be eliminated in fast neutron reactors by fission or transmutation to short half-life isotopes [1-5]. Such separations reduce the volume, radiotoxicity, and the thermal load of nuclear waste that will eventually be disposed of in a geological repository.

Reprocessing of used nuclear fuel is accomplished primarily using liquid-liquid extraction methods. In these systems, complexing agents with an affinity for specific elements are added to improve separation factors, as is the case for separation of trivalent actinides from lanthanides. The use of *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid (CDTA) has been suggested in the Actinide Lanthanide Separation (ALSEP) and Group Actinide Extraction (GANEX) processes to prevent the coextraction of the fission products Zr and Pd with the targeted actinide elements [1, 5, 6]. Thus, understanding Pu(IV) complexation with CDTA is of importance from the standpoint of predicting Pu behavior in processes such as ALSEP and GANEX.

The chemical structure of CDTA (Fig. 1) is closely related to that of ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (EDTA), the difference being a cyclohexane ring in

CDTA replacing the ethylene group found in EDTA. The consequence of this cyclohexane ring makes CDTA have a more rigid structure compared to EDTA and alters the thermodynamics of complexation with metal cations. While a few studies have reported stability constants for Pu(IV) with EDTA, and one study is available for Pu(III) with CDTA, no thermodynamic data are available for the complexation of Pu(IV) with CDTA [7-13]. Additionally, the acid dissociation constants of CDTA have only been reported at a few different ionic strengths, with no attempt to describe the ionic strength dependence of the protonation reactions. Modeling the ionic strength dependence of these equilibrium constants would allow for the extrapolation of their values to other ionic strengths, providing more accurate parameters for predicting speciation were data might not be available.

This work reports information for the complexation of Pu(IV) with CDTA, including the determination of the corresponding stability constants in $NaClO_4$ media. The complexation of Pu(IV) with CDTA and the associated thermodynamic data of the complex(es) had not been quantified, and this work results in the identification of new Pu(IV)-CDTA complexes and speciation information that is necessary for understanding Pu(IV)-CDTA behavior in advanced nuclear fuel reprocessing systems. Measurement of CDTA acid dissociation constants were performed using potentiometry at ionic strengths of 0.10-2.00 $mol \cdot L^{-1}$ $NaClO_4$, and the ionic strength dependence described with the Specific ion Interaction Theory. A liquid-liquid extraction method was used to determine the stability constants of Pu(IV)-CDTA in 1.00 $mol \cdot L^{-1}$ $(Na,H)ClO_4$. The Pu(IV)-CDTA complexation studies were carried out with tracer concentrations of ^{238}Pu in acidic solutions to minimize hydrolysis, colloid formation, and disproportionation of Pu(IV).

2 Experimental

2.1 Materials

All chemicals were reagent grade and used without further purification unless specified and are listed in Table 1. Aqueous solutions were prepared with distilled, deionized water (Millipore Synergy, 18.2 MΩ·cm^{-1}). Anhydrous $NaClO_4$ (98.0-102.0%, ACS certified, Alfa Aesar) or the monohydrate (≥ 99.0%, HLPC grade, Fluka Analytical), potassium hydrogen phthalate (KHP) (99+%, Acros Organics), and *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid monohydrate ($H_4CDTA·H_2O$) (> 99.0%, TCI) were dried in an oven at 110 °C for 1 hr followed by cooling in a desiccator. Sodium perchlorate and $NaNO_2$ (99.6%, ACS certified, Baker Analyzed) solutions were made by dissolving a weighed amount of reagent in water. A solution of 50 wt % NaOH (pellets, ≥ 97.0%, ACS certified, Fisher) was produced from which carbonate was allowed to precipitate overnight. Dilutions of NaOH were made from this solution with an appropriate amount of $NaClO_4$ to fix the ionic strength, and then standardized by titrations of KHP to a phenolphthalein endpoint using a Brinkmann Metrohm 765 Dosimat. Carbonate content in the NaOH solutions was estimated from the protolytic impurity level obtained from analyzing the Gran titrations in the program GLEE (Protonic Software) (a protolytic impurity level < 2% was desired), and as such, it was found necessary to replace these solutions on a weekly basis [14, 15]. Stock solutions of $HClO_4$ were prepared from dilutions of 70% perchloric acid (redistilled, Alfa Aesar) in $NaClO_4$ solution of desired ionic strength and standardized against standardized NaOH. Solutions of 5.00×10^{-3} mol·L^{-1} CDTA were prepared by adding weighed portions of the dried reagent to $NaClO_4$ solution of appropriate ionic strength, and then adding approximately one mole ratio of standardized NaOH to the CDTA suspension under gentle heating to completely dissolve before dilution to the final volume. 2-Thenoyltrifluoroacetone (TTA) (99%, Aldrich) was dissolved in

p-xylene (99%, Acros) to obtain a 0.100 mol·L^{-1} TTA stock solution. This solution was protected from light and stored in a covered glass bottle when not in use.

2.2 Pu(IV) Stock Solution

A ^{238}Pu(IV) stock of 6×10^{-7} mol·L^{-1} total Pu in 1 mol·L^{-1} HCl was used. The isotopic composition was verified by α-spectroscopy and liquid scintillation counting as 99.5 ± 0.4% ^{238}Pu and 0.5 ± 0.4% $^{239+240}$Pu by activity percent. The stock was previously purified (within one year) and adjusted to Pu(IV) by anion exchange as previously described [16, 17]. Specifically, 2 mL of Pu in 8 mol·L^{-1} HNO_3 was adjusted to Pu(IV) by adding 100 µL of saturated $NaNO_2$ and then loaded onto a column containing 2 mL of Bio Rad AG 1-X8 (100-200 mesh) anion exchange resin. The column was rinsed with 3 bed volumes of 8 mol·L^{-1} HNO_3 and then Pu was eluted as Pu(III) with 15 vol % HI/HCl. A few drops of concentrated HNO_3 were added to the eluent and heated to near dryness multiple times to remove HI and oxidize Pu back to Pu(IV), before final dissolution in 1 mol·L^{-1} HCl. The Pu oxidation state was verified by a liquid-liquid extraction method using 0.025 mol·L^{-1} 1-phenyl-3-methyl-4-benzoyl-2-pyrazolin-5-one (PMBP) (99%, Aldrich) in *p*-xylene which quantitatively extracts only the 4+ oxidation state from 1 mol·L^{-1} HCl [18, 19]. The results from this extraction indicated that the stock was 96 ± 2% Pu(IV).

2.3 Potentiometric Titration

Potentiometric titrations for the quantification of the acid dissociation constants, pK_a, of CDTA were performed with a Mettler Toledo Titration Excellence T50 autotitrator equipped with a Mettler Toledo DGi111-SC combination glass electrode, Mettler Toledo DT1000 temperature probe, Mettler Toledo compact propeller stirrer, and controlled with LabX 2016 software (Mettler Toledo, version 7.0.0). The inner fill solution of the glass electrode was replaced with 3 mol·L^{-1}

NaCl to avoid precipitation of $KClO_4$ in the electrode frit. All titrations were performed under an argon atmosphere (Ar was bubbled through solutions of 1 mol·L^{-1} NaOH and water to remove CO_2 and to hydrate the gas) in a 100 mL water-jacketed titration cell connected to an external circulating water bath (Fisher Scientific Isotemp 3016D). Volumetric pipettes for transferring solution into the titration cell were calibrated daily by weighing dispensed volumes of water. The circulating water bath temperature was adjusted such that the temperature of the solution in the titration cell was maintained at 25.0 ± 0.1 °C as confirmed by the temperature probe. Typically, this required setting the bath temperature to 25.1 or 25.2 °C. At least 100 data points were collected for each titration curve with a 30 second equilibration time between each addition of titrant. The volume of titrant dispensed in each addition was adjusted such that the titration concluded within 1 hr to minimize potential variations due to electrode drift. The glass electrode was calibrated to give pC_H (= $-\log_{10}$ [H^+]) via Gran titrations at each ionic strength [20]. A 2.000 mL aliquot of standardized 0.1000 mol·L^{-1} $HClO_4$ was added to 50.00 mL of $NaClO_4$ solution and titrated with standardized 0.1000 mol·L^{-1} NaOH/$NaClO_4$ of the same ionic strength. The Gran titration data was analyzed in the program GLEE (Protonic Software) for determination of the standard electrode potential and the electrode slope factor using data from the acidic (pC_H 2.5-3.2) and basic (pC_H 10.8-11.3) regions of the strong acid-base titration curves [14, 15]. The potential readings obtained from these titrations were first used to calculate the value of pK_w at each ionic strength and were subsequently used in the Gran analysis to define the relationship between electrode potential and pC_H. Accurate pK_w values are crucial to obtain accurate pK_a values. The slope factors ranged from 58.72 to 59.30 mV over the course of this work were within 1% of the Nernstian value. A Gran titration was performed before every replicate CDTA titration to account for any drift in electrode response between runs. Determination of the pK_a values of

CDTA in 0.10-2.00 mol·L^{-1} $NaClO_4$ were performed by acidifying 50.00 mL of 5.00×10^{-3} mol·L^{-1} CDTA to ca. pC_H 2 by adding a known amount of standardized 0.1000 mol·L^{-1} $HClO_4$/$NaClO_4$, and then titrating with standardized 0.1000 mol·L^{-1} NaOH/$NaClO_4$ of the same ionic strength. Four replicate titrations were performed at each ionic strength. Fitting of the protonation constants of CDTA was performed in the program Hyperquad2013 (Protonic Software) [21, 22].

2.4 Liquid-Liquid Extraction

Liquid-liquid extractions were performed by contacting equal volumes of aqueous and organic phases (500 µL each) in 1.5 mL screw cap microcentrifuge tubes with at least triplicate samples for each data point. The samples were vigorously shaken to emulsion on a vortex mixer for 30 min at room temperature (23 ± 1 °C); preliminary experiments indicated this was sufficient shaking time to reach extraction equilibrium (Fig. S1, supplementary material). After mixing, the phases were separated by centrifuging for 1 min at 5000 rpm, and an aliquot of 200 µL from each phase was then mixed with 5 mL of Perkin Elmer Ultima Gold™ LLT liquid scintillation cocktail and counted on a Perkin Elmer Tri-Carb 2900 TR liquid scintillation analyzer. An energy window of 100-2000 keV was used, with sample count times of 30 min, or until a 1% error (±2σ) in the count rate was achieved. Backgrounds were typically 6-7 cpm.

Slope-analysis experiments were performed to elucidate the TTA and H^+ stoichiometries of the extracted Pu(IV)-TTA species. The TTA dependence was determined by contacting varied concentrations of TTA (0.010-0.050 mol·L^{-1}) in *p*-xylene with aqueous solutions of ca. 11,000 cpm ^{238}Pu (ca. 6×10^{-9} mol·L^{-1} total Pu(IV)) in 1.00 mol·L^{-1} $HClO_4$ and 1×10^{-3} mol·L^{-1} $NaNO_2$ to maintain Pu in the 4+ oxidation state. To determine the H^+ dependence, a constant concentration of 0.030 mol·L^{-1} TTA in *p*-xylene was used, varying the concentration of

standardized $HClO_4$ in the aqueous phase from 0.75 to 1.00 mol·L^{-1} with the addition of $NaClO_4$ to maintain the ionic strength at 1.00 mol·L^{-1}. To determine the Pu(IV)-CDTA stability constants, ca. 6×10^{-9} mol·L^{-1} total Pu(IV) and varied concentrations of CDTA (0 to 1.00×10^{-3} mol·L^{-1}) were added to the aqueous phase with 0.020 mol·L^{-1} TTA in the *p*-xylene organic phase. These experiments were performed at different concentrations of standardized $HClO_4$ from 0.10 to 0.50 mol·L^{-1} (there was no complexation between Pu(IV) and CDTA observed at > 0.50 mol·L^{-1} $HClO_4$) while maintaining the ionic strength at 1.00 mol·L^{-1} with $NaClO_4$ at room temperature (23 ± 1 °C).

3 Results and Discussion

3.1 Measurement of pK_w

The electrode potential readings obtained over the course of the Gran titrations were used to calculate the autoprotolysis constant of water, pK_w, in solutions of 0.10-2.00 mol·L^{-1} $NaClO_4$ [23-26]. Accurate pK_w values are crucial to obtain accurate pK_a values. During the titration of a strong acid with a strong base, the measured electrode potential in the acidic region (before the equivalence point) of the titration curve can be written as:

$$E = E° + \ln(10)\frac{RT}{F}\log_{10}[H^+]\gamma_{H^+} + E_j \quad (1)$$

where E is the measured electrode potential, $E°$ is the standard electrode potential, R is the gas constant, T is the absolute temperature, F is the Faraday constant, γ_{H^+} is the activity coefficient of H^+, and E_j is the junction potential. At constant ionic strength, the activity coefficients and the junction potential are constants, and can be combined into the standard electrode potential to provide a new constant, $E°'$, which at 25 °C is:

$$E = E^{\circ\prime} + (59.16\ \text{mV}) \log_{10} [\text{H}^+]$$
$$= E^{\circ\prime} - (59.16\ \text{mV}) \text{p}C_{\text{H}} \quad (2)$$

Following a similar argument, the electrode potential response in the basic region of the titration curve can be written:

$$E = E^{\circ} + \ln(10) \frac{RT}{F} \log_{10} \left(\frac{K_{\text{w}}}{[\text{OH}^-]\gamma_{\text{OH}^-}} \right) + E_j$$
$$= E^{\circ\prime} - (59.16\ \text{mV}) \text{p}K_{\text{w}} + (59.16\ \text{mV}) \text{p}C_{\text{OH}} \quad (3)$$

Plots of E vs. pC_{H} in the acidic region, or vs. pC_{OH} in the basic region, have y-intercepts of $E_{\text{a}}^{\circ} = E^{\circ\prime}$ (Eq. 2) and $E_{\text{b}}^{\circ} = E^{\circ\prime} - (59.16\ \text{mV})\text{p}K_{\text{w}}$ (Eq. 3) respectively. The pC_{H} in the acidic region and the pC_{OH} in the basic region are calculated from the known amounts of standardized strong acid or from the excess standardized strong base added during the titration. The value of pK_{w} is determined from E_{a}° and E_{b}°:

$$\text{p}K_{\text{w}} = \frac{E_{\text{a}}^{\circ} - E_{\text{b}}^{\circ}}{59.16\ \text{mV}} \quad (4)$$

Titration data from at least four Gran titrations at each ionic strength were generated (Fig. 2) to determine E_{a}° and E_{b}°, and Eq. 4 was used to calculate pK_{w}. The averaged values of the obtained pK_{w} values are presented with Table 2 with errors corresponding to $\pm 3\sigma$ from quadruplicate titrations. Our reported values agree well with those in the literature in $NaClO_4$ media, and there is an exceptional agreement with the values reported in the NIST stability constant database [27-31]. However, a slight discrepancy was observed between the NIST value of 13.95 ± 0.01 in 2.00 mol·L^{-1} $NaClO_4$, which was higher than our value of 13.87 ± 0.03 but still agree within 1%. Our experimentally determined pK_{w} values were used for the analysis of the Gran titration curves for electrode calibration and when refining the CDTA pK_{a} values.

3.2 CDTA Acid Dissociation Constants

The acid dissociation constants of CDTA were determined in ionic strengths of 0.10-2.00 mol·L^{-1} $NaClO_4$ via potentiometric titration. CDTA is a hexaprotic, weak acid with stepwise acid dissociation constants, K_{ai}, corresponding to the following equilibrium:

$$H_{6-i+1}CDTA^{6-i+1-4} \rightleftharpoons H_{6-i}CDTA^{6-i-4} + H^+ \quad (5)$$

$$K_{ai} = \frac{[H_{6-i}CDTA^{6-i-4}][H^+]}{[H_{6-i+1-4}CDTA^{6-i+1-4}]} \quad (6)$$

Representative titration curves of CDTA at each ionic strength are displayed in Fig. 3. Fitting the titration data in the program Hyperquad2013 from four replicate titrations at each ionic strength yielded the values for pK_{a2} through pK_{a6} and are summarized in Table 2 with errors reported as $\pm 3\sigma$ from quadruplicate titrations. The speciation of CDTA in 1.00 mol·L^{-1} $NaClO_4$ is presented in Fig. S2 in the supplementary material. The values reported in the NIST database are only listed in ionic media of Na^+ salts and only a few additional references report these values specifically in $NaClO_4$ [27, 32-34]. Our results in 0.50 and 1.00 mol·L^{-1} $NaClO_4$ are in good agreement with the corresponding conditions by Chinea et al. [32] and Anderegg [33]. At an ionic strength of 0.10 mol·L^{-1}, the NIST database provides values for pK_{a3}, pK_{a4}, and pK_{a5} only. No previously reported values at 2.00 mol·L^{-1} ionic strength were identified. Attempts to include pK_{a1} in the data fitting resulted in a failure in refinement, i.e. the free concentrations of every species at each pC_H could not be calculated. This is explained when considering that the corresponding species H_6CDTA^{2+} likely contributes < 1% of the CDTA speciation at pC_H 2; the lowest pC_H value in the collected titration curves, and thus the mass balance expressions for C_{CDTA} and C_H could not be solved when that species was included in the chemical model. Though attempts to measure pK_{a1} were made using lower starting pC_H (< 2), electrode response suffered due to changes in electrode

junction potential which resulted in unacceptable errors. Generally, the electrode junction potential of a glass electrode varies as a function of $[H^+]$ and γ_{H^+} at $pC_H < 2$ and is no longer a constant term under such conditions. This meant that electrode response was no longer a linear function of pC_H alone, and led to large $|pC_H^{meaured} - pC_H^{calculated}|^2$ residuals which resulted in high errors in this region of the titration curves. Indeed, higher errors are also reflected in the values that were determined for pK_{a2} which had values < 2. The only reported values for pK_{a1} are 0.96 measured by Beck and Görög [33, 35] via solubility experiments in dilute $HClO_4$ at 20 °C, and 1.09 ± 0.02 in 1 mol·L^{-1} KCl at 25 °C by Merciny et al. [13].

3.3 SIT Parameters

The variation of pK_w and the CDTA pK_a values with ionic strength were modeled following the Specific ion Interaction Theory (SIT) approach [36]. Within the SIT model, the equilibrium constants are described as a function of ionic strength by:

$$pK_w + \Delta z^2 D + \log_{10} a_{H_2O} = pK_w^\circ + \Delta\varepsilon I_m \quad (7)$$

$$pK_{ai} + \Delta z^2 D = pK_{ai}^\circ + \Delta\varepsilon I_m \quad (8)$$

where K_w° and K_{ai}° are the thermodynamic equilibrium constants at zero ionic strength, a_{H_2O} is the activity of water, I_m is the ionic strength in molality (mol·kg^{-1}), D is the Debye-Hückel term equal to $(0.509 \cdot I_m^{1/2})/(1 + 1.5 \cdot I_m^{1/2})$ at 25 °C, Δz^2 is the change in squared charge over the course of the reaction given by:

$$\Delta z^2 = \sum \left(v_i z_i^2\right)_{products} - \sum \left(v_j z_j^2\right)_{reactants} \quad (9)$$

$\Delta\varepsilon$ is the SIT parameter that is the difference in the individual parameters that describe specific ion interactions in a given background electrolyte medium:

$$\Delta\varepsilon = \sum (\nu_i \varepsilon_i)_{\text{products}} - \sum (\nu_j \varepsilon_j)_{\text{reactants}} \quad (10)$$

where ν are stoichiometric coefficients. Tabulated values of a_{H_2O} in various background electrolyte media are accessible in the literature [36]. The SIT parameters are determined using Eqs. 7 and 8; plots of ($pK_w + \Delta z^2 D + \log_{10} a_{H_2O}$) or ($pK_{ai} + \Delta z^2 D$) as functions of I_m produce linear relationships with slopes equal to $\Delta\varepsilon$ and y-intercepts equal to $pK_i°$. Using this approach however, requires converting the equilibrium constants on the molar scale (K_C) to the molal scale (K_m) by [36]:

$$pK_m = pK_C - \sum \nu_i \log_{10} \vartheta \quad (11)$$

where ϑ is the ratio between molality and molarity for a given background electrolyte. The value of $\Sigma\nu_i$ in the case of the stepwise dissociation constants equals 1. The determined pK_w and CDTA pK_a values were converted to the molal scale with Eq. 11 and then the SIT parameters determined from the error weighted least squares regression of the SIT plots. These plots are shown in Fig. 4 and the resulting SIT parameters are displayed in Table 3.

The value of pK_w decreases with an increasing ionic strength from 0.10 to 0.50 mol·L^{-1} $NaClO_4$; pK_w then increases from ionic strength from 0.50 to 2.00 mol·L^{-1} $NaClO_4$. The resulting SIT analysis leads to $pK_w° = 14.00 \pm 0.03$ and $\Delta\varepsilon = 0.13 \pm 0.02$ kg·mol^{-1}. There is agreement between our measured value of $pK_w°$ and those reported by NIST and Du et al. [27, 29]. A discrepancy in our value of $\Delta\varepsilon$ is observed when compared to the higher value of $\Delta\varepsilon = 0.1910$ kg·mol^{-1} reported by Du et al. The work by Du et al. also utilized potentiometric titration to measure pK_a values for acetic acid, HF, and pK_w at varying ionic strengths of $NaClO_4$, but the method for calculating pK_w from their data was not explicitly stated. However, it is inferred that pK_w was used as an adjustable fit parameter and obtained from the first derivative analysis of

pK_a titrations of acetic acid and HF. Additionally, the changes in a_{H_2O} with ionic strength was not included in the SIT model of Du et al. If the a_{H_2O} term is not included in the SIT fitting of our pK_w data, pK_w° remains unchanged but we observed an increase of slope resulting in a higher value of $\Delta\varepsilon$. The absence of the contribution of a_{H_2O} in the SIT model is a likely explanation for why the value from Du et al. is higher than our result. Finally, Du et al. did not report any error associated to $\Delta\varepsilon$, while we report data with a $\pm 3\sigma$ error; the two results may in fact overlap at the 99% confidence interval.

The SIT parameters for the CDTA pK_a values had not yet been reported in the literature. The pK_a values decrease with an increasing ionic strength from 0.10 to 0.50 mol·L^{-1} $NaClO_4$, and then increase from 0.50 to 2.00 mol·L^{-1} $NaClO_4$. An exception to this trend was observed for pK_{a4} which was found to continuously decrease, i.e. become more acidic, from 0.10 to 2.00 mol·L^{-1} $NaClO_4$ and is reflected in the SIT parameter as having a negative value, $\Delta\varepsilon_4 = -0.11 \pm 0.03$ kg·mol^{-1}. The equilibrium reaction of pK_{a4} corresponds to the deprotonation of the final carboxylate group of CDTA. The increasing acidity of this carboxylate group with an increasing ionic strength maintained by $NaClO_4$ suggests stronger specific ion interactions between (Na^+, H_2CDTA^{2-}) than (H^+, H_2CDTA^{2-}), thus the increased acidity of that proton. There is perhaps increasing association/complexation of Na^+ with the fully deprotonated carboxylate groups that is thermodynamically more favorable than the (likely) rapid isomeric equilibrium of that proton between the four carboxylate groups of CDTA. Calorimetry experiments or van't Hoff analysis could be performed to determine if there is an enthalpic or entropic driving force that can further explain this phenomenon.

3.4 Pu(IV)-TTA Extraction Stoichiometry

The extraction of Pu(IV) with TTA can be expressed by:

$$Pu^{4+} + 4HTTA_{(org)} \rightleftharpoons Pu(TTA)_{4\,(org)} + 4H^{+} \quad (12)$$

with an extraction equilibrium constant, K_{ex}:

$$K_{ex} = \frac{[Pu(TTA)_4]_{(org)}[H^{+}]^4}{[Pu^{4+}][HTTA]^4_{(org)}} \quad (13)$$

where HTTA is the enol form of TTA that exchanges H^+ with the aqueous phase as it extracts a metal cation into the organic phase [37]. Perchlorate is a weakly complexing anion and complexation with Pu(IV) is negligible, therefore ClO_4^- is not expected to participate in the extraction equilibrium. The distribution ratio of Pu(IV) is the analytical concentration of Pu(IV) in the organic phase divided by the analytical concentration of Pu(IV) in the aqueous phase after extraction and was determined radiometrically by measuring the count rate of ^{238}Pu in each phase. Thus, the distribution ratio in the absence of CDTA, D_0, is expressed as:

$$D_0 = \frac{[Pu(TTA)_4]_{(org)}}{[Pu^{4+}] + \sum [Pu(OH)_h^{4-h}]} = \frac{[Pu(TTA)_4]_{(org)}}{[Pu^{4+}]\left(1 + \sum \beta_{1\text{-}h0}[H^{+}]^{-h}\right)} \quad (14)$$

where β_{1-h0} are the hydrolysis constants for Pu(IV), taken from Baes and Mesmer which contains a complete set of Pu(IV) hydrolysis constants at 1 mol·L^{-1} (Na,H)ClO_4 ionic strength [38]. Equation 13 can be written in terms of D_0 by combining with Eq. 14, after which taking the logarithm yields:

$$\log_{10}\left\{D_0\left(1 + \sum \beta_{1\text{-}h0}[H^{+}]^{-h}\right)\right\} = \log_{10} K_{ex} + 4\log_{10}[HTTA]_{(org)} - 4\log_{10}[H^{+}] \quad (15)$$

From Eq. 15, plots of $\log_{10}\{D_0(1 + \sum\beta_{1-h0}[H^+]^{-h})\}$ vs. $\log_{10}[HTTA]_{(org)}$ or $\log_{10}[H^+]$ provide expected slopes of 4 and −4 respectively based on the expected stoichiometries of TTA and H^+ given in Eq. 12. The results of these slope-analysis experiments are plotted in Fig. 5 and gave the

expected slopes of 3.9 ± 0.1 for the TTA dependence and −3.8 ± 0.2 for the H^+ dependence from the error weighted least squares regression. This indicates that the extraction mechanism in Eq. 12 does indeed describe the extraction of Pu(IV) with TTA and that $Pu(TTA)_4$ is the only species extracted into the organic phase. Additionally, these results verified that Pu remained in the 4+ oxidation state during the extractions; slopes significantly different from 4 would have indicated reduction or oxidation of Pu(IV) had occurred [39, 40]. This data was also used to calculate the extraction equilibrium constant with Eq. 15; our results indicate $\log_{10} K_{ex} = 6.02 \pm 0.06$ (1.00 mol·L^{-1} (Na,H)ClO_4/*p*-xylene/23 ± 1 °C).

Comparing the values of K_{ex} for the Pu(IV)-TTA system (Table 4), our value is observed to be lower than those previously reported in different organic diluents. Values measured in benzene have been reported in the review article by Poskanzer et al. [41] as $\log_{10} K_{ex} = 6.8$ (1 mol·L^{-1} $HClO_4$/benzene) and Ramakrishna et al. [42] report $\log_{10} K_{ex} = 7.3$ (1.0-2.0 mol·L^{-1} $HClO_4$/benzene/25 °C), while values using toluene have been reported by Nash et al. [43] as $\log_{10} K_{ex} = 6.6 \pm 0.1$ (2.0 mol·L^{-1} (Na,H)ClO_4/toluene/25.0 °C) and by Xia et al. [39, 40] as $\log_{10} K_{ex} = 7.08 \pm 0.01$ (2.0 mol·L^{-1} $HClO_4$/toluene/25 °C). No studies using *p*-xylene have previously been reported and we cannot make a direct comparison. This is of importance because the extraction of Zr(IV) with TTA in different aliphatic and aromatic diluents from 1 mol·L^{-1} HNO_3 leads to decreasing K_{ex} values in aromatic diluents following the trend benzene>toluene>nitrobenzene [44]. The authors attributed the variation in K_{ex} to the changes in the dielectric constant and dipole moment of the organic phase diluent. This concept also seems to apply to the Pu(IV)-TTA system, where the K_{ex} value varies depending on the diluent used; appearing to decrease following trend benzene>toluene>*p*-xylene. A potentially linear trend is observed between K_{ex} and the density of the organic diluent decreasing on the order of

benzene>toluene>*p*-xylene, however no apparent relationships are observed between K_{ex} and other solvent parameters such as the dielectric constant or dipole moment of the organic diluent. The spread found in the literature K_{ex} values, which differ by almost one order of magnitude under the same reported experimental conditions, and the limited number of diluents explored make defining an analytical trend difficult, and a systematic study of diluent effects on the liquid-liquid extraction of Pu(IV) may be warranted.

3.5 Pu(IV)-CDTA Complexation

The complexation of Pu(IV) with CDTA can be described by the following equilibrium:

$$Pu^{4+} + hH^{+} + xCDTA^{4-} \rightleftharpoons Pu(H_hCDTA_x)^{4+h-4x} \tag{16}$$

with a stability constant:

$$\beta_{1hx} = \frac{[Pu(H_hCDTA_x)^{4+h-4x}]}{[Pu^{4+}][H^{+}]^{h}[CDTA^{4-}]^{x}} \tag{17}$$

By convention, negative values of h indicate a hydroxo species. The distribution ratio of Pu(IV) in the presence of CDTA in the aqueous phase, D, is defined:

$$\begin{aligned} D &= \frac{[Pu(TTA)_4]_{(org)}}{[Pu^{4+}] + \sum [Pu(OH)_h^{4-h}] + \sum [Pu(H_hCDTA_x)^{4+h-4x}]} \\ &= \frac{[Pu(TTA)_4]_{(org)}}{[Pu^{4+}]\left(1 + \sum \beta_{1-h0}[H^{+}]^{-h} + \sum \beta_{1hx}[H^{+}]^{h}[CDTA^{4-}]^{x}\right)} \end{aligned} \tag{18}$$

Combining Eqs. 14 and 18 gives:

$$\frac{1}{D} = \frac{1}{D_0} + \sum \frac{\beta_x^{app}}{D_0}[CDTA^{4-}]^{x} \tag{19}$$

where β_x^{app} is an apparent stability constant defined as:

$$\beta_x^{app} = \frac{\sum \beta_{1hx}}{\left(1 + \sum \beta_{1\text{-}h0}[H^+]^{-h}\right)}[H^+]^h \quad (20)$$

At a fixed $[H^+]$, plots of $1/D$ against the concentration of free CDTA, $[CDTA^{4-}]$, have a y-intercept proportional to D_0 and coefficients proportional to β_x^{app}. The distribution ratio was measured varying the concentration of CDTA in solutions of standardized 0.10-0.50 mol·L^{-1} $HClO_4$ with 1.00 mol·L^{-1} (Na,H)ClO_4 total ionic strength, and then plotted according to Eq. 19. The concentration of free CDTA was calculated at each $[H^+]$ using our measured pK_a values and the value of pK_{a1} = 0.96 from Beck and Görög at 1.00 mol·L^{-1} $NaClO_4$ ionic strength [33, 35]. The distribution data was found to follow a linear trend with respect to $1/D$ vs. $[CDTA^{4-}]$ at each $[H^+]$ and fit with error weighted least squares. Representative plots are shown in Fig. 6 and the distribution data can be found in the supplementary material (Tables S1-S5). The linear fits of $1/D$ vs. $[CDTA^{4-}]$ indicate a Pu(IV)-CDTA stoichiometry of 1:1, i.e. $x = 1$, and the β^{app} values were obtained from the slopes of the linear regression at each $[H^+]$ according to Eq. 19. If no protonated Pu(IV)-CDTA complexes are present, there should be little variation in the values of β^{app} with changes in acidity. However, the measured β^{app} values (Table S6) were found to increase in magnitude with increasing $[H^+]$, indicating the formation of one or more protonated Pu(IV)-CDTA species. The plot of β^{app} vs. $[H^+]$ in Fig. 7 followed 2nd-order polynomial behavior, implying the presence of multiple protonated complexes. Thus, the definition of β^{app} in Eq. 20 can be expressed in terms of the individual Pu(IV)-CDTA stability constants as [45-47]:

$$\beta^{app}\left(1 + \sum \beta_{1\text{-}h0}[H^+]^{-h}\right) = \beta_{101} + \beta_{111}[H^+] + \beta_{121}[H^+]^2 \quad (21)$$

The values of β_{101}, β_{111}, and β_{121} were determined from the coefficients of the 2nd-order polynomial fit and are listed in Table 4.

An aqueous Pu(IV)-CDTA speciation plot (Fig. 8) was developed, using the acid dissociation constants and stability constants determined in this work and the Pu(IV) hydrolysis constants from Baes and Mesmer [38]. The modeling conditions reflect the solution conditions that were used in the liquid-liquid extraction experiments from which the stability constants were measured, and therefore only a pC_H range of −1 to 3 was modeled to remain representative of the acidic conditions explored in the experiments. According to the speciation model, the protonated Pu(IV)-CDTA complexes start to form at p$C_H \sim 0$. Initially, we attempted to determine the stability constants in 1.00 mol·L^{-1} $HClO_4$ (i.e. p$C_H = 0$) but we did not observe any changes in the distribution ratio with varied CDTA concentration. This observation was an indication that no Pu(IV)-CDTA complexation was occurring under these conditions and indeed matches what is predicted by the speciation model. There is a mixture of the protonated complexes $Pu(H_2CDTA)^{2+}$ and $Pu(HCDTA)^{+}$ between pC_H 0 and 1, where $Pu(HCDTA)^{+}$ becomes the primary Pu(IV) species at a pC_H of 0.8. The protonated complexes are deprotonated and disappear as the pC_H is increased, forming the 1:0:1 complex, $PuCDTA^0$, as the dominant Pu(IV) species at p$C_H > 2$. Of additional note, Pu(IV) is fully complexed upon reaching pC_H 1 and the hydrolysis of Pu(IV) is effectively suppressed when CDTA is in stoichiometric excess.

The only other reported study of Pu complexation with CDTA was a potentiometric study of Pu(III), and the reported stability constant for the Pu(III)-CDTA complex was $\log_{10}\beta_{101} = 17.70 \pm 0.02$ (1 mol·L^{-1} KCl, 25.00 ± 0.01 °C) [13]. The greater value of $\log_{10}\beta_{101} = 24.2 \pm 0.3$ (1.00 mol·L^{-1} (Na,H)ClO_4, 23 ± 1 °C) we obtained for the Pu(IV)-CDTA system follows the expected trend of increasing complexation strength on the order of Pu(III) < Pu(IV), due to the increased cationic charge and Lewis acidity of Pu(IV) compared to Pu(III). While no other Pu(IV)-CDTA studies have been reported, comparisons to Pu(IV)-EDTA

complexes can be informative due to the similar structures of the two ligands. Foreman et al. [9] calculated a Pu(IV)-EDTA stability constant of $\log_{10}\beta_{101} = 24.2$ in 1 mol·L^{-1} HNO_3 with spectrophotometry and Cauchetier et al. [10] report $\log_{10}\beta_{101} = 25.6$ in 0.1 mol·L^{-1} ionic strength of unspecified background electrolyte. Using a liquid-liquid extraction method, Thakur et al. [11] report $\log_{10}\beta_{101} = 24.55 \pm 0.22$ from an acidic solution of 1.0 mol·L^{-1} $HClO_4$/4.0 mol·L^{-1} $NaClO_4$ and 25 °C but did not report any protonated complexes as they did not perform experiments at varied acid concentration, which is necessary in order to observe those complexes. Perhaps the most complete study of Pu(IV)-EDTA solution equilibria was performed by Boukhalfa et al. [12] who utilized potentiometry, spectrophotometry, and cyclic voltammetry to identify Pu(IV)-EDTA and ternary mixed-ligand complexes in solution. At a 1:1 metal to ligand ratio they found the 1:0:1 complex, $PuEDTA^0$, to dominate in acidic solutions of pH < 4 ($\log_{10}\beta_{101} = 26.44 \pm 0.20$, 1.0 mol·L^{-1} $NaClO_4$, 25 °C), followed by the formation of hydroxo species at higher pH. When they changed the metal to ligand ratio to 1:2, they observed the formation of bis-EDTA complexes with Pu(IV) at near neutral pH, where the $PuEDTA^0$ species was still the dominant complex under acidic pH. In our experiments CDTA was present in great stoichiometric excess relative to Pu(IV), but it is unlikely that similar bis-CDTA complexes would form under the acidic conditions of 0.10-0.50 mol·L^{-1} $HClO_4$ studied, as was the case for the Pu(IV)-EDTA system.

Metal-ligand complex stability constants of EDTA and CDTA generally increase in the order EDTA < CDTA. This is indeed the case for other tetravalent cations, such as Th(IV), for which $\log_{10}\beta_{101}$ values of 22.3 with EDTA and 24.5 with CDTA (0.5 mol·L^{-1} Na^+ salt, 25 °C) were reported [27]. This free energy relationship can be attributed to two factors: (1) the increase in total basicity (ΣpK_a) of CDTA ($\Sigma pK_a = 23.5 \pm 0.2$, 1.00 mol·L^{-1} $NaClO_4$, present work) compared to EDTA ($\Sigma pK_a = 20.9 \pm 0.3$, 1.0 mol·L^{-1} $NaClO_4$, [27]), and (2) a thermodynamic

effect where the carboxylate groups on CDTA are pre-organized in an orientation appropriate for binding a metal cation because of its rigid cyclohexane backbone, while the more flexible EDTA molecule has an energy cost associated with orienting the ligand into the required binding geometry. Regarding the second reason, the stronger metal-ligand complexes with CDTA would likely be represented thermodynamically by having a more favorable change in the reaction entropy compared with EDTA complexes. Therefore, we anticipated a larger β_{101} for Pu(IV)-CDTA than for Pu(IV)-EDTA based on this free energy relationship. Yet, our value of β_{101} for Pu(IV)-CDTA is slightly lower than the aforementioned values reported for Pu(IV)-EDTA. However, the absence of protonated Pu(IV)-EDTA species in the literature, which likely do form under the acidic conditions that were studied, could result in inaccurately high values of $\beta_{101}^{\mathrm{EDTA}}$, explaining this apparent non-congruence. A comprehensive study of Pu(IV) complexes with EDTA and CDTA at varied temperatures would be beneficial to better understand the underlying thermodynamics of these systems and provide a better understanding of the similarities and differences between these two systems.

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Conflict of Interest

The authors declare no conflict of interest.

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Table 1 Description of the materials used in this work

Material	Abbreviation	Source	Mass fraction purity[a]
AG 1-X8 anion exchange resin (100-200 mesh)		Bio-Rad Laboratories	
trans-1,2-Diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid monohydrate	$H_4CDTA \cdot H_2O$	TCI	> 99.0%
Hydrochloric acid	HCl	BDH Chemicals	36.5-38.0%
Nitric acid	HNO_3	BDH Chemicals	68-70%
Perchloric acid	$HClO_4$	Alfa Aesar	70%
1-Phenyl-3-methyl-4-benzoyl-2-pyrazolin-5-one	PMBP	Sigma-Aldrich	99%
Potassium hydrogen phthalate	KHP	Acros Organics	> 99%
Sodium hydroxide (pellets)	NaOH	Fisher Scientific	≥ 97.0%
Sodium nitrite	$NaNO_2$	J. T. Baker	99.6%
Sodium perchlorate (anhydrous)	$NaClO_4$	Alfa Aesar	98.0-102.0%
Sodium perchlorate (monohydrate)	$NaClO_4 \cdot H_2O$	Fluka Analytical	≥ 99.0%
2-Thenoyltrifluoroacetone	TTA	Sigma-Aldrich	99%
Ultima Gold LLT liquid scintillation cocktail		PerkinElmer	
p-Xylene		Acros Organics	99%

[a]Purities as provided by the supplier

596 **Table 2** Autoprotolysis of water and acid dissociation constants for CDTA in $NaClO_4$ media

Ionic strength	T (°C)	pK_w	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	pK_{a5}	pK_{a6}	Ref.
0.10 mol·L^{-1} $NaClO_4$	25.0 ± 0.1	13.78 ± 0.02		1.6 ± 0.5	2.59 ± 0.07	3.72 ± 0.03	6.13 ± 0.02	9.80 ± 0.09	p.w.[a]
0.10 mol·L^{-1} Na^+ salt	25.0	13.78 ± 0.01			2.48 ± 0.08	3.50 ± 0.05	6.07 ± 0.02		27
0.10 mol·L^{-1} $NaClO_4$	25	13.79 ± 0.03							28
0.10 mol·L^{-1} $NaClO_4$	25	13.80 ± 0.02							29
0.50 mol·L^{-1} $NaClO_4$	25.0 ± 0.1	13.74 ± 0.02		1.6 ± 0.2	2.48 ± 0.04	3.41 ± 0.05	5.85 ± 0.05	9.35 ± 0.05	p.w.
0.50 mol·L^{-1} Na^+ salt	25.0	13.73 ± 0.04						11.3	27
0.50 mol·L^{-1} $NaClO_4$	25	13.77 ± 0.01							29
0.50 mol·L^{-1} $NaClO_4$	25	13.73							31
0.50 mol·L^{-1} $NaClO_4$	25			1.91 ± 0.03	2.45 ± 0.02	3.35 ± 0.01	5.80 ± 0.02	9.31 ± 0.07	32
1.00 mol·L^{-1} $NaClO_4$	25.0 ± 0.1	13.76 ± 0.02		1.7 ± 0.1	2.46 ± 0.02	3.27 ± 0.04	5.86 ± 0.04	9.27 ± 0.04	p.w.
1.0 mol·L^{-1} Na^+ salt	25.0	13.77 ± 0.04		1.6 ± 0.1	2.42 ± 0.01	3.21 ± 0.04	5.84	9.22	27
1.0 mol·L^{-1} $NaClO_4$	25	13.81 ± 0.04							28
1.0 mol·L^{-1} $NaClO_4$	25	13.82 ± 0.02							29
1.05 mol·kg^{-1} $NaClO_4$	25	13.78 ± 0.01							30
1.0 mol·L^{-1} $NaClO_4$	20	13.95		1.72	2.41	3.52	5.87	9.30	33
1.0 mol·L^{-1} $NaClO_4$	21			1.78 ± 0.02	2.30 ± 0.02	3.50 ± 0.03			34
Dilute $HClO_4$	20		0.96	1.92					33, 35
1 mol·L^{-1} KCl	25.00 ± 0.01		1.09 ± 0.02	1.68 ± 0.02	2.32 ± 0.01	3.18 ± 0.01	5.98 ± 0.01	12.13 ± 0.01	13
1.50 mol·L^{-1} $NaClO_4$	25.0 ± 0.1	13.82 ± 0.02							p.w.
2.00 mol·L^{-1} $NaClO_4$	25.0 ± 0.1	13.87 ± 0.03		1.9 ± 0.1	2.55 ± 0.07	3.02 ± 0.05	6.06 ± 0.04	9.31 ± 0.03	p.w.
2.0 mol·L^{-1} $NaClO_4$	25.0	13.95 ± 0.01							27

597 [a]p.w. = present work

598 The standard uncertainties are $u(T) = 0.1$ °C. The expanded uncertainties are $u(K_i) = K_i \cdot \sqrt{(3\sigma \cdot K_i^{-1})^2 + (u(T) \cdot T^{-1})^2}$ where σ is the standard deviation
599 from replicates with $n = 4$ (99% confidence level).

Table 3 SIT parameters for the dissociation constants of water and CDTA from $NaClO_4$ media at 25.0 ± 0.1 °C

Ionic strength ($mol \cdot L^{-1}$)	ϑ ($L \cdot kg^{-1}$)[a]	a_{H_2O}[a]	Constant	Value	Δz^2	$\Delta\varepsilon$ ($kg \cdot mol^{-1}$)	Ref.
0.10	1.0075	0.9966	$pK_w°$	14.00 ± 0.04	2	0.13 ± 0.02	p.w.[b]
0.50	1.0265	0.9833		13.997 ± 0.003			27
1.00	1.0515	0.9660		14.013	2	0.1910	29
1.50	1.0780	0.9476	$pK_{a1}°$				
2.00	1.1062	0.9279	$pK_{a2}°$	1.52 ± 0.04	0	0.15 ± 0.03	p.w.
			$pK_{a3}°$	2.78 ± 0.05	2	0.07 ± 0.05	p.w.
			$pK_{a4}°$	4.17 ± 0.04	4	−0.11 ± 0.03	p.w.
			$pK_{a5}°$	6.75 ± 0.03	6	0.30 ± 0.01	p.w.
			$pK_{a6}°$	10.64 ± 0.06	8	0.23 ± 0.02	p.w.

[a]From Ref. [36]

[b]p.w. = present work

The standard uncertainties are $u(T) = 0.1$ °C. The expanded uncertainties are $u(K_i°) = K_i° \cdot \sqrt{(3\sigma \cdot K_i^{\circ -1})^2 + (u(T) \cdot T^{-1})^2}$ and $u(\Delta\varepsilon) = \Delta\varepsilon \cdot \sqrt{(3\sigma \cdot \Delta\varepsilon^{-1})^2 + (u(T) \cdot T^{-1})^2}$ where σ is the standard deviation from replicates with $n = 4$ (99% confidence level).

Table 4 Equilibrium constants for the liquid-liquid extraction of Pu(IV) with TTA and complexation reactions with CDTA

Reaction	Medium	T (°C)	Constant	Value	Ref.
$Pu^{4+} + 4HTTA_{(org)} \rightleftharpoons Pu(TTA)_{4\,(org)} + 4H^+$	1.00 mol·L^{-1} (Na,H)ClO$_4$/*p*-xylene	23 ± 1	$\log_{10} K_{ex}$	6.02 ± 0.06	p.w.[a]
	1 mol·L^{-1} HClO$_4$/benzene			6.8	41
	1.0-2.0 mol·L^{-1} HClO$_4$/benzene	25		7.3	42
	2.0 mol·L^{-1} (Na,H)ClO$_4$/toluene	25.0		6.6 ± 0.1	43
	2.0 mol·L^{-1} HClO$_4$/toluene	25		7.08 ± 0.01	39, 40
$Pu^{4+} + CDTA^{4-} \rightleftharpoons PuCDTA^0$	1.00 mol·L^{-1} (Na,H)ClO$_4$	23 ± 1	$\log_{10} \beta_{101}$	24.2 ± 0.3	p.w.
$Pu^{4+} + H^+ + CDTA^{4-} \rightleftharpoons Pu(HCDTA)^+$	1.00 mol·L^{-1} (Na,H)ClO$_4$	23 ± 1	$\log_{10} \beta_{111}$	25.4 ± 0.2	p.w.
$Pu^{4+} + 2H^+ + CDTA^{4-} \rightleftharpoons Pu(H_2CDTA)^{2+}$	1.00 mol·L^{-1} (Na,H)ClO$_4$	23 ± 1	$\log_{10} \beta_{121}$	25.8 ± 0.1	p.w.

[a]p.w. = present work

The standard uncertainties are $u(T) = 1$ °C. The expanded uncertainties are $u(K_{ex}) = K_{ex} \cdot \sqrt{(2\sigma \cdot K_{ex}^{-1})^2 + (u(T) \cdot T^{-1})^2}$ and $u(\beta) = \beta \cdot \sqrt{(2\sigma \cdot \beta^{-1})^2 + (u(T) \cdot T^{-1})^2}$ where σ is the standard deviation from replicates with $n = 3$ (95% confidence level).

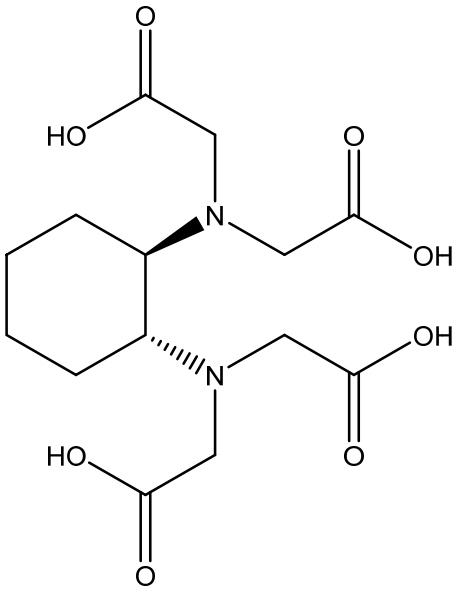


Fig. 1 Chemical structure of *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid (CDTA)

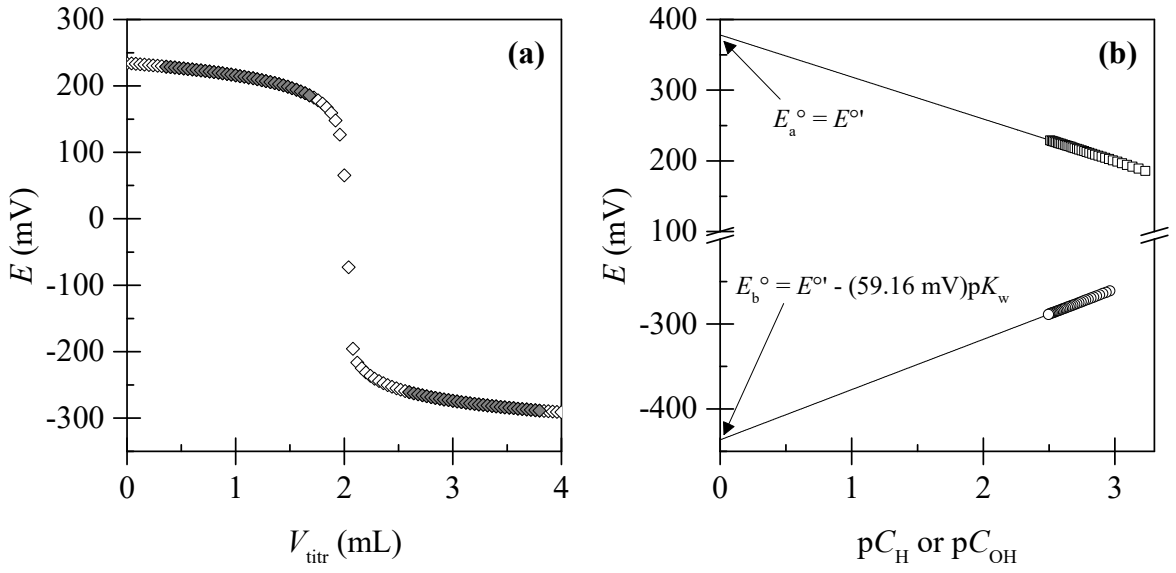


Fig. 2 (a) Gran titration plot used for electrode calibration at 1.00 mol·L^{-1} $NaClO_4$ and 25.0 ± 0.1 °C. Titrant: 0.1000 mol·L^{-1} NaOH/0.90 mol·L^{-1} $NaClO_4$. Titrand: 2.000 mL of 0.1000 mol·L^{-1} $HClO_4$/0.90 mol·L^{-1} $NaClO_4$ added to 50.00 mL of 1.00 mol·L^{-1} $NaClO_4$. The shaded data points were used to construct the plots in **(b)** for the determination of pK_w. In this example, $E_a°$ = 387.2 ± 0.2 mV and $E_b°$ = −436.5 ± 0.2 mV, giving a pK_w value of 13.77 ± 0.01 using Eq. 4

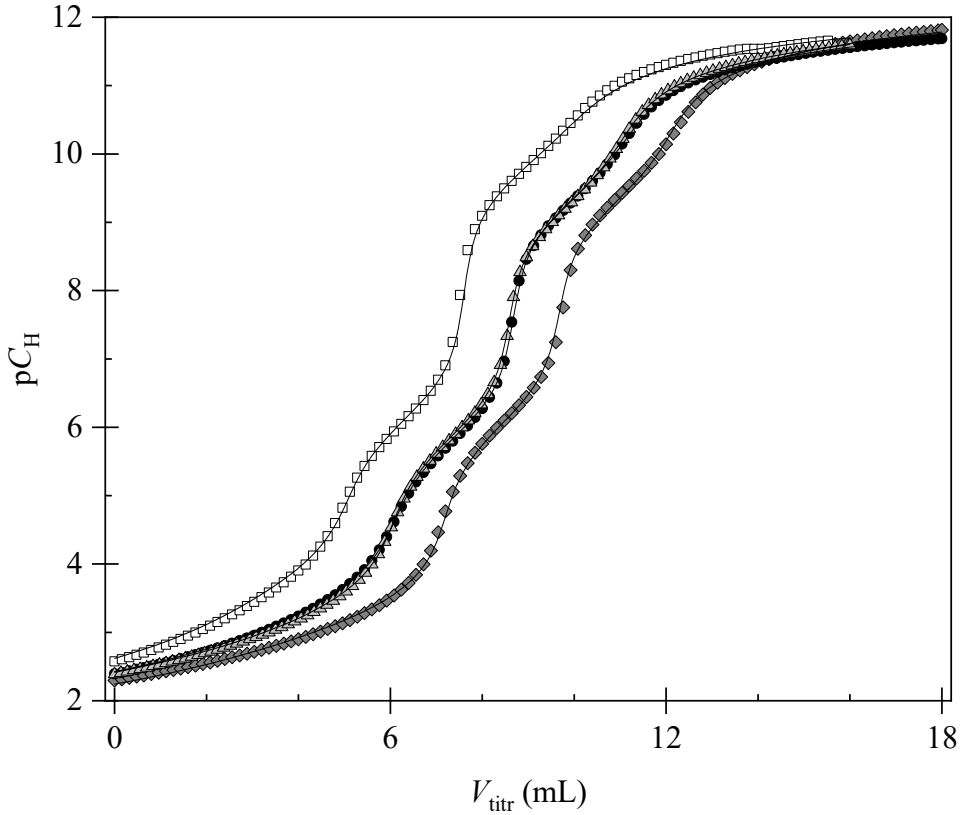
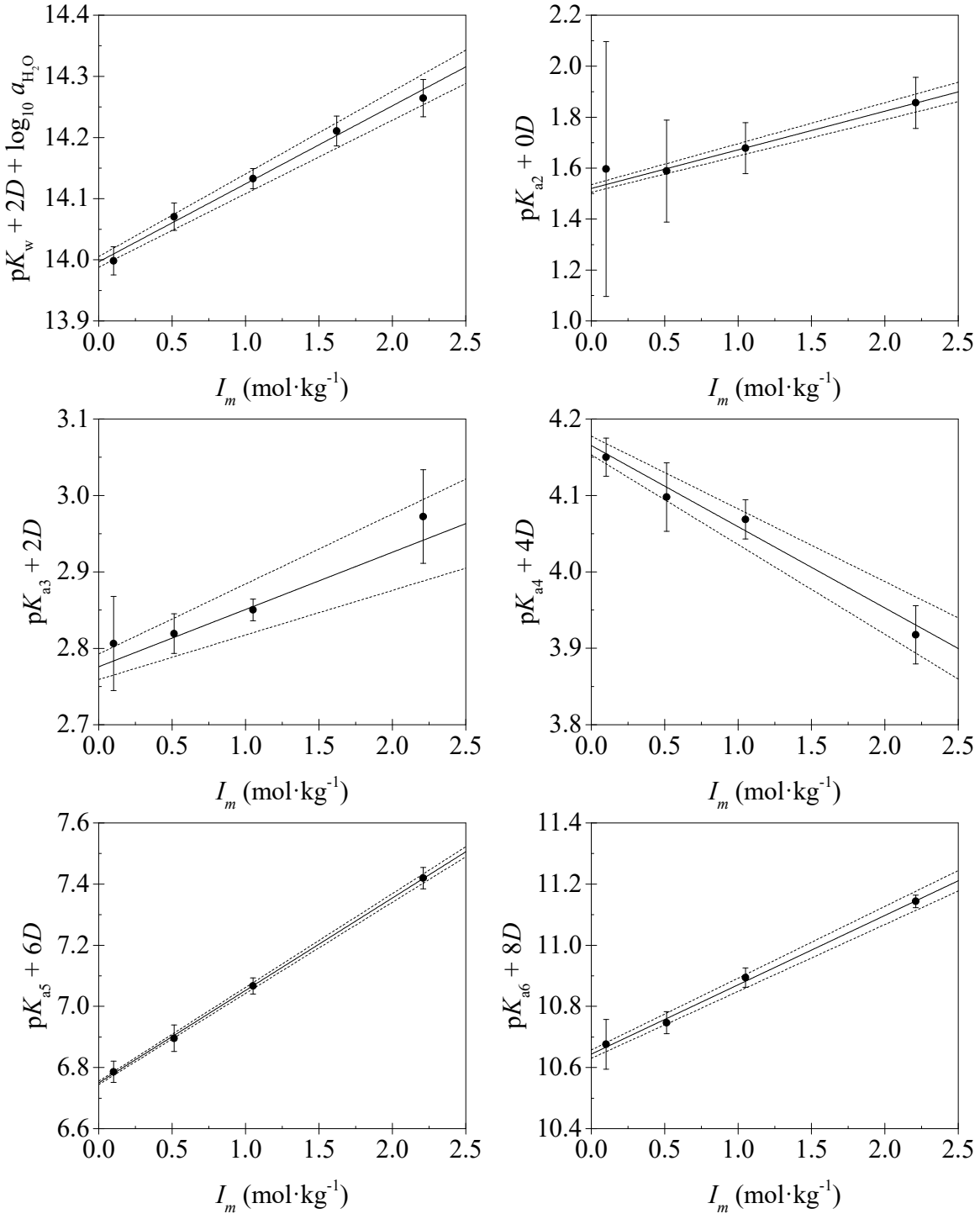


Fig. 3 Titration curves of CDTA at 0.10 mol·L^{-1} (□), 0.50 mol·L^{-1} (●), 1.00 mol·L^{-1} (△), and 2.00 mol·L^{-1} (◆) $NaClO_4$ ionic strength and 25.0 ± 0.1 °C. Titrand: 50.00 mL of 5.00×10^{-3} mol·L^{-1} CDTA/$NaClO_4$. Titrant: 0.1000 mol·L^{-1} NaOH/$NaClO_4$. Data points represent experimental data and solid lines are the calculated fits using the pK_w and pK_a values presented in Table 2



627
628 **Fig. 4** SIT plots of pK_w and CDTA pK_{ai} vs. I_m (molal scale) in $NaClO_4$ media at 25.0 ± 0.1 °C.
629 Error bars represent ±3σ from replicates (n = 4). Solid lines are the error weighted linear fits
630 obtained using Eqs. 7 or 8, while dashed lines represent the error limits obtained from the error
631 weighted least squares regression

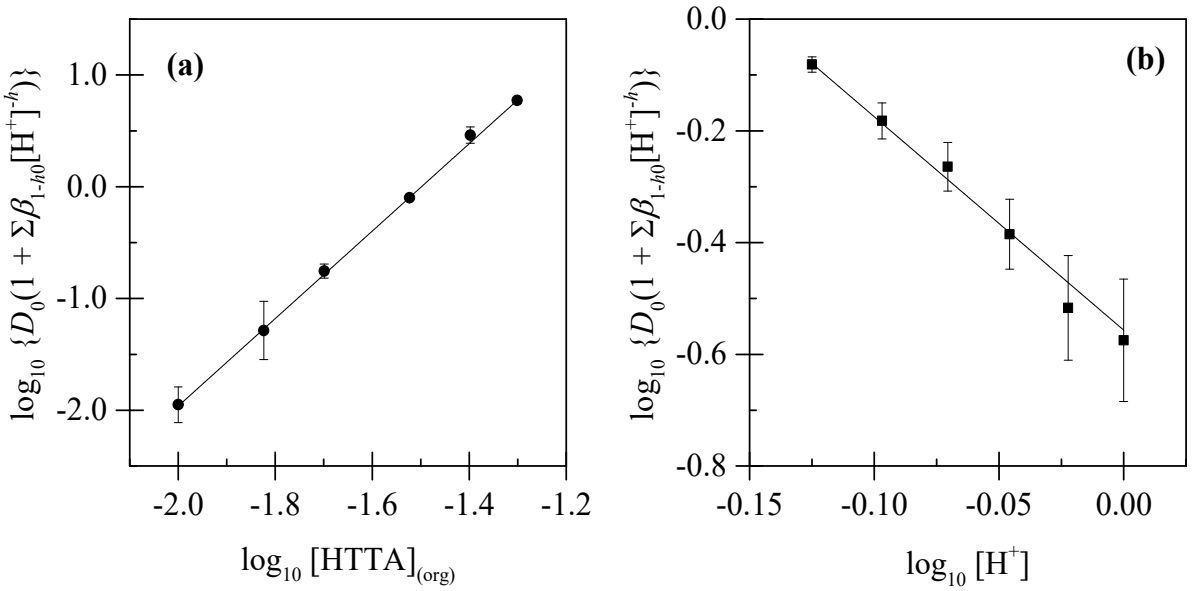


Fig. 5 Slope-analysis plots for the extraction of Pu(IV) from 1.00 mol·L^{-1} (Na,H)ClO$_4$ with TTA in *p*-xylene at 23 ± 1 °C. Error bars represent ±2σ from replicates (n = 3). **(a)** TTA dependence: ^{238}Pu(IV)/1.00 mol·L^{-1} HClO$_4$/0.010-0.050 mol·L^{-1} TTA/*p*-xylene. Slope = 3.9 ± 0.1. **(b)** H^+ dependence: ^{238}Pu(IV)/0.75-1.00 mol·L^{-1} HClO$_4$/NaClO$_4$/0.030 mol·L^{-1} TTA/*p*-xylene. Slope = −3.8 ± 0.2

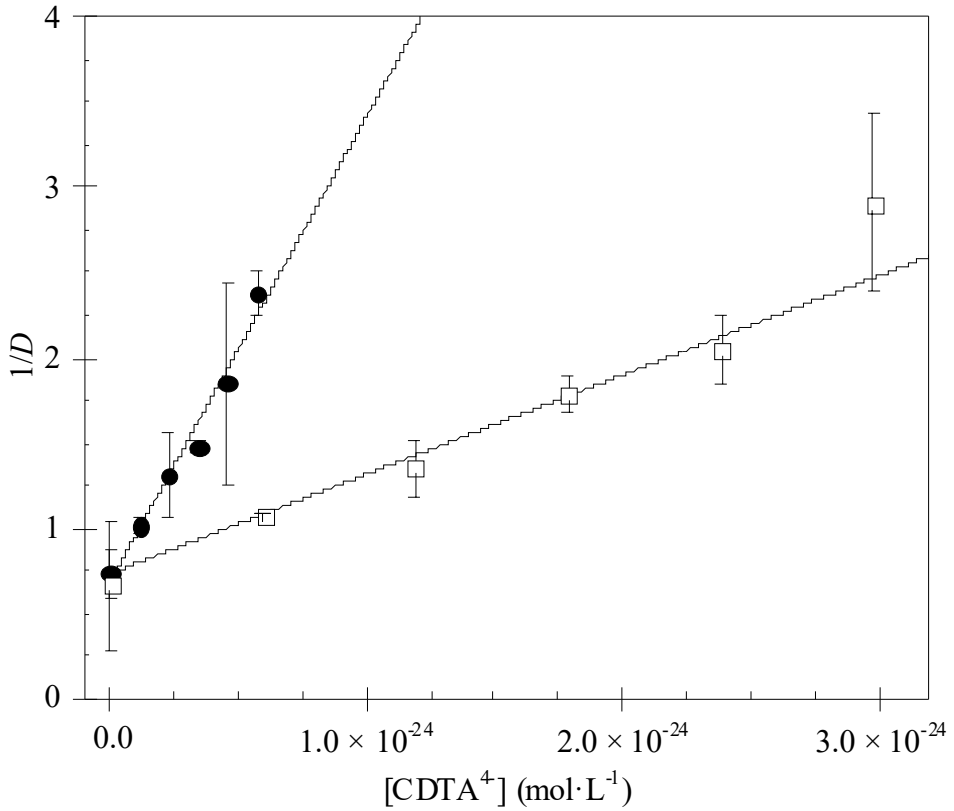


Fig. 6 Representative plots of $1/D$ vs. $[CDTA^{4-}]$ from the extraction system of $^{238}Pu(IV)$/1.00 mol·L^{-1} (Na,H)ClO_4/0.020 mol·L^{-1} TTA/*p*-xylene/23 ± 1 °C, at acidities of 0.40 mol·L^{-1} $HClO_4$ (●) and 0.30 mol·L^{-1} $HClO_4$ (□). Error bars represent $\pm 2\sigma$ from replicates ($n = 3$). The value of $1/D_0$ is obtained from the *y*-intercepts and the slopes are proportional to β^{app} from the error weighted least squares fitting. The changes in slope at different acidities indicate the presence of protonated Pu(IV)-CDTA complexes

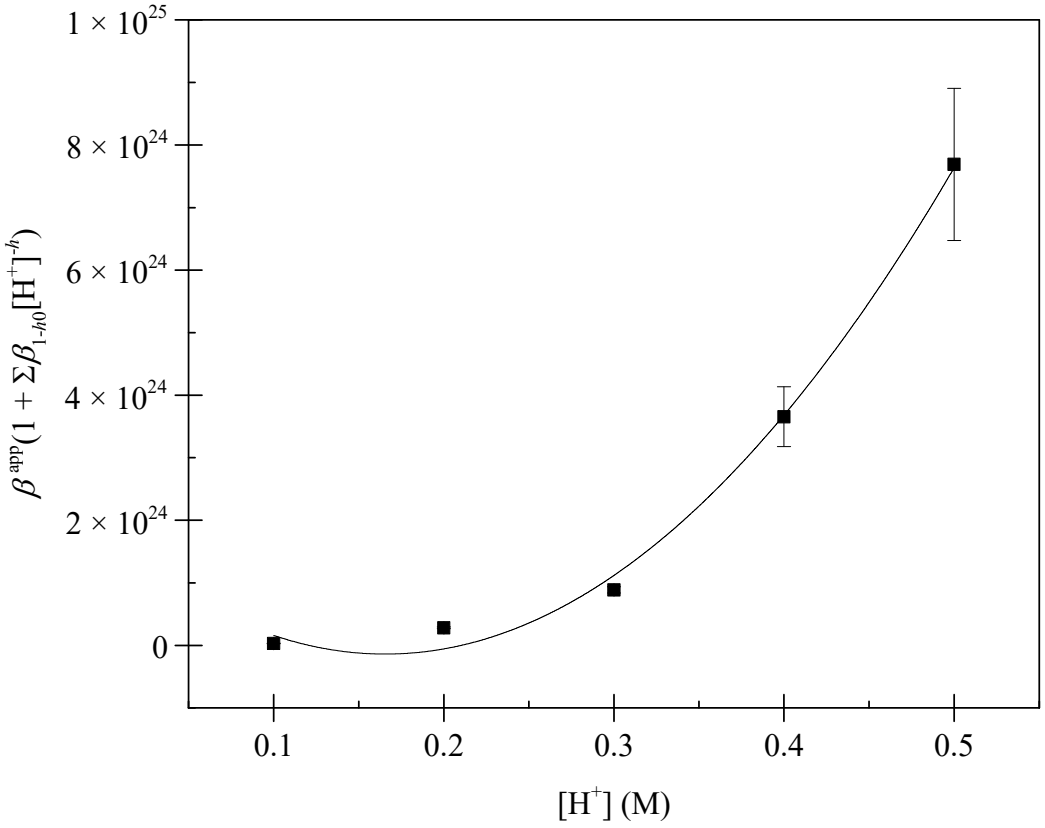


Fig. 7 Variation in the hydrolysis corrected, apparent stability constants of Pu(IV)-CDTA with $[H^+]$ at a total ionic strength of 1.00 mol·L^{-1} (Na,H)ClO$_4$ and 23 ± 1 °C. Error bars represent ±2σ from replicates (n = 3). This data can be found in the supplementary material (Table S6)

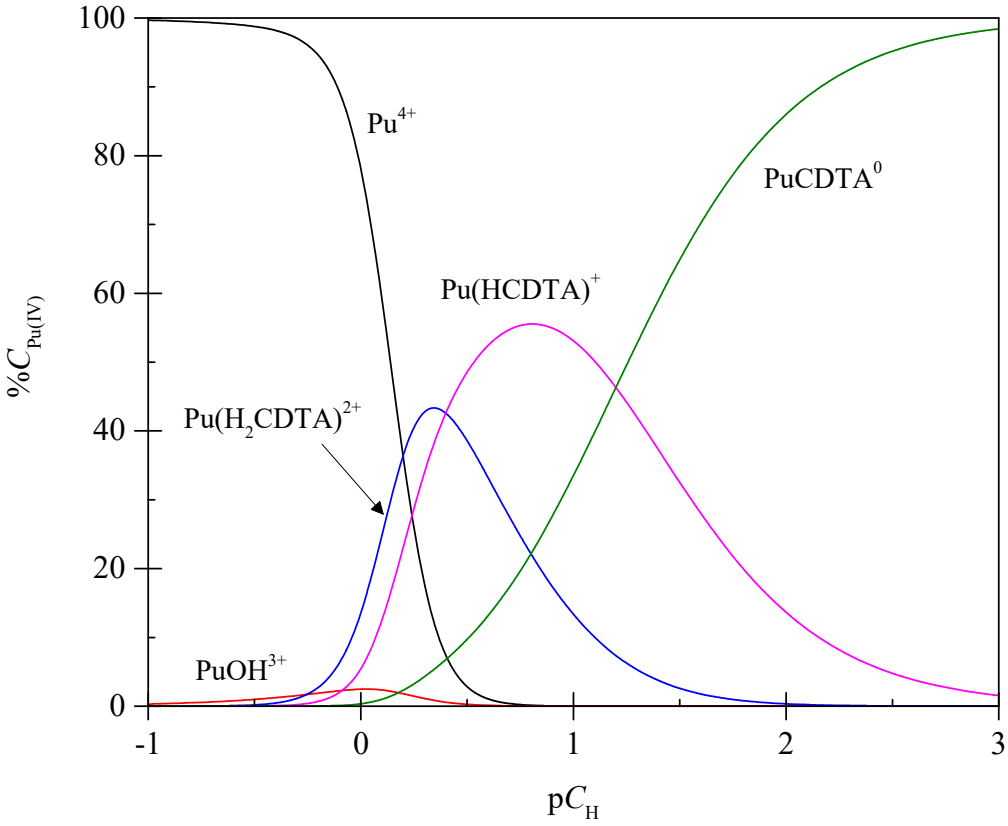


Fig. 8 Pu(IV)-CDTA speciation diagram constructed using [Pu(IV)] = 5×10^{-8} mol·L^{-1}, [CDTA] = 1×10^{-3} mol·L^{-1}, and the stability constants reported in this work at 1.00 mol·L^{-1} (Na,H)ClO$_4$ and 23 ± 1 °C