HEXAVALENT GROUP ACTINIDE SEPARATION: EXPLORATORY RESEARCH WITH COPPER (III) PERIODATE

by

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Applied Chemistry).

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ABSTRACT

More significant development of nuclear energy will require scientific advances in the proper management and disposal of used fuel. To reduce the long-term radiotoxicity hazard associated with nuclear waste, the most viable approach is the closed nuclear fuel cycle where actinides, namely U, Np, Pu, and Am, are recovered for transmutation into short-lived radioisotopes. If transmutation of actinides is to be completed, these actinides need be selectively recovered from fission products prior to fast reactor fuel assemblies. Separation of americium from trivalent lanthanides and trivalent actinides is one of the most difficult elemental separation steps due to their similar chemical behavior. One separation method under consideration is oxidization of americium to the hexavalent state, forming a linear dioxo cation (AmO$_2^{2+}$). Forcing americium to the hexavalent state provides a path for achieving a group hexavalent actinide separation from lanthanides, trivalent actinides, and remaining fission products. This work evaluates Cu$^{3+}$ periodate as an oxidant to accomplish a group hexavalent actinide separation with diamyl amylphosphonate (DAAP) and N$_2$N-dialkylamide (monoamide) extractants.

Oxidation of Np, Pu, and Am in molar nitric acid and subsequent extraction by DAAP was demonstrated using radiotracer methods and UV-Vis-NIR spectroscopy. The UV-Vis-NIR measurements showed Am$^{3+}$, AmO$_2^{+}$, and AmO$_2^{2+}$ species were present during extraction process while NpO$_2^{2+}$ and PuO$_2^{2+}$ displayed more stability in solution. Due to AmO$_2^{2+}$ reduction, phase contact times were limited to 5 seconds to obtain satisfactory extraction values. The interaction of Cu$^{3+}$ periodate with other metals encountered in the fuel cycle was also studied, and found to inhibit AmO$_2^{2+}$ extraction as well as form precipitates.

Straight and branched acyl chain monoamides were synthesized to study their selectivity towards hexavalent actinides. The branched monoamides were shown to be selective for PuO$_2^{2+}$
over Pu$^{4+}$. A UV-Vis analysis of organic phase Pu$^{4+}$ and PuO$_2^{2+}$ showed two species are extracted by straight and branched monoamide ligands. One species was a dinitrato charge neutral species extracted by monoamide, and the second was anionic species extracted by a protonated monoamide. Desirable AmO$_2^{2+}$ extraction values were achieved using straight chain monoamides pretreated with an oxidant while branched monoamides showed room for improvement.
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CHAPTER 1
INTRODUCTION

1.1 History of Americium

Americium, element 95, is a manmade element that was first isolated in 1944 at the Metallurgical Laboratory at the University of Chicago by Glenn T. Seaborg et. al.\textsuperscript{1,2} Production of americium was achieved by bombarding \(^{239}\text{Pu}\) with neutrons at Clinton Laboratories in Tennessee and the Hanford Engineer Works in Washington state which resulted in successive \((n,\gamma)\) reactions:

\[
^{\text{239}}\text{Pu}(n,\gamma)^{\text{240}}\text{Pu}(n,\gamma)^{\text{241}}\text{Pu}(n,\gamma)^{\beta^-} \rightarrow ^{\text{241}}\text{Am} + \bar{\nu}_e
\]

Neutron bombardment followed by beta decay of \(^{241}\text{Am}\) results in the production of \(^{242}\text{Cm}\), and is why Am and Cm were co-discovered between 1944 and 1945. Separation of Am and Cm from plutonium was done by dissolving the irradiated Pu tailings in acidic media and oxidizing Pu to the hexavalent state to generate a soluble fluoride compound. Seaborg assumed the new elements would behave more like lanthanides and maintain a trivalent state which form insoluble fluoride compounds in acidic media.\textsuperscript{1} The precipitate was redissolved to oxidize any residual Pu to Pu(VI) and reprecipitate the target elements.

The discovery of the two new elements was announced on the national radio program Quiz Kids on November 11\textsuperscript{th}, 1945 when a child asked Glenn T. Seaborg if any new elements like neptunium or plutonium had been discovered in the Metallurgical Laboratory. Since the discovery had been declassified, Seaborg confirmed the discovery of element 95 and 96. An official announcement was made the following week at an American Chemical Society symposium on November 16, 1945 at Northwestern University.\textsuperscript{3} Less than a year later, the name americium was suggested for element 95 to parallel its lanthanide homologue, europium. Curium was selected for element 96 after Pierre and Marie Curie since its homologue, gadolinium, was name after the
scientist Johan Gadolin. Prior to the established nomenclature, Tom Morgan, a scientist working with the new elements, referred to the elements as “pandemonium” and “delirium” due to how arduous it was to separate them from the lanthanide elements due to their near identical chemistries.

Currently, there are 20 isotopes of Am (\(^{230}\)Am to \(^{249}\)Am) that have half-lives varying from 17 seconds to 7364 years. The two primary isotopes are \(^{241}\)Am and \(^{243}\)Am which have half-lives of 432.6 and 7364 years, respectively. Kilogram amounts of these two isotopes have been produced from the Manhattan Project and commercial nuclear power reactors. The primary use of \(^{241}\)Am is in household smoke detectors, but is also used as a neutron source due to the \((\alpha,n)\) reaction when in the presence of beryllium. The specific activity of \(^{243}\)Am is lower than \(^{241}\)Am (approximately 17x), and is useful for experimental studies when exposure to radiation is of concern. Americium-243 is used as a target to produce heavier actinides such as \(^{249}\)Bk and \(^{252}\)Cf. Due to the limited commercial uses of the Am isotopes and long half-life’s, recovery of Am from used nuclear fuel rods has not been implemented in industrial reprocessing schemes. Instead, current schemes are designed to dispose used nuclear fuel in geological repositories. Currently, no geological repository has been established for the disposal of high-level waste (HLW). Disposing of used nuclear fuel in repositories is referred to as the open fuel cycle since it does not seek to recover fissionable U and Pu materials that can be recycled and used to produce more energy. This method increases the volume of high level waste (HLW) waste to be disposed of in non-existent geological repositories and results in inefficient use of uranium and plutonium resources.

Advanced nuclear fuel cycles aim to improve uranium fuel efficiency and decrease the amount of HLW, the overall radiotoxicity, and secondary waste produced during reprocessing. Recycling used nuclear fuel is referred to as the closed nuclear fuel cycle. One way to achieve a
closed nuclear fuel cycle is to selectively recover uranium, neptunium, plutonium, and americium after their production and partial consumption in a conventional (pressurized water or boiling water) nuclear reactor. After recovery, these actinides could be either placed back into a conventional reactor, plutonium or maybe uranium, for further power production, or transmuted in a fast neutron spectrum reactor, neptunium and americium, to decrease the decay timelines associated with these elements. Curium can also be produced in a conventional reactor and, if transmutation of americium is sought, it may be of interest to separate the americium from the curium. The curium isotope generally produced in a reactor, $^{244}\text{Cm}$, has an 18.1 year half-life. When $^{244}\text{Cm}$ decays to $^{240}\text{Pu}$ ($t_{1/2} - 6530$ years), the radioactivity decreases by several orders of magnitude and the fuel fabrication process is greatly simplified.

Separation of americium from curium is thought to be one of the hardest elemental separations in the periodic table due to their similar atomic radii and mutual stability as trivalent cations in aqueous solution. Due to their comparable chemistries, the trivalent $5f$ actinides follow trivalent $4f$ lanthanides in currently operated nuclear fuel cycles. Several options have been considered to accomplish an Am/Cm separation that would be compatible with advanced nuclear fuel cycle goals. One possible route is to remove Am from Cm and lanthanides after the hexavalent actinides (U, Np, and Pu) have been removed. This method involves a highly selective ligand that preferentially binds to Cm$^{3+}$ over Am$^{3+}$, utilizing the small differences in atomic radii. Alternatively, Am$^{3+}$ can be oxidized to AmO$_2^{+}$ (pentavalent) or AmO$_2^{2+}$ (hexavalent) cations which allows ligands to selectively remove Cm$^{3+}$ and trivalent lanthanides from the oxidized Am cations. Either method increases the amount of secondary waste volumes. A more direct approach is to remove Am along with U, Np, and Pu through a redox-based process.
1.2 Separation Chemistry of Americium

The ground state electron configuration of Am is $5f^7s^2$ and is similar to the ground state configuration of the lanthanide (Ln) series, $4f^{n-6}s^2$ (n = 6 to 14), which primarily prefer a trivalent state in solution. The similar Ln$^{3+}$ chemical behavior in solution is due to the $5d$ and $6s$ orbitals spatially extending beyond the valence $4f$ orbitals. Since the valence electrons are buried within the $6s$ and $5d$ orbitals the $4f$ electrons cannot participate in chemical bonding. Addition of more electrons across the series results in a lanthanide contraction going from 1.27 Å for La$^{3+}$ (CN = 9) to 0.985 Å for Yb$^{3+}$ (CN = 8). Due to the propensity to form Ln$^{3+}$ in solution and the similar atomic radii the lanthanides behave similar chemically.

Chemistry of the light actinides (Ac to Pu) is more complex due to the $6d$ and $5f$ orbitals being closer in energy than their lanthanide counterparts. In fact, the $6d$ orbitals are lower in energy than the $5f$ causing thorium’s ground state configuration to be $6d^27s^2$. Moving to heavier actinides, the energy of the $5f$ decreases and eventually become lower than the $6d$ orbitals causing plutonium’s ground state configuration to be $5f^67s^2$. The energy gap continues to widen and causes the heavy actinides (Cm to Lr) to have more lanthanide like behavior since the $5f$ valence electrons participate in bonding to a lesser degree. The ability of the $5f$ and $6d$ electrons to participate in bonding allows the light actinides to experience higher oxidation states (up to VII) and exhibit a more complex chemical behavior.

Americium straddles the light and heavy actinide chemical characteristics. As a light actinide, various oxidation states can be achieved under well controlled conditions. Owing to the heavy actinide characteristics, in solution americium is most stable as a trivalent cation, Am$^{3+}$, and has a 1.09 Å atomic radii (CN = 8) which is similar to trivalent lanthanides (Nd$^{3+}$ = 1.109 Å, CN = 8). As a result, when americium and lanthanides are encountered together in a sample, such as
used nuclear fuel rod, the separation of the constituents from each other is largely dictated by the trivalent actinide/lanthanide chemistries, and becomes a difficult task due to the similar atomic radii and identical oxidation states.

Although precipitation methods were developed for the initial purification of Am from plutonium and lanthanides, a solvent based separation process is preferred for high throughput extraction of americium.\textsuperscript{21} Solvent extraction relies on the ability for a target element, the solute, to be dispersed between two immiscible liquid phases.\textsuperscript{22} Initially, the solute is dissolved in one of the two phases, organic or aqueous. The two phases are then mixed together and the solute is distributed between the two phases until it reaches an equilibrium. Once equilibrium is reached, the solute has a certain concentration in the organic phase and another in the aqueous phase. The distribution of the solute between the solvents is referred to as the distribution value, represented by the equation:

\[ D = \frac{[M]_{org}}{[M]_{aq}} \]

Where D is the distribution value, brackets represent the concentration of the solute, M, in the organic (org) or the aqueous (aq) phase. A distribution value of 1 would mean the solute concentration is equivalent in the organic and aqueous phases. In other words, 50% of the solute is the aqueous phase and 50% is in the organic phase.

When elements are dissolved in solution they will exist in their ionic form, having a charge associated with them. The d-block and f-block metals, as discussed previously, will exist in various oxidation states as a cation. Since organic phases are non-polar the solute remains in the organic phase by forming a charge neutral adduct. The extraction of a metal into the organic phase, forming a charge neutral adduct, is done either with a solvating ligand or via ion exchange by an organic
When using solvating ligands, the metal cation becomes charge balanced through interactions with anionic species in solution. The extraction equation takes the general form of:

$$M_{aq}^{x+} + xA_{aq}^- + zL_{org} \rightarrow (MA_xL_z)_{org}$$

Where $M$ is the metal cation, $x$ is the cation charge, $A$ is the anion, $L$ is the ligand, and $z$ is the number of ligands needed to extract the charge neutral metal species. Conversely, instead of utilizing surrounding anionic species, organic acids exchange a proton ($H^+$) into the aqueous phase when extracting a metal cation. The extraction equation can be generally written as:

$$M_{aq}^{x+} + xHL_{org} \rightarrow (ML_x)_{org} + xH^+_{aq}$$

Where $M$ is the metal cation, $x$ is the cation charge, $HL$ is the organic acid, and $H^+$ is the proton that exchanges with the metal cation into the aqueous phase. Between the two ligand extraction types, solvating ligands perform better when the organic phase is mixed with aqueous phases containing molar acid concentrations. Ion exchange ligands perform best with sub molar acidic aqueous phases (pH 0 to pH 6).

Using ion exchange ligands, the TALSPEAK (Trivalent Actinide – Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes) process was developed in 1964 by Weaver and Kappelmann to separate $\text{Am}^{3+}$ and $\text{Cm}^{3+}$ from the lanthanides. The process utilizes di-(2-ethylhexyl)phosphoric acid (HDEHP), Figure 1.1, as an ion exchange ligand to extract the trivalent lanthanides. The HDEHP ligand exchanges three protons to extract the trivalent lanthanides and form a charge neutral species. Since HDEHP form dimers, and so while there is a three proton transfer, six HDEHP molecules are present in the extracted adduct. The separation of Am and Cm from the lanthanides occurs through the use of diethyleneetriaminepentaacetic acid (DTPA), Figure 1.1, to hold back $\text{Am}^{3+}$ and $\text{Cm}^{3+}$ in the aqueous phase in the presence of a buffer, lactic acid. Diethyleneetriaminepentaacetic acid is able...
to hold back Am$^{3+}$ over the trivalent lanthanides due to the slight extension of the $5f$ electrons compared to the $4f$ electrons of the lanthanides. The variance in the electronic structure between the hard acid actinide and lanthanide cations results in the actinides having a slightly softer character, and can bind more strongly to the hard base donor atoms like O and N.$^{24,25}$ A drawback to the TALSPEAK process is the slow kinetics and tight control of pH and lactic acid concentrations required. Solvating ligands provide faster kinetics and aren’t susceptible to small changes in the pH.

![Diagram of (A) di-(2-ethylhexyl)phosphoric acid (HDEHP) (B) diethylenetriaminepentaacetic acid (C) lactic acid molecules utilized in the TALSPEAK process to aid in purification of Am.]

The TALSPEAK process works without changing americium’s oxidation state. This is due to the high reduction potential required to oxidize Am$^{3+}$ to the hexavalent state, AmO$_2^{2+}$ (AmO$_2^{2+}$/Am$^{3+}$ 1.69 V).$^{26}$ Asprey et. al. first achieved hexavalent americium in 1950 by oxidizing
it with ammonium peroxydisulfate in 0.2 M nitric and perchloric acids. They found when peroxydisulfate was added, an AmF$_3$ precipitate did not form and indicated a different oxidation state was present in solution. Furthermore, they added sodium acetate to the solution which produced a yellow compound, NaAmO$_2$Ac$_3$, which is analogous to UO$_2^{2+}$ and PuO$_2^{2+}$. They also characterized the species using UV-Vis spectroscopy and found a large peak at 991 nm resulted after addition of oxidant, and noticed the 991 nm peak decreased over time producing AmO$_2^{2+}$. Shortly after the production of AmO$_2^{2+}$, it was realized addition of Ag$^+$ to the solution improved the oxidation and provided quantitative oxidation of Am$^{3+}$ to AmO$_2^{2+}$. From the use of the oxidants, the AmO$_2^{2+}$/Am$^{3+}$ reduction potential was estimated to be 2 volts since S$_2$O$_8^{2-}$/2SO$_4^{2-}$ reduction potential is 2.05 volts and Ag$^{2+}$/Ag$^+$ is 1.98 volts. Schulz established the reduction potentials using electrolytic oxidation of Am$^{3+}$ in perchloric acid media and found the AmO$_2^{2+}$/Am$^{3+}$ reduction potential to be 1.68 V vs. SCE (saturated calomel electrode), Figure 1.2. The high reduction potential of the AmO$_2^{2+}$/Am$^{3+}$ couple limited the oxidizing materials to strong oxidants such as (sodium, potassium, or ammonium) persulfates, ozone, and sodium perxenate.

Figure 1.2: Latimer diagram of Am reduction potentials (volts) in perchloric acid vs. SCE (saturated calomel electrode).

Once the different oxidation states were established, separation methods exploited americium’s different oxidation states to purify americium from trivalent lanthanides and curium.
The first methods utilized the formation of precipitates.\textsuperscript{13,28,30} After oxidizing Am\textsuperscript{3+} to AmO\textsubscript{2}\textsuperscript{2+} in 0.3 M perchloric acid, addition of 2 M sodium acetate generated an acetate solid of NaAmO\textsubscript{2}(O\textsubscript{2}C\textsubscript{2}H\textsubscript{3})\textsubscript{3}. The precipitate had no AmO\textsubscript{2}\textsuperscript{2+} or Am\textsuperscript{3+} absorption lines in the compound and indicated any reduced species remained in solution.\textsuperscript{28} Similarly, treatment of AmO\textsubscript{2}\textsuperscript{2+} generated no precipitate. However, a precipitate formed when a mixed Am\textsuperscript{3+}/AmO\textsubscript{2}\textsuperscript{2+} solution was treated with hydrofluoric acid due to Am\textsuperscript{3+} forming a AmF\textsubscript{3} precipitate.\textsuperscript{28} Taking advantage of trivalent actinides and lanthanides complexing with fluoride, oxidized americium was also ran over a column contained calcium fluoride.\textsuperscript{13} Hexavalent americium moves through the column while the trivalent species replace the calcium cation to bind with fluoride.

A solution based method developed in the late 1960’s by F. L. Moore used americium’s pentavalent state to achieve separation.\textsuperscript{8} First, the americium was oxidized using Ag\textsuperscript{+}/ammonium persulfate in dilute nitric acid. Ammonium acetate-acetic acid buffer was added to adjust the pH to 4.8 – 5.2 and reduce AmO\textsubscript{2}\textsuperscript{2+} to AmO\textsubscript{2}\textsuperscript{2+}. For the separation, 0.5 M 2-thenoyltrifluoroacetone in xylene was mixed with the solution. The 2-thenoyltrifluoroacetone extractant recovers trivalent actinides/lanthanides while the pentavalent AmO\textsubscript{2}\textsuperscript{2+} species remained in the organic phase. In the presence of fission product metal ions, a 91 ± 1% recovery of americium was achieved. Another method used bis(2,6-dimethyl-4-heptyl)phosphoric acid (HD(DIBM)P) to selectively extract AmO\textsubscript{2}\textsuperscript{2+} over Cm\textsuperscript{3+}.\textsuperscript{14} Americium was oxidized using the standard Ag\textsuperscript{+} and potassium persulfate oxidant in 0.025 to 0.2 M HNO\textsubscript{3}. Under 0.025 M HNO\textsubscript{3} conditions, an americium distribution value of 49 was achieved with 0.60 M HD(DIBM)P in n-heptane while Cm distribution values were below 6 x 10\textsuperscript{-6}.

While these oxidation separation methods showed promise, there were several drawbacks. As mentioned, the precipitation method is good at the bench scale, but is not suitable for high
throughput purification of Am from fission products. The HD(DIBM)P method was the most promising method, but works only under mildly acidic (\(pH = 1.6\)) conditions as persulfate does not oxidize Am in strong acid conditions. The current processes for recovery of used nuclear fuel materials employ molar nitric acid conditions. Therefore, methods for oxidizing americium under stronger nitric acid conditions have been investigated recently.

1.3 Actinide Recovery in Molar Nitric Acid Solutions

The current employed process for separation of nuclear fuel is based off the PUREX process (Plutonium Uranium Reduction EXtraction). The PUREX process utilizes the solvating ligand tri-n-butyl phosphate (TBP), Figure 1.3, to selectively remove \(\text{Pu}^{4+}\) and hexavalent, linear dioxo-cations \(\text{UO}_2^{2+}\) and \(\text{NpO}_2^{2+}\) from the fission products, \(\text{Cm}^{3+}\) and \(\text{Am}^{3+}\) in molar nitric acid solutions.\(^{32}\) As mentioned previously, the cations complex with nitrate anions and are subsequently extracted as a charge neutral species by TBP into an organic diluent such a kerosene or n-dodecane. The chemical equation for \(\text{Pu}^{4+}\) and \(\text{UO}_2^{2+}\) are as follows:

\[
\text{Pu}^{4+} + 4\ \text{NO}_3^{-} + \text{TBP}_{\text{org}} \rightarrow (\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP})_{\text{org}}
\]

\[
\text{UO}_2^{2+} + 2\ \text{NO}_3^{-} + \text{TBP}_{\text{org}} \rightarrow (\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP})_{\text{org}}
\]

Oxidation of \(\text{Am}^{3+}\) to the hexavalent state produces the linear dioxo-cation \(\text{AmO}_2^{2+}\), and can be separated using similar chemistry that removes \(\text{UO}_2^{2+}\), \(\text{NpO}_2^{2+}\), and \(\text{PuO}_2^{2+}\).\(^{20,33}\) The high reduction potential \(\text{Am}^{3+}\) to \(\text{AmO}_2^{2+}\) of 1.68 V (in 1 M HClO\(_4\)) requires the process to use strong oxidizers that work in molar nitric acid solutions.\(^{26,34-36}\) Recently, \(\text{Am}^{3+}\) was oxidized electrochemically over 7 hours to obtain 40% \(\text{AmO}_2^{+}\) and 53% \(\text{AmO}_2^{2+}\) using a terpyridine-derivitized indium-tin-oxide (ITO) electrode in 0.1 M nitric acid.\(^{34}\) While this technique was a significant technical breakthrough, limitations using the current ITO electrode for fuel cycle applications still exist. A group actinide recovery would be aided by oxidizing Am in molar acid
conditions more compatible with solvating extractants favored in fuel cycle separations, and having the majority of Am in the hexavalent state, as opposed to the less charge dense and poorly extracted pentavalent state.\(^{37}\)

Beginning in the 1950’s, the most commonly published method has used peroxydisulfate to oxidize Am.\(^{8,9,11-15,27,28,30,38}\) Addition of silver nitrate into the method was found to increase the oxidation efficiency of Am\(^{3+}\) to AmO\(_2^{2+}\).\(^{38}\) Kamoshida demonstrated Am oxidation in 1 M HNO\(_3\) using peroxydisulfate and silver; however, only 90% AmO\(_2^{2+}\) was generated in 1 M HNO\(_3\) with 1.5 M (NH\(_4\))\(_2\)S\(_2\)O\(_8\)/0.01 M AgNO\(_3\).\(^{15}\) Increasing the nitric acid concentration increased the decomposition of peroxydisulfate to peroxide, a reducing agent relative to AmO\(_2^{2+}\).\(^{11}\) Furthermore, peroxydisulfate decomposes to sulfate which is undesirable in waste reprocessing and interferes with waste vitrification.\(^{39}\)

\[
\text{Figure 1.3: Molecular structure of (A) tri-}n\text{-butylphosphate (TBP) ligand used in the PUREX process and (B) structure of diamyl amylphosphonate (DAAP) ligand.}
\]

Under molar acid concentrations, sodium bismuthate was shown to sufficiently oxidize Am\(^{3+}\) to AmO\(_2^{2+}\) in 0.5 to 2 M HNO\(_3\) by Hara and Suzuki in 1976.\(^{35}\) A total of 20 minutes was required to quantitatively oxidize Am in 0.5 M HNO\(_3\) at 20\(^\circ\) C while 2 M HNO\(_3\) required 40 minutes. Furthermore, increased temperatures decreased the time needed to achieve complete oxidation. Extractions using sodium bismuthate to form AmO\(_2^{2+}\) in molar nitric acid and extraction by TBP or diamyl amylphosphonate (DAAP), Figure 1.3, weren’t completed until the late 2000’s by Mincher et. al.\(^{33,40,41}\) In Mincher’s studies, americium was oxidized for 2 hours in 0.5 to 4.0 M
HNO₃ solutions and achieved quantitative oxidation (determined by UV-Vis). The actinides U, Np, Pu, and Am underwent sodium bismuthate treatment followed by extraction with 30% TBP in n-dodecane, Figure 1.4. The results show all four hexavalent actinides are extracted in appreciable amounts by the TBP solution. Most noteworthy result is the Am distribution value greater than 1 at 2 M HNO₃ and approaches 2 at 4 M HNO₃.

Figure 1.4: Extraction of the hexavalent actinides U, Np, Pu, and Am all treated by sodium bismuthate oxidation. The extraction of untreated Am⁴⁺ is also shown. Reprinted with permission.

Diamyl amylphosphonate (DAAP) was used in the subsequent studies since DAAP is a phosphonate extractant. The phosphonates have slightly more basic phosphoryl group compared to TBP’s phosphate oxygen.⁴⁰,⁴¹ Distribution values of 6 were achieved for sodium bismuthate oxidized americium extractions in up to 6 M HNO₃; however, results between the two studies for the same acid ranges (0.5 to 6 M HNO₃) were not consistent. The sodium bismuthate treated process has two major drawbacks. One is the long oxidation times (over 2 hours) needed prior to extraction. Secondly, sodium bismuthate is not soluble in the aqueous and organic phases. The
insolubility of sodium bismuthate potentially complicates the engineering design for liquid-liquid extractions using this oxidant. The recovery of oxidized Am using sodium bismuthate as an oxidant and octylphenyldiisobutylcarbamoylmethylphosphine (CMPO) as an extracting ligand was also considered.\textsuperscript{10} In this instance, the undesired recovery of Bi(III), present from reduction of Bi(V), out-competed Cm\textsuperscript{3+} and trivalent lanthanides for the CMPO ligand. Due to these short-comings, a soluble, strong oxidizer with innocuous degradation products is desirable for Am oxidation and extraction under molar acid concentrations.

<table>
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<th>HNO\textsubscript{3} (M)</th>
<th>% AmO\textsubscript{2}\textsuperscript{2+}</th>
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<tr>
<td>0.25</td>
<td>99.6</td>
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<tr>
<td>0.50</td>
<td>99.8</td>
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<tr>
<td>0.75</td>
<td>99.6</td>
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<tr>
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<tr>
<td>2.0</td>
<td>99.0</td>
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<td>3.0</td>
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Recently, Sergey I. Sinkov and Gregg J. Lumetta showed that Cu\textsuperscript{3+} periodate (Cu\textsuperscript{3+}/Cu\textsuperscript{2+} 2.0 V in water) was able to oxidize Am\textsuperscript{3+} to AmO\textsubscript{2}\textsuperscript{2+} in molar nitric acid.\textsuperscript{36} The study showed that periodate (IO\textsubscript{4}\textsuperscript{-} and/or H\textsubscript{5}IO\textsubscript{6}) does not oxidize americium in going from the heptavalent to pentavalent state (IO\textsubscript{4}\textsuperscript{-}/IO\textsubscript{3}\textsuperscript{-} 1.589 V).\textsuperscript{42} Furthermore, Sinkov found that an Am-iodate precipitate did not form which customarily happens with Am\textsuperscript{3+} and iodate, Am(IO\textsubscript{3})\textsubscript{3}.\textsuperscript{43-45} This indicated that periodate is stable in the acidic aqueous media and does not readily reduce to iodate under the conditions studied. Sinkov also determined by UV-Vis spectroscopy that a 10:1 molar excess of Cu\textsuperscript{3+} periodate:americium was needed to quantitatively oxidize americium, Table 1.1. Most
importantly, americium oxidation occurs rapidly in the aqueous media, and \( \text{Cu}^{3+} \) periodate and its reduced products are soluble in the aqueous phase. These are both advantages over the insoluble sodium bismuthate. The preliminary study by Sinkov and Lumetta paved the way for hexavalent actinide separation methods using the strong, soluble oxidant \( \text{Cu}^{3+} \) periodate with solvating extractant ligands, which is the focus of this dissertation.

### 1.4: C,H,O,N Based Extractants for Hexavalent Actinide Separation

The recovery of \( \text{UO}_2^{2+} \) and \( \text{Pu}^{4+} \) from irradiated U and Th fuels has been realized through the PUREX\textsuperscript{46} and THOREX (THORium EXtraction)\textsuperscript{47} processes, respectively. These processes utilize tri-n-butyl phosphate (TBP) and a hydrocarbon diluent such as kerosene or n-dodecane to remove the desired metal. Use of TBP in used nuclear fuel separation processes, while demonstrated as effective and viable, has several adverse effects, including: the inability to incinerate used solvent leading to large volumes of secondary low-level radioactive waste, generation of radiolytic degradation products that decreases the stripping efficiency of TBP, and third phase formation at high metal loading that impedes phase disengagement.\textsuperscript{48–52} An advancement in nuclear power technology would include the development of alternative extractants that overcome these unfavorable aspects in nuclear fuel recovery.

First explored by Siddall, the N,N-dialkyl aliphatic amide class of extractants has been reported to have several favorable features over organophosphorous ligands.\textsuperscript{48} Following the CHON principle (reagents composed exclusively of carbon, hydrogen, oxygen, and nitrogen), the incinerable nature of N,N-dialkyl amides decreases secondary waste volumes. Furthermore, the formation of innocuous degradation products (aqueous soluble carboxylic acids and amines) does not hinder stripping efficiency. This decreases the need for scrubbing steps that remove degradation products in engineered scale separations leading to a more simplified process. In
optimizing phase interaction and metal extraction, the synthetic tunability of dialkyl amides allows for systematic evaluations of their chemical and physical properties. For example, Siddall’s work supports the hypothesis that the interaction between the metal cation and monoamide ligand occurs at the acyl oxygen. Furthermore, it has been shown, by Siddall and others, that the identity of the acyl group has a profound effect on the extraction capabilities of the monoamide. Grouped as either a straight or branched monoamide (Figure 1.5) to describe the nature of the alkyl chain, the straight chain monoamides extract hexavalent and tetravalent actinides. Conversely, the branch chained monoamide selectively extracts hexavalent actinides. The hexavalent selectivity is a promising feature for group actinide separations being studied as a part of the oxidation of Am to the hexavalent state.

Figure 1.5: Structure of straight chain N,N-dihexylbutyramide (A) and branched N,N-dihexyl(2-methyl)butyramide (B).

1.5 Thesis Purpose and Outline

This dissertation focuses on developing a hexavalent group actinide separation process for the application of increased nuclear fuel economy and decreased radiotoxicity. The first chapter assesses whether a solvent extraction using Cu\(^{3+}\) periodate as an oxidant and diamyl amylphosphonate as an extractant can be achieved in the absence and presence of fission products typically encountered in the fuel process. The second chapter studies Cu\(^{3+}\) periodate’s ability to oxidize NpO\(_2^+\) and Pu\(^{4+}\), and uses UV-Vis-NIR to measure Np, Pu, and Am speciation in the organic and aqueous phases during solvent extraction. The third chapter consists of excerpts from
a review paper written on monoamides. The review focuses on branched monoamide’s ability to selectively extract hexavalent actinides over tetravalent actinides. The fourth chapter looks at how changes in monoamide chain length effects extraction of \( \text{Pu}^{4+} \), \( \text{PuO}_2^{2+} \), and \( \text{AmO}_2^{2+} \) species. The chapter also looks at hexavalent actinide extraction by monoamides using sodium bismuthate as an oxidant. Chapter 5 concludes the dissertation by summarizing the findings and makes suggestions for future research for achieving a hexavalent group actinide separation process.
CHAPTER 2

HEXAVALENT AMERICIUM RECOVERY USING COPPER(III) PERIODATE

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2.1 Abstract

Separation of americium from the lanthanides is considered one of the most difficult separation steps in closing the nuclear fuel cycle. One approach to this separation could involve oxidizing americium to the hexavalent state to form a linear dioxo cation while the lanthanides remain as trivalent ions. This work considers aqueous soluble Cu³⁺ periodate as an oxidant under molar nitric acid conditions to separate hexavalent Am with diamyl amylphosphonate (DAAP) in n-dodecane. Initial studies assessed the kinetics of Cu³⁺ periodate auto-reduction in acidic media to aid in development of the solvent extraction system. Following characterization of the Cu³⁺ periodate oxidant, solvent extraction studies optimized the recovery of Am from varied nitric acid media and in the presence of other fission product, or fission product surrogate, species. Short aqueous/organic contact times encouraged successful recovery of Am (distribution values as high as 2) from nitric acid media in the absence of redox active fission products. In the presence of a post-PUREX simulant aqueous feed, precipitation of tetravalent species (Ce, Ru, Zr) occurred and the distribution values of ²⁴¹Am were suppressed, suggesting some oxidizing capacity of the Cu³⁺ periodate is significantly consumed by other redox active metals in the simulant. The manuscript demonstrates Cu³⁺ periodate as a potentially viable oxidant for Am oxidation and recovery and

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notes the consumption of oxidizing capacity observed in the presence of the post-PUREX simulant feed will need to be addressed for any approach seeking to oxidize Am for separations relevant to the nuclear fuel cycle.

2.2 Introduction

Advanced nuclear fuel cycles aim to improve uranium fuel efficiency and decrease the amount of high-level waste (HLW), the overall radiotoxicity, and secondary waste produced during reprocessing. Only approximately five percent of the uranium in a nuclear fuel rod is consumed before fission products, particularly the lanthanides, prevent the efficient consumption of uranium in the power reactor. Lanthanides have relatively high neutron capture cross sections and recover neutrons through (n, γ) reactions that would otherwise forward the fission process in the reactor. One way to improve uranium fuel efficiency and decrease the amount of HLW developed during nuclear power production is to selectively recover uranium, neptunium, plutonium, and americium from the fission products after their production and partial consumption in a conventional (pressurized water or boiling water) nuclear reactor. After recovery, these actinides could be either returned to a conventional reactor (plutonium or uranium) for further power production or transmuted in a fast neutron spectrum reactor (neptunium and americium) to decrease the decay timelines associated with these elements.\(^5\)

The accessible redox chemistry of uranium, neptunium, and plutonium allows for relatively straightforward recovery of these elements away from the fission products, especially the lanthanides. Separation of americium from the lanthanides is thought to be one of the most difficult separations in closing the nuclear fuel cycle due to their mutual stability as trivalent cations in aqueous solution and affinity for hard acid donors.\(^5\) As a result of their comparable chemistry, the trivalent 5\(f\) actinides follow trivalent 4\(f\) lanthanides in currently operated nuclear fuel cycles.
Several options have been considered to accomplish trivalent actinides/lanthanide separations that would be compatible with advanced nuclear fuel cycle goals. Many of these approaches utilize soft donor (nitrogen, sulfur) complexants or extractants to selectively interact with the actinides over the lanthanides.\textsuperscript{55–58} These systems can produce separation factors as high as 10,000 between americium and europium but require the use of synthetically complex extractants, can be kinetically slow, or can be prohibitively sensitive to the harsh radiation environment presented from the irradiated nuclear fuel.\textsuperscript{59–61} Additionally, these methods would require the development of at least two separation steps, since the soft donor chemistry has not been optimized for the group recovery of uranium, neptunium, plutonium, and americium from the fission products. A more direct approach is to remove Am along with U, Np, and Pu after oxidation of the transuranics to the hexavalent state.\textsuperscript{13–15} This would decrease the amount of secondary waste volumes and would function more similarly to the internationally familiar plutonium uranium redox extraction (PUREX) process.

The PUREX process utilizes tri-n-butyl phosphate (TBP) to selectively remove hexavalent, linear dioxo actinides (e.g., UO$_2^{2+}$) and tetravalent actinides (e.g., Pu$^{4+}$), from the remaining fission products, Cm$^{3+}$ and Am$^{3+}$, in molar nitric acid solutions.\textsuperscript{32} Oxidation of Am$^{3+}$ to the hexavalent state produces the linear dioxo-cation AmO$_2^{2+}$, which can be separated using chemistry similar to that which removes UO$_2^{2+}$, NpO$_2^{2+}$, and PuO$_2^{2+}$.\textsuperscript{20,33} The significant 1.68 V oxidation potential of the AmO$_2^{2+}$/Am$^{3+}$ couple requires the process to use strong oxidizing agents.\textsuperscript{26,34} Several approaches have been used for americium oxidation, but these approaches are only effective in dilute (<0.1 M H$^+$) acid media,\textsuperscript{34} only oxidize americium to the pentavalent state, or use the insoluble sodium bismuthate oxidant.\textsuperscript{10,33,40,41} Possible separations in an advanced nuclear fuel cycle would benefit from separations compatibility with higher acid media, a soluble oxidant that
would simplify solvent extraction operations and have the majority of Am in an extractatable hexavalent state, as opposed to the less charge dense and poorly extracted pentavalent state.\textsuperscript{37}

Utilizing the strong Cu\textsuperscript{3+} to Cu\textsuperscript{2+} reduction potential (2.4 V), copper(III) periodate recently demonstrated effective oxidization of Am\textsuperscript{3+} to AmO\textsubscript{2}\textsuperscript{2+} in 0.25 to 3.5 M HNO\textsubscript{3} solutions.\textsuperscript{36} The oxidation of Am\textsuperscript{3+} to AmO\textsubscript{2}\textsuperscript{2+} was monitored using UV–visible spectroscopy. A 10:1 molar excess ratio of Cu\textsuperscript{3+} periodate to Am\textsuperscript{3+} resulted in 99\%+ conversion of Am\textsuperscript{3+} to AmO\textsubscript{2}\textsuperscript{2+} in 0.25 - 2 M HNO\textsubscript{3}. At 3 M HNO\textsubscript{3}, the conversion was 98\% and further decreased to 76.8\% in 3.5 M HNO\textsubscript{3}. Using the same stoichiometric ratio, NaBiO\textsubscript{3} in 3.5 M HNO\textsubscript{3} was found to oxidize only 19\% of Am\textsuperscript{3+}. Increasing the molar ratio of Cu\textsuperscript{3+} periodate to 20:1, Am\textsuperscript{3+} was oxidized with 95\% efficiency in 3.5 M HNO\textsubscript{3}. Post-oxidation, the resulting Cu\textsuperscript{2+} and periodate ions have the advantage of being soluble in nitric acid. There was an indication that periodate formed a complex with AmO\textsubscript{2}\textsuperscript{2+} in 0.25 M HNO\textsubscript{3} but was not present at elevated nitric acid concentrations.\textsuperscript{36} Similarly, the periodate anion has been reported to form complexes with UO\textsubscript{2}\textsuperscript{2+} at low acid conditions (pH 2.6).\textsuperscript{62}

The effective oxidation of Am\textsuperscript{3+} by Cu\textsuperscript{3+} periodate and benign degradation products in molar nitric acid are favorable for solvent extraction processes. However, the oxidation of Am\textsuperscript{3+} competes with the autoreduction of Cu\textsuperscript{3+} periodate in nitric acid. The autoreduction can explain why 20:1 Cu\textsuperscript{3+} periodate to Am molar ratio in 3.5 M HNO\textsubscript{3} was necessary for quantitative oxidation to occur. This manuscript assesses the reduction kinetics of Cu\textsuperscript{3+} periodate in nitric acid to evaluate whether its lifetime is suitable for application in solvent extraction processes. Following the reduction studies, oxidation of\textsuperscript{241}Am by Cu\textsuperscript{3+} periodate and extraction by diamyl amylphosphonate (DAAP) conditions were optimized, and separation of\textsuperscript{241}Am from a trivalent lanthanide surrogate,\textsuperscript{244}Cm, was demonstrated. A final study considers the recovery of americium from an aqueous nuclear fuel simulant feed that might be anticipated after uranium, neptunium, and plutonium recovery that
would happen during an initial PUREX-type cleanup to focus on fission product impacts on this chemistry. This manuscript will refer to this as a “post-PUREX” simulant.

2.3 Experimental Section

Synthesis of copper(III) periodate followed a method using potassium persulfate to oxidize copper. Using a 500 mL round-bottom flask, 3.12 g of CuSO$_4$·5H$_2$O (Mallinckrodt), 5.34 g of NaIO$_4$ (Acros organics), 16.04 g of KOH (Fisher), and 2.51 g of K$_2$S$_2$O$_8$ (Hach) were dissolved in 0.2 L of 18 MΩ H$_2$O. The mixture was refluxed for 30 min and then allowed to cool to room temperature. When cool, the solution was filtered through a glass fritted funnel. The filtrate was chilled in an ice bath to remove potassium sulfate. The solution was filtered once more through the glass fritted funnel. An 8 M NaNO$_3$ solution was added to the filtrate until crystals began to form. The solution sat overnight to allow the crystals to precipitate out. After crystallization, the solution was an opaque yellow color. The dark brown crystals were collected by filtration and rinsed with 18 MΩ H$_2$O until they began to dissolve in order to remove any excess KOH. Lastly, the crystals were dried in a lyophilizer, Labconco freeZone 6.

The copper percent was established by dissolving a known amount of copper(III) periodate in 4 M H$_2$SO$_4$. The brown copper(III) periodate color faded to the familiar light blue Cu(II) color. The absorbance of the Cu(II) peak at 805 nm was compared to a calibration plot of CuSO$_4$ in 4 M H$_2$SO$_4$. The copper percent was found to be 9.86 ± 0.03 wt %, which is higher than another reported literature value of 7.53% using the molecular formula Na$_5$[Cu{IO$_5$(OH)}$_2$]·12H$_2$O or 7.37% with Na$_5$[Cu{IO$_5$(OH)}$_2$]·14H$_2$O stoichiometry. The higher value is due to the lyophylizer’s ability to remove nearly all hydrated water. As a result, the stoichiometry was calculated to be Na$_5$[Cu{IO$_5$(OH)}$_2$]·H$_2$O using a measured average hydration state from copper mass analysis of 9.86%. Copper(III) periodate was dissolved in water for UV–vis spectroscopy analysis and
displayed the characteristic peaks at 420, 261, and 210 nm (Figure 1.1). An FT-IR was collected on a copper(III) periodate sample containing 7.1% Cu (close to 7.37% of Na$_5$[Cu{IO$_5$(OH)$_2$}\cdot 14$H$_2$O] and lyophilizer dried copper(III) periodate (9.86 ± 0.03 wt % Cu) (Figure 1.2).

Reduction of Cu$^{3+}$ periodate was monitored via UV–vis on an Olis RSM 1000 instrument. The stopped-flow mode was utilized to observe the reduction of the Cu$^{3+}$ peak (420 nm) at 21 scans per second for 1s. To monitor the reduction, equal volumes of 400 μM Copper(III) periodate in 18 MΩ H$_2$O and HNO$_3$ (Optima grade, Fisher) solution were injected into the stop-flow. Since equal volumes were mixed, the data is reported as the final HNO$_3$ concentration whereas the initial concentration of HNO$_3$, prior to injection, was twice the molarity. The stopped-flow mode is limited to the 235 nm collection window and cannot collect absorbance values below 250 nm, eliminating the ability to monitor periodate during the reduction. Using the normal scanning mode,
excess Cu$^{3+}$ periodate was reduced in a pH 3 HNO$_3$ solution. This allowed qualitative information to be collected on the periodate anion.

Prior to extraction studies, the $^{241}$Am stock from Eckert and Ziegler in 1 M HCl was converted to HNO$_3$ media by sequential evaporations of HCl, dilutions with optima HNO$_3$, and final dissolution in 0.1 M HNO$_3$. Solvent extraction experiments were carried out by weighing 20 mg of Cu$^{3+}$ periodate in a 2 mL glass vial. Extractant solution of 1 M DAAP (Eichrom) in n-dodecane (Fisher) was pre-equilibrated with equal volumes of the appropriate nitric acid solution for 15 min. The nitric acid solutions were freshly made with optima HNO$_3$ and 18 MΩ H$_2$O. The 0.1 M HNO$_3$ 241Am stock was spiked into the nitric acid solution being studied, 0.5–5 M HNO$_3$. Carrying out one extraction at a time, 500 μL of Am spiked nitric acid was added to 20 mg Cu$^{3+}$ periodate (62 mM) immediately followed by addition of 500 μL of pre-equilibrated 1 M DAAP.
The $^{241}\text{Am}$ activity of each sample was 0.0010 μCi resulting in a 2.6 nM $^{241}\text{Am}$ concentration. For complete oxidation, the 20:1 molar excess of $\text{Cu}^{3+}$ periodate to the tracer 2.6 nM $^{241}\text{Am}$ would equal an unfeasible 17 ng of $\text{Cu}^{3+}$ periodate. The 62 mM $\text{Cu}^{3+}$ periodate used is in significant ($\sim 10^7$) molar excess. This amount minimizes any effect from $\text{Cu}^{3+}$ periodate autoreduction and ensures $^{241}\text{Am}$ should be thoroughly oxidized prior to contact with the extractant solution. The vial was shaken by hand for 5 s and centrifuged for 30 s to promote phase disengagement. Both phases were sampled and counted on a Packard Cobra II autogamma counter and were found to have mass recoveries of 98 ± 4%.

The ability to oxidize and extract Am from solutions encountered in nuclear fuel recycling was tested on a post-PUREX simulant feed obtained from Pacific Northwest National Laboratory. This simulant contains Fe, Pr, Eu, Gd, La, Mo, Nd, Ru, Sm, Sn, Te, Zr, Sr, Pr, Y, and Ce in 2.9 M HNO$_3$. An analysis of the listed elements was completed on the simulant before and after contact with $\text{Cu}^{3+}$ periodate in 1:1 mol ratio using an inductively coupled plasma–optical emission spectrometer (ICP-OES). This analysis was completed using an iCAP 6500 Duo ICP-OES in axial mode purchased from Thermo Scientific (Waltham, MA). A five point calibration curve was prepared from gravimetric dilution of 1000 ppm single element standards obtained from High Purity Standards (Charleston, SC). The calibration curve standards and dissolved samples were prepared with 2% optima nitric acid. The elements Y and Ce could not be quantified using ICP-OES due to peak interference from other lanthanide elements. Cerium was of particular interest due to its ability to form a tetravalent cation, and its interaction with $\text{Cu}^{3+}$ periodate was therefore monitored using UV–vis spectroscopy. Extraction experiments were completed in the same manner as previously described. Since the post-PUREX simulant is in 2.9 M HNO$_3$, the aqueous phase oxidation time was monitored from 10 to 50 s prior to mixing with pre-equilibrated 1 M
DAAP for 5 s. The aqueous–organic contact times were adjusted from 5 to 30 s while maintaining a 10 s aqueous oxidation time. The $^{241}$Am mass recoveries were found to be $83 \pm 1\%$.

Curium extractions were done following the method described for Am. However, since $^{244}$Cm is not a strong gamma emitter, phases were counted using a Packard Tri-Carb 2500 Liquid Scintillation Counter. Triplicate extraction samples were collected and are reported as the mean value with less than 2% standard deviation. Each sample contained an initial $^{244}$Cm activity of 0.040 μCi, and mass recovery was 100 ± 2%. All extraction experiments were carried out with triplicate samples at room temperature, 24 ± 2 °C.

Caution! The isotopes $^{241}$Am and $^{244}$Cm are radioactive. All manipulations of the radioactive elements were safely handled in a radioactive designated fume hood.

2.4 Results and Discussion

2.4.1 Copper(III) Periodate Reduction

Reduction of Cu$^{3+}$ periodate was first monitored using UV-vis spectroscopy with 0.001 M HNO$_3$ solution in excess of Cu$^{3+}$ periodate and is presented in Figure 2.3. During reduction of Cu$^{3+}$ periodate, the periodate absorbance decreased and shifted to lower wavelengths. The Cu$^{3+}$ peak decreased linearly over time. The autoreduction of Cu$^{3+}$ periodate in excess nitric acid, presented in Figure 2.4A, followed pseudo-first order decay, and the rate of this reduction was seen to have an acid dependence. Figure 2.5 shows that the reduction rate increases as the concentration of acid increases from 0.05 to 0.5 M HNO$_3$. Figure 2.5 also demonstrates a saturation effect with respect to acid concentration on the rate of reduction. The role of periodate on Cu$^{3+}$ periodate autoreduction was also considered by adding sodium periodate in the presence of 0.5 M HNO$_3$, shown in Figure 2.4B. The observed reduction rate constants of Cu$^{3+}$ periodate in varying amounts of excess sodium periodate are presented in Table 2.1. Rate constant values show the reduction
rates decrease as the molar concentration of sodium periodate increases relative to Cu\(^{3+}\) periodate. This behavior matches what has been observed in the literature for Cu\(^{3+}\) periodate reduction under alkaline conditions.\(^{64,65}\)

While reduction of higher oxidation state metal periodates under basic conditions or neutral pH conditions has been assessed in the prior literature, reports in acidic media are nonexistent.\(^{64–66}\) This is a reflection of the limited stability of these metal salts under acidic conditions. The information presented in Figure 2.5 and Table 2.1 suggests the autoreduction mechanism for Cu\(^{3+}\) periodate under acidic conditions proceeds via a dissociative process.

![Figure 2.3: UV-Vis spectrum of Cu\(^{3+}\) periodate reduction in 0.001 M HNO\(_3\). The Cu\(^{3+}\) peak at 420 nm decreases over time. The periodate peak decreases and shifts to lower wavelengths.](image)
Table 2.1: Pseudo-1st Order Rate Constant for Cu$^{3+}$ Periodate Reduction in 0.5 M HNO$_3$ with Excess Periodate (Moles Cu$^{3+}$ periodate/Moles sodium periodate)$^a$

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>k (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4</td>
<td>1.38 ± 0.03</td>
</tr>
<tr>
<td>1:3</td>
<td>1.53 ± 0.07</td>
</tr>
<tr>
<td>1:2</td>
<td>1.62 ± 0.10</td>
</tr>
<tr>
<td>1:1</td>
<td>1.87 ± 0.09</td>
</tr>
<tr>
<td>1:0</td>
<td>2.04 ± 0.09</td>
</tr>
</tbody>
</table>

$^a$The rate of reduction decreases as concentration of periodate increases.

Table 2.2: Equilibrium Constants of Various Periodate Species at 25 °C$^a$

<table>
<thead>
<tr>
<th>Equation</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_5$IO$_6$ ⇌ H$_4$IO$_6^-$ + H$^+$</td>
<td>K = 5.1 x 10$^{-4}$</td>
</tr>
<tr>
<td>H$_4$IO$_6^-$ ⇌ H$_3$IO$_6^{2-}$ + H$^+$</td>
<td>K = 4.9 x 10$^{-9}$</td>
</tr>
<tr>
<td>H$_3$IO$_6^{2-}$ ⇌ H$_2$IO$_6^{3-}$ + H$^+$</td>
<td>K = 2.5 x 10$^{-12}$</td>
</tr>
<tr>
<td>H$_4$IO$_6^-$ ⇌ IO$_4^-$ + 2H$_2$O</td>
<td>K = 29</td>
</tr>
</tbody>
</table>

$^a$As pH increases, a progressive deprotonation and dehydration of periodate species occurs.$^{66}$
Prior to mixing, the Cu$^{3+}$ periodate solution has a pH of 10.33. Under these conditions, the Cu$^{3+}$ periodate complex predominately takes the form of [Cu(H$_2$IO$_6$)$_2$]$^{5-}$ with two orthoperiodate ions complexed to the Cu$^{3+}$. At this degree of protonation, orthoperiodate allows for bidentate coordination to the metal; therefore, the two ligands satisfy the coordination number of the square-planar Cu$^{3+}$. This configuration gives the Cu$^{3+}$ redox stability in solution. Studies in alkaline media have suggested that when one orthoperiodate ion dissociates from the complex the Cu$^{3+}$ becomes accessible to reductants. This dissociation process matches the observations made under acidic conditions in this study. The small protonation equilibrium constants of H$_3$IO$_6^{2-}$, H$_4$IO$_6^-$, and H$_5$IO$_6$ indicate protonation is thermodynamically favorable under acidic conditions. The equilibrium constants for these are listed in Table 2.2. As one of the orthoperiodate anions leaves the Cu$^{3+}$ complex, the periodate becomes protonated and reformation of the complex with Cu$^{3+}$ is inhibited. This results in the coordination environment around the complex being unfilled and leaves the Cu$^{3+}$ available to complex with reductants causing Cu$^{3+}$ reduction to proceed more readily under higher acid concentrations.

Figure 2.5: Acid dependency of observed rate constants for the reduction of Cu$^{3+}$ periodate upon mixing with nitric acid.
The chemical species most likely being oxidized by Cu\(^{3+}\) is H\(_2\)O to O\(_2\). The high concentration (relative to other species in solution) and oxidation potential for the H\(_2\)O to O\(_2\) (1.22 V in pH 0) is well within the oxidative capacity of Cu\(^{3+}\) (2.4 V in water at 25°C).\(^{42}\) Addition of excess periodate, Table 2.1, in the system momentarily shifts the protonation equilibrium of orthoperiodate ligands and impedes the reduction rate. The observations made in this kinetic study appear to suggest the autoreduction of Cu\(^{3+}\) periodate proceeds via a dissociative process; however, these results alone are insufficient to fully interpret the reaction mechanism and rate law. The acid saturation effect on the rate (Figure 2.5) does however suggest the reduction rate of Cu\(^{3+}\) periodate will not be further affected by the higher acid concentrations relevant to the americium oxidation.

### 2.4.2 Actinide Solvent Extraction Studies

The impact of copper periodate on a uranium recovery by DAAP, a solvating ligand, in molar acid media (a standard solvent extraction reaction without the possibility of reduction of the metal ion) is presented in Figure 2.6. Metal ion extraction by DAAP from nitrate media generally proceeds as follows

\[
M^{x+} + x\text{NO}_3^- + y\text{DAAP} \rightarrow M(\text{NO}_3)_x(\text{DAAP})_y
\]

Where no overbar denotes a species in the organic phase and \(y\) varies between two and three depending on how many extractants are required to saturate the extracted metal’s coordination sphere. A slight decrease in uranium recovery is observed when the acid concentration is 0.5 M HNO\(_3\). This may be related to periodate complexing of the uranyl cation at low acidities.\(^{41,62}\) This study observed \(D = 79 \pm 14\) when Cu\(^{3+}\) periodate is present and 87 \(\pm 18\) without periodate at 24 °C. Distribution ratios are within experimental error in the presence and absence of Cu\(^{3+}\) periodate between 1 and 5 M HNO\(_3\). The results show Cu\(^{3+}\) periodate did not impact extraction of uranyl
cation by DAAP in molar nitric acid; therefore, it seems possible that Cu$^{3+}$ periodate would not impact other hexavalent actinide chemistries in the separation system.

![Figure 2.6: Distribution of $^{233}$U from 0.5 M to 5 M HNO$_3$ and 1 M DAAP in n-dodecane in the presence (square) and absence (circle) of Cu$^{3+}$ periodate.](image)

Distribution values for $^{241}$Am using 1 M DAAP from 0.5 to 5 M HNO$_3$ oxidized by Cu$^{3+}$ periodate and in the absence of Cu$^{3+}$ periodate are presented in Figure 2.7. All values presented in Figure 2.7 are the mean of triplicate samples with a relative standard deviation less than 13%.

The results show americium has higher recovery when Cu$^{3+}$ periodate oxidizes Am than when no oxidizer is present. Since DAAP preferentially extracts hexavalent cations over trivalent cations, this suggests oxidation of the Am to the hexavalent state is occurring in the solvent extraction system. A UV-vis analysis, Figure 2.8, shows the AmO$_2^{2+}$ peak at 666 nm in 1 M HNO$_3$ which matches that observed by Sinkov and Lumetta and confirms AmO$_2^{2+}$ is present prior to extraction by DAAP.$^{36}$ Under both extraction conditions, the distribution ratios increase between 0.5 and 1 M HNO$_3$. After reaching a maximum distribution ratio of 0.99 ± 0.04 at 1 M HNO$_3$, the distribution...
ratios steadily decrease as nitric acid concentration increases. The same trend is observed when the Cu$^{3+}$ periodate oxidant is not present and trivalent americium should predominantly be in solution. This suggests the suppressed distribution ratio is due to the increased competition of nitric acid, which is known to be extracted by solvating organophosphorus extractants, like diamyl amyl phosphonate.$^{67}$

![Figure 2.7: Distribution of 241Am in the presence of Cu$^{3+}$ periodate oxidant (red ■) and absence of any oxidant (blue ▲) from 0.5 to 5 M HNO$_3$ and 1 M DAAP in n-dodecane.](image)

To evaluate the robustness of $^{241}$Am recovery, one study considered the general presence of organic reductants by varying the aqueous/organic phase mixing times. The distribution ratios shown in Figure 2.9 as mean values with less than 8% relative standard deviation, decreased as the contact time between the two phases increased from 5 to 30 s. A second test considered the role of aqueous reductants by varying the americium/Cu$^{3+}$ periodate contact time from 10 to 50 s prior to contact with 1 M DAAP for 5 s. The americium/Cu$^{3+}$ contact data, also presented in Figure 2.9 as a triplicate mean with less than 6% relative standard deviation, shows the distribution remains constant under extended oxidation times prior to interfacing with the organic phase. While
optimizing extraction conditions, a dark brown to yellow color in the aqueous phase, indicating the presence of Cu$^{3+}$ periodate, was observed to subside after mixing aqueous/organic phases for 35 – 40 s. In the americium/Cu$^{3+}$ contact experiments, the aqueous solution remained dark brown even at 50 s prior to contact with the organic phase. The presence of oxidant continues to reoxidize any reduced species of americium and makes it available for extraction by DAAP. Absence of Cu$^{3+}$ periodate in the aqueous phase after contact with 1 M DAAP for 40 s versus its persistence after 50 s without organic contact suggest 1 M DAAP in $n$-dodecane solution encourages reduction. This suggest reduction of either americium or Cu$^{3+}$ periodate by the organic phase may be a limiting factor in a solvent extraction system designed to recover hexavalent americium under acidic conditions.

![UV-Visible spectrum](image)

Figure 2.8: UV-Visible spectrum of 3.0 mM Am in 1 M HNO$_3$ with 20 mg of Cu$^{3+}$ periodate. Due to $^{241}$Am high specific activity, $^{243}$Am was used for the UV-Vis analysis, and the spectrum was collected using a Spectral 420 CCD Array UV-Vis Spectrometer. The sharp peak at 666 nm is indicative of AmO$_2^{2+}$. The Cu$^{3+}$ periodate is present as indicated by the large shoulder below 660 nm. The spectrum is consistent with spectra presented by Sinkov.$^{36}$
2.4.3 Extraction Reproducibility Using DAAP

Comparing literature uranium distribution values at 2 M HNO₃, Siddall reported D = 450 with 1.1 M DAAP in n-dodecane at 30 °C. Mincher et al. reported D = 350 at 2 M HNO₃ for 1 M DAAP in n-dodecane at 19 °C. Results from this study, D = 80, are slightly higher than Brahmananda Rao et al. who reported D = 65 for 2 M HNO₃ with 1.1 M DAAP/n-dodecane at 30 °C. The literature presents significant variability in metal distribution values between studies for even more straightforward, redox inert systems.

The Am studies in this work present differences in Am partitioning and seemed to be dependent on the DAAP chemical lot used from Eichrom. Under similar conditions, Am extractions completed with DAAP lot #ER-145-135 (Figure 2.7) and lot #998082 (Figure 2.9),
produced distribution ratios of 0.99 ± 0.04 and 1.8 ± 0.2, respectively, at 1 M HNO$_3$. A recent report from Idaho National Laboratory (INL) has observed similar variations in Am recovery based on the DAAP lot. $^{69}$ Lot numbers for INL investigations were ER-145-141 and 998107. A definitive origin for the variations in metal ion partitioning may stem from the synthesis of the DAAP molecule. DAAP is frequently synthesized using a Michaelis-Becker or Michaelis-Arbuzov reaction.$^{68}$ Either of these reactions could allow for the formation of trace phosphinates instead of a phosphate. Trace phosphinates could impact radiotracer distribution studies and might be below the detection limit of the 400 MHz liquid NMR use for characterization. An early report from Horwitz notes distillation of DAAP at 105 °C prior to completing investigations.$^{70}$ This may be a crucial step in improving the reproducibility of studies using DAAP with radiotracers.

### 2.4.4 Americium Separation from a Trivalent f-Element

The efficacy of americium separation from a trivalent $f$-element that should be inert to oxidation under these conditions, curium, was assessed using the optimized Cu$^{3+}$ periodate extraction by DAAP. The distribution ratios of $^{241}$Am and $^{244}$Cm in the presence of varying acid content are presented in Figure 2.10 as the mean of triplicate samples with less than 10% relative standard for $^{241}$Am. Distribution values of Cm in the presence of Cu$^{3+}$ periodate are presented in Figure 2.10 as a mean of triplicate samples with less than 2% for $^{244}$Cm. As the data shows, the extraction of Cm does not substantially increase in the presence of Cu$^{3+}$ periodate. The oxidation and increased extraction of $^{244}$Cm are unlikely since the 3.0 V Cm$^{4+}$ to Cm$^{3+}$ electrochemical potential is well above the 2.4 V Cu$^{3+}$ to Cu$^{2+}$ potential. The increase could be a result of minor salting out effect by the periodate anion. However, it could also be from $^{244}$Cm to decay to $^{240}$Pu. The $^{240}$Pu would be oxidized to hexavalent state and extracted out.
Figure 2.10: Distribution of $^{241}$Am in the presence of Cu$^{3+}$ periodate (red ■), $^{244}$Cm in the presence of Cu$^{3+}$ periodate (gray ●), $^{244}$Cm in the absence of Cu$^{3+}$ periodate (○), and separation factors $D_{\text{Am}}/D_{\text{Cm}}$ (blue ▲) from 0.5 to 5 M HNO$_3$ with 1 M DAAP in n-dodecane.

Previous efforts have compared the selectivity of oxidized Am recovery with more redox inert Cm. The overall trend and distribution ratios are comparable to Mincher et al., who also shows $^{244}$Cm distributions decrease with increased nitric acid concentration. The separation factors ($D_{\text{Am}}/D_{\text{Cm}}$), presented in Figure 2.10, of $^{241}$Am from $^{244}$Cm are 5.4, 6.4, 6.2 for 2, 3, and 4 M HNO$_3$, respectively. The oxidized $^{241}$Am/$^{244}$Cm separation factor at 3 M HNO$_3$ of 6.4 is comparable to the dipicolinic acid-functionalized crown ether Am$^{3+}$/Cm$^{3+}$ separation strategy that presents a separation factor of 6.5. The Cu$^{3+}$ periodate oxidized $^{241}$Am had a higher separation factor of 5.4 at 2 M HNO$_3$ compared to a separation factor of approximately 2 for $^{243}$Am oxidized...
by sodium bismuthate. At 4 M HNO₃, the sodium bismuthate oxidized ⁴¹⁺ Am was found to have a separation factor of approximately 9 while this study achieved a value of 6.2. The results show separation of Cu³⁺ periodate oxidized ⁴¹⁺ Am from a trivalent f-element is plausible over a broad range of acid conditions. In fact, the best separations are observed at acid concentrations comparable to the PUREX process, between 3 and 4 M HNO₃.

### 2.4.5 Post-PUREX Am Recovery

Table 2.3: Determined Metal Concentration (mM) in PNNL Post-PUREX Simulant by ICP-OES Before and After Addition of Cu³⁺ Periodate to the Solution

<table>
<thead>
<tr>
<th>element</th>
<th>Post-PUREX stock concentration (mM)</th>
<th>Post-PUREX after Cu³⁺ periodate addition (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.096 ± 0.003</td>
<td>0.121 ± 0.004</td>
</tr>
<tr>
<td>Sr</td>
<td>2.26 ± 0.07</td>
<td>2.12 ± 0.07</td>
</tr>
<tr>
<td>Zr</td>
<td>7.4 ± 0.2</td>
<td>0.062 ± 0.002</td>
</tr>
<tr>
<td>Mo</td>
<td>4.4 ± 0.1</td>
<td>3.16 ± 0.09</td>
</tr>
<tr>
<td>Ru</td>
<td>2.73 ± 0.08</td>
<td>0.038 ± 0.001</td>
</tr>
<tr>
<td>Pd</td>
<td>0.090 ± 0.003</td>
<td>0.120 ± 0.004</td>
</tr>
<tr>
<td>Sn</td>
<td>0.111 ± 0.003</td>
<td>0.0049 ± 0.0002</td>
</tr>
<tr>
<td>Te</td>
<td>0.55 ± 0.02</td>
<td>0.53 ± 0.02</td>
</tr>
<tr>
<td>La</td>
<td>2.23 ± 0.07</td>
<td>2.15 ± 0.06</td>
</tr>
<tr>
<td>Pr</td>
<td>1.81 ± 0.05</td>
<td>1.89 ± 0.06</td>
</tr>
<tr>
<td>Nd</td>
<td>7.3 ± 0.2</td>
<td>6.8 ± 0.2</td>
</tr>
<tr>
<td>Sm</td>
<td>2.96 ± 0.09</td>
<td>1.21 ± 0.04</td>
</tr>
<tr>
<td>Eu</td>
<td>0.295 ± 0.009</td>
<td>0.286 ± 0.009</td>
</tr>
<tr>
<td>Gd</td>
<td>0.232 ± 0.007</td>
<td>0.223 ± 0.007</td>
</tr>
</tbody>
</table>

The same experimental design was applied to separate ⁴¹⁺ Am from the post-PUREX simulant obtained from Pacific Northwest National Laboratory. Prior to the ⁴¹⁺ Am extractions, Cu³⁺ periodate was added to the simulant in a 1:1 molar ratio (Cu³⁺ periodate to total metal concentration) to observe any effects. Upon addition, a white precipitate formed. To assess which metals formed the precipitate, ICP-OES analysis was completed on the simulant before and after Cu³⁺ periodate addition (Table 2.3). Of the listed metals, the concentration of Zr, Sn, and Ru decreased substantially from 7.4, 0.111, and 2.73 mM to 0.062, 0.0049, and 0.038 mM,
respectively. Precipitation of Zr\(^{4+}\) by periodate has been demonstrated previously under similar nitric acid conditions.\(^{71}\) The study found the precipitate to be a 1:1 composition of Zr\(^{4+}\) to periodate with the formula ZrHIO\(_6\)-4H\(_2\)O. Tetravalent Sn has also been reported to form a precipitate with periodate as SnIO\(_6\)^-.\(^{66,72}\) A ruthenium periodate solid complex has been reported to form as Na\(_6\)[Ru(OH)\(_2\)(IO\(_6\))\(_2\)].\(^{73,74}\)

![Figure 2.11: The UV-Vis spectra of 15 mM H\(_2\)Ce(NO\(_3\))\(_6\) in 3 M HNO\(_3\) (black). Addition of 20 mg Cu\(^{3+}\) periodate caused a light yellow to white precipitate to form. The solution was centrifuged prior to recollecting a UV-Vis spectra. The results show the amount of Ce\(^{4+}\) dropped significantly, and there was an ingrowth of Cu\(^{2+}\) from reduction of Cu\(^{3+}\) (blue). Similarly, addition of 20 mg sodium periodate resulted precipitate formation and a decrease of the Ce\(^{4+}\) signal in the UV-Vis spectrum (orange).](image)

To a lesser extent, Mo (4.4 to 3.16 mM) and Sm (2.96 to 1.21 mM) concentrations also decreased. The Mo periodate species has been found to be dependent on pH.\(^{66}\) In acidic solutions, an IMo\(_6\)O\(_{24}\)^{5+} complex forms where on orthoperiodate molecule is surrounded by six MoO\(_6\) molecules.\(^{75}\) Literature on lanthanide periodate complexes is sparse, and literature on Sm periodate
solid precipitate is nonexistent. It is not apparent what caused the Sm concentration to decrease because trivalent lanthanide Sm is not expected to complex well with periodate. Cerium, on the other hand, has a 1.72 V Ce$^{4+}$ to Ce$^{3+}$ potential and can be oxidized by Cu$^{3+}$ (2.4 V).\textsuperscript{42} Cerium is present in the post-PUREX simulant but could not be analyzed using ICP-OES due to interfering peaks. Instead, the UV-vis of Ce$^{4+}$ in 3 M HNO$_3$ was monitored before and after addition of periodate and Cu$^{3+}$ periodate (Figure 2.11). After addition of periodate or Cu$^{3+}$ periodate, a light yellow to white precipitate formed and was separated from the solution via centrifugation. The supernatant spectra clearly show a decrease in the Ce$^{4+}$ shoulder peak corresponding to the precipitation of Ce$^{4+}$ with periodate. The solid Ce$^{4+}$ complex has been reported to form in nitric acid as CeHIO$_6$.\textsuperscript{76} The precipitation of Ce$^{4+}$ foreshadows the effect of periodate on actinides not discussed in this manuscript, namely, Th, Np, and Pu. As a tetravalent, precipitation of Th$^{4+}$ with periodate has been demonstrated to form a ThHIO$_6$ complex. The elements Np and Pu are expected to be oxidized given their NpO$_2^{2+}$ to NpO$_2^{+}$ 1.24 V and PuO$_2^{2+}$ to Pu$^{4+}$ 1.05 V potentials. On the basis of the Ce$^{4+}$ precipitation, incomplete oxidation of Pu$^{4+}$ could cause a precipitation to form. Oxidation of Np and Pu by Cu$^{3+}$ periodate studies are currently being assessed.

To date, the recovery of hexavalent americium in the presence of other species anticipated to be present in a used nuclear fuel aqueous processing stream has not been considered. This study considered how americium recovery, while in the presence of Cu$^{3+}$ periodate, would be affected by the presence of other metals found in the nuclear fuel recycling process. The oxidation time of the post-PUREX simulant containing $^{241}$Am with Cu$^{3+}$ periodate was increased from 10 to 50 s prior to contact with DAAP for 5 s. During oxidation time, the precipitate formed and was separated out from the solution via centrifugation. Shown in Figure 2.12, the distribution of $^{241}$Am did not change with contact time.
The average $^{241}$Am distribution ratio of 0.40 ± 0.03 is higher than the 0.19 ± 0.01 value obtained for Am$^{3+}$ under the same acidic conditions (3 M HNO$_3$). This indicates $^{241}$Am is still being oxidized and extracted by DAAP. On the other hand, the 0.40 distribution ratio is lower than the 1.8 ± 0.2 distribution ratio obtained in the absence of other metals at 3 M HNO$_3$ (Figure 2.10). Holding the oxidation time constant at 10 s, the mixing time between aqueous and organic phases was increased from 5 to 30 s. The results, Figure 2.12, show the distribution ratio begins at 0.39 ± 0.03 and decreases to 0.27 ± 0.03 as contact times increases. The decreasing distribution ratio is similar to the trend observed in the aqueous HNO$_3$ contacts. This further shows that while Am is being extracted, it is most likely reduced to the unfavorably extracted trivalent and pentavalent...
cations. The mass balance of $^{241}$Am in both experiments with the used nuclear fuel simulant was $81 \pm 1\%$.

The lower mass balance can be indicative of this phase formations or integration of Am into a precipitate. A third phase was not observed and can be ruled out. Sykora et al.\textsuperscript{44} have noted the formation of an Am$^{3+}$ precipitate upon mixing with periodate, and several papers have discussed hydrothermal synthesis of Am crystals with iodate, the reduced form of periodate.\textsuperscript{43–45}

In addition to precipitate formation of the other metal species, it is possible that Am$^{3+}$ precipitated out resulting in the 81% mass balance. It should be noted that periodate itself, although a strong oxidizer ($1.65$ V IO$_4^-$ to IO$_3^-$), does not have the capacity to oxidize Am$^{3+}$ to AmO$_2^{2+}$ and AmO$_2^{2+}$ periodate precipitates have not been observed.\textsuperscript{36,43,45} Although the $^{241}$Am distribution ratio was suppressed, any separation process developed to streamline advanced fuel cycle separations by americium oxidation will need to address the possibility of distribution ratio suppression in the presence of other metal species that will be oxidized by the strong oxidizers being studied (Cu$^{3+}$ periodate, sodium bismuthate, electrochemical or silver ozone).

2.5 Conclusion

The oxidant Cu$^{3+}$ periodate was found to autoreduce in nitric acid via an inner sphere mechanism. Addition of excess sodium periodate decreased the rate of Cu$^{3+}$ reduction and indicated dissociation of the periodate anion from the metal cation complex as the rate limiting step. Although oxidations of Am$^{3+}$ is competing with the autoreduction of Cu$^{3+}$ periodate, extraction of oxidized $^{241}$Am by DAAP was achieved. Extending the $^{241}$Am oxidation time in nitric acid did not impact the distribution values but values decreased with increased aqueous/organic contact times. The inability of Cu$^{3+}$ periodate to oxidize and affect the extraction of Cm resulted in practical separation of oxidized $^{241}$Am from trivalent $f$-element under molar acid conditions.
analogous to the currently employed PUREX used in the nuclear fuel cycle process. The post-PUREX simulant investigations suggest further research in this area will need to address recovery of americium in the presence of other species that will most likely be present during used nuclear fuel recycle. Future experiments will extend the use of Cu\(^{3+}\) as an oxidizer to other actinides, investigate the use of other extractants for oxidized Am recovery, and examine the partitioning of fission products in the solvent extraction system.
CHAPTER 3

ORGANIC AND AQUEOUS REDOX SPECIATION OF COPPER (III) PERIODATE

OXIDIZED TRANSURANIUM ACTINIDES

Kevin McCann, Sergey I. Sinkov, Gregg J. Lumetta, Jenifer C. Shafer

3.1 Abstract

A hexavalent group actinide separation process could streamline used nuclear fuel recycle and waste management. The limiting factor to such a process compatible with current fuel dissolution practices is obtaining and maintaining hexavalent Am, AmO$_2^{2+}$, in molar nitric acid due to the high reduction potential of the Am(VI)/Am(III) couple (1.68 V vs SCE). Two strong oxidants, sodium bismuthate and Cu$_3^+$ periodate, have demonstrated quantitative oxidation of Am under molar acid conditions and better than 50% recovery by diamyl amylphosphonate (DAAP) is possible under these same conditions. This work considers the use of Cu$_3^+$ periodate to oxidize Np(V) to Np(VI) and Pu(IV) to Pu(VI) and recover these elements by extraction with DAAP. A metal:oxidant ratio of 1:1.2 and 1:3 was necessary to quantitatively oxidize Np(V) and Pu(IV), respectively, to the hexavalent state. Extraction of hexavalent Np, Pu, and Am by 1 M DAAP in n-dodecane was measured using UV-Vis (PuO$_2^{2+}$, AmO$_2^{2+}$) and NIR (NpO$_2^{2+}$). Distribution values of AmO$_2^{2+}$ were found to match previous tracer level studies. The organic phase spectra of Np, Pu, and Am are presented and molar absorptivities are calculated for characteristic peaks. Hexavalent Pu was found to be stable in the organic phase while NpO$_2^{2+}$ showed some reduction to NpO$_2^+$ and Am was present as Am$_3^{3+}$, AmO$_2^+$, and AmO$_2^{2+}$ species in aqueous and organic phases during the extraction experiments. These results demonstrate, for the first time, the ability

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to recover macroscopic amounts of americium that would be present during fuel reprocessing and are the first characterization of Am organic phase oxidation state speciation relevant to a hexavalent group actinide separation process under acidic conditions.

3.2 Introduction

The management of use nuclear fuel (UNF) is a challenge faced around the world with a variety of approaches employed. The United States (U.S.) currently participates in an open nuclear fuel cycle where UNF, upon removal from a reactor, is planned for direct disposal in a permanent geological repository. The use of an open nuclear fuel cycle has two main disadvantages. One disadvantage arises from the nuclear fuel being removed from a power reactor when approximately five percent of the available energy has been consumed. This removal is necessary due to the ingrowth of neutron siphoning fission products formed over the course of uranium and plutonium fission. These fission products recover neutrons via neutron capture reactions that compete with the neutron induced fission reactions that propagate the nuclear chain reaction necessary for energy production. The second drawback is the U.S. currently does not have a sited geological repository for commercial high-level waste. Even if the formerly considered site for high level waste, Yucca Mountain, were to open, the current UNF inventory would exceed its the capacity. The limiting capacity of a given geological repository and limited utilization of the uranium and plutonium resources encourages consideration of alternative strategies to manage used nuclear fuel.

Other nations, such as United Kingdom, France, and Japan participate in a partially closed nuclear fuel cycle, where UNF is recycled to more fully recover energy from the fuel and decrease nuclear waste volume. Recycling of UNF is enabled by separating uranium and plutonium from neutron siphoning fission products, namely lanthanides, which force the removal of the inefficient nuclear fuel from the reactor. This separation is frequently accomplished using the Plutonium
Uranium Reduction Extraction process (PUREX) or some close derivative. Under current use, the PUREX process seeks to separate only uranium and plutonium from used nuclear fuel, but recovery and fission-based transmutation of neptunium and americium, radionuclides that contribute significantly to the UNF heat load or long waste management timelines, could increase the capacity and decrease the waste management timelines of a given repository. Recovery and transmutation of the actinides uranium through americium actinides is frequently referred to as a closed nuclear fuel cycle.

A complication associated with the closed nuclear fuel cycle is efficient recovery of Am from fission product lanthanides. The separation of Am from the lanthanides is difficult due to their common oxidation states, comparable atomic radii and tendency to participate in largely ionic interactions caused by the contraction of the 4f and 5f orbitals within the 6s and 7s valence shells. A common approach is to use soft-donor, such as nitrogen, ligands that will selectively complex Am over the lanthanides since the actinides seem able to participate in limited covalent interactions with these donors. An approach like this is non-ideal since an earlier separation step, and therefore an additional reprocessing facility, is necessary to recover U, Np, and Pu. A more streamlined approach, where U through Am actinides are co-recovered in a single step, would be preferred to minimize the number of necessary reprocessing facilities and cost.

The group separation of the U through Am actinides has been proposed by recovering these elements using their common hexavalent state, where the actinides form an extractable and unique linear dioxo cation (AnO$_2^{2+}$). While uranium generally prefers the hexavalent state, and neptunium or plutonium can be readily oxidized to the hexavalent state$^{42}$, oxidation of americium requires the use of strong oxidants, such as sodium bismuthate or Cu$^{3+}$ periodate, that can overcome the AmO$_2^{2+}$/Am$^{3+}$ 1.68 V standard reduction potential.$^{34}$ Several recent reports have
demonstrated recovery of americium under these highly oxidizing conditions, but assessment of the americium oxidation state recovered into the organic phase has yet to be completed. The reduction of \( \text{AmO}_2^{2+} \) to the poorly extracted \( \text{AmO}_2^+ \) in the organic phase has been cited as a potential reason for the short aqueous/organic contact times necessary for effective Am recovery. Finally, while the solubility of \( \text{Cu}^{3+} \) periodate may make it a viable oxidant for this separations approach, the efficiency of Np and Pu oxidation by \( \text{Cu}^{3+} \) periodate has not been assessed.

This study characterizes the organic and aqueous phase redox speciation of the redox variable Np, Pu, and Am transuranic species as well as the efficacy of Np and Pu oxidation to the hexavalent state by \( \text{Cu}^{3+} \) periodate under relevant conditions to UNF processing. These assessments were completed using UV-visible spectroscopy, a technique being developed for on-line monitoring systems to allow real time analysis of actinide concentrations during reprocessing. To complete these studies, the conditional extinction coefficients in the aqueous and organic phases were assessed.

This study has several significant findings: 1) The efficacy of \( \text{Cu}^{3+} \) periodate as an oxidant to drive Np(V) and Pu(IV) to the hexavalent state is demonstrated and increasing excesses of \( \text{Cu}^{3+} \) periodate are necessary to complete quantitative oxidation moving from Np to Pu to Am. 2) These are the first distribution values assessed for using macroscopic amounts of americium in a solvent extraction system relevant to a hexavalent group actinide separation process under acidic conditions. The comparability of the macroscopic measurements to radionuclide studies is an encouraging validation of radionuclide techniques to effectively model more applicable fuel cycle conditions where millimolar amounts of americium will be present. 3) This is the first characterization of americium redox speciation in the organic phase following oxidation by either sodium bismuthate or \( \text{Cu}^{3+} \) periodate and recovery by diamyl amylphosphonate (DAAP).
Reduction of AmO$_{2}^{2+}$ to AmO$_{2}^{+}$ was observed and provides further evidence that Am reduction to lower oxidation states following extraction to the organic phase is a limiting factor in development of hexavalent-based U, Np, Pu, Am actinide separations.

### 3.3 Experimental

The Cu$^{3+}$ periodate oxidizer was synthesized following previously described procedure.$^{63,85}$ Manipulation of radioactive elements $^{237}$Np, $^{239}$Pu, and $^{243}$Am was done in radioactive designated fume hoods in the Radiochemical Processing Laboratory at Pacific Northwest National Laboratory. All UV-Vis measurements were collected using Ocean Optics fiber optic cables and a Spectral 420 Spectrophotometer. The oxidation state of $^{237}$Np was carefully controlled by first converting a $^{237}$Np stock to NpO$_{2}^{2+}$. The NpO$_{2}^{2+}$ stock was reduced to NpO$_{2}^{+}$ by addition of hydrazine. The NpO$_{2}^{+}$ stock was diluted in a sealable glass test tube to 800 µL in 1 M HNO$_{3}$ (Optima grade, Fisher) for a final concentration of 10 mM (8 µmol) NpO$_{2}^{+}$. The oxidation of 8 µmol NpO$_{2}^{+}$ was done incrementally by adding 2.4 µmol solid Cu$^{3+}$ periodate (30% of 8 µmol) to the vial, a UV-Vis spectrum was measured, Cu$^{3+}$ periodate addition and measurement was repeated two more times, and 2.8 µmol Cu$^{3+}$ periodate was added for the final measurement. To obtain Pu$^{4+}$, 30% H$_{2}$O$_{2}$ was added to the stock solution to reduce any higher oxidation state Pu species. Tetravalent $^{239}$Pu was then diluted to 800 µL in 1 M HNO$_{3}$ for a final 12.5 mM concentration (10 µmol) Pu$^{4+}$. Copper(III) periodate was added incrementally in three 6 µmol additions to the Pu$^{4+}$ solution. For the final addition, 7 µmol Cu$^{3+}$ periodate was added to the solution.

Extraction studies of $^{237}$NpO$_{2}^{2+}$, $^{239}$PuO$_{2}^{2+}$, and $^{243}$Am (initially in the +6 oxidation state) from HNO$_{3}$ by 1 M DAAP (Eichrom, used as received) were monitored using UV-Vis for $^{239}$Pu and $^{243}$Am, and an Ocean Optics NIR-512 spectrophotometer was used to monitor $^{237}$Np. A NpO$_{2}^{+}$/NpO$_{2}^{2+}$ stock solution was diluted to 14 mM in 2 M HNO$_{3}$. To oxidize NpO$_{2}^{+}$ to the
hexavalent state 20 mg Cu\(^{3+}\) periodate was added to the solution, and monitored using UV-Vis to ensure the solution was 100% NpO\(_2^{2+}\). An equal volume (800 µL) of 1 M DAAP pre-equilibrated with nitric acid in n-dodecane was added to the oxidized NpO\(_2^{2+}\) solution and vortexed for 5 seconds. Near-infrared spectra of the two phases, separated by centrifugation, were collected and then the solutions were vortexed again for 5 seconds. This was repeated 5 times for a collective total of 30 second phase mixing time. The same procedure was repeated for 3.1 mM PuO\(_2^{2+}\) solution. Hexavalent Pu was obtained by oxidizing a stock solution with HClO\(_4\). The HClO\(_4\) was evaporated off until wet crystals formed and was diluted with HNO\(_3\). The evaporation and dilution of PuO\(_2^{2+}\) containing stock was completed with 1 M HNO\(_3\) two additional times. Hexavalent \(^{243}\)Am separations were done by adding 20 mg Cu\(^{3+}\) periodate to 3.0 mM \(^{243}\)Am\(^{3+}\) in 1, 2, 3, and 4 M HNO\(_3\) solutions. These solutions were then contacted with an equal volume of nitric acid, pre-equilibrated 1 M DAAP. The phases were vortexed for 5 seconds, and separated by centrifugation. Americium oxidation state speciation was determined by using polynomial fits to baseline the Am\(^{3+}\) (503 nm), AmO\(_2^{+}\) (513 m), and AmO\(_2^{2+}\) (666 nm) UV-Vis peaks in the aqueous phases and Beer’s law.

### 3.4 Stoichiometric oxidation Results and Discussion

The aqueous NpO\(_2^{+}\) UV-Vis spectrum undergoes several changes after the addition of Cu\(^{3+}\) periodate. Figure 3.1 shows a shoulder appear below 500 nm. Within the shoulder region, the 428 and 476 nm peak decrease in intensity, and the 476 nm peak broadens. The intensity of the broad peak at 555 nm increases while the 770 nm broad peak decreases. The most prominent peak at 617 nm and two sharp peaks at 688 nm and 917 nm decrease. These changes are consistent with a decrease in NpO\(_2^{+}\) concentration. The concomitant ingrowth of the shoulder peak, broadening of 428 nm peak, and increased intensity of the 555 nm peak indicate NpO\(_2^{2+}\) is being generated. The
ingrowth of a large, broad peak between 580 and 950 nm is a signature of Cu$^{2+}$ and is consistent with reduction of Cu$^{3+}$ to Cu$^{2+}$. To remove the Cu$^{2+}$ interference, the 688 nm peak was baselined using a polynomial fit, and changes in aqueous NpO$_2^+$ concentration was calculated using Beer’s Law. A molar absorptivity of 2.1 M$^{-1}$cm$^{-1}$ was calculated using the baselined 688 nm peak (Figure 3.2) prior to Cu$^{3+}$ periodate addition.

![Absorbance vs Wavelength graph](image)

**Figure 3.1:** Oxidation of 8.0 µmol NpO$_2^+$ in 1 M HNO$_3$ (black dotted line) to NpO$_2^{2+}$ (blue) by incremental addition of Cu$^{3+}$ periodate (2.4 µmol Cu$^{3+}$ periodate = red, 4.8 µmol = orange, 7.2 µmol = green, 10 µmol = blue).
Figure 3.2: UV-Vis of NpO$_2^{+}$ oxidation to NpO$_2^{2+}$ by Cu$^{3+}$ periodate. A polynomial fit (dot black line) was used to remove Cu$^{2+}$ peak interference from the 688 nm NpO$_2^{+}$ peak (left). The baseline corrected 688 nm peak used to calculate NpO$_2^{+}$ concentration (right).

Three sequential additions of Cu$^{3+}$ periodate (2.4 µmol each) to a NpO$_2^{+}$ solution (8.0 µmol total) in 1 M HNO$_3$ resulted in 2 µmol (83% efficiency), 1.9 µmol (79% efficiency) and 1.8 µmol (75% efficiency) of NpO$_2^{2+}$ formation. All NpO$_2^{+}$ was converted to NpO$_2^{2+}$ when 2.8 µmol Cu$^{3+}$ periodate was added in the final addition. The slight decrease from 2 µmols to 1.8 µmols NpO$_2^{+}$ being oxidized after each addition is most likely due to the ingrowth of a broad NpO$_2^{2+}$ peak that interferes with the 687 nm NpO$_2^{+}$ signature. Oxidation of NpO$_2^{+}$ to NpO$_2^{2+}$ is a one electron transfer process; similarly, Cu$^{3+}$ is reduced by one electron to Cu$^{2+}$ during the process. Therefore, a 1:1 mole ratio of NpO$_2^{+}$ to Cu$^{3+}$ would theoretically produce 100% NpO$_2^{2+}$. However, the first three measurements show an 81% oxidation efficiency in 1 M HNO$_3$ for a 1:1 mole ratio of NpO$_2^{+}$ to Cu$^{3+}$ periodate. The 81% oxidation efficiency perhaps occurs due to Cu$^{3+}$ periodate oxidizing water or from reduction by nitric acid before it can oxidize NpO$_2^{+}$.$^{85}$ Therefore, to achieve complete NpO$_2^{+}$ oxidation under these conditions a 1:1.2 mole ratio is required.

In nuclear fuel processing schemes Pu is primarily found in the Pu$^{4+}$ state and requires a two electron oxidation to achieve the hexavalent state. Due to the one electron reduction of Cu$^{3+}$ to Cu$^{2+}$, a 1:2 stoichiometric ratio of Pu$^{4+}$:Cu$^{3+}$ is theoretically required to oxidize Pu$^{4+}$ to PuO$_2^{2+}$. 


Upon addition of 6 µmol Cu$^{3+}$ periodate to the 10.2 µmol Pu$^{4+}$ solution, a pink precipitate formed making the solution opaque and unsuitable for a UV-Vis measurement. The vial was centrifuged to concentrate the precipitate at the bottom and a clear supernatant for UV-Vis analysis was made available. Figure 3.3 shows a comparison of the before and after oxidized plutonium containing solution. Prior to oxidation the solution is 99%+ Pu$^{4+}$ as indicated by the shoulder peak below 400 nm, the sharp peak at 476 nm and broad peaks from 500 to 900 nm.$^{2,87-89}$ In nitric acid solution Pu$^{4+}$, slowly disproportionates to Pu$^{3+}$ and PuO$_2^{2+}$. The small peak at 832 nm shows some PuO$_2^{2+}$ is present. After the oxidation, there is an ingrowth of the prominent PuO$_2^{2+}$ peak at 832 nm occurs, as well as sharp peaks at 623, 504, 458 nm and two broad peaks at 521 and 467 nm. The high molar absorptivity of the 832 nm peak encouraged the use of the peak at 623 nm for quantification of PuO$_2^{2+}$. The 623 nm molar absorptivity was calculated as 4.0 M$^{-1}$cm$^{-1}$ and was used to determine the aqueous PuO$_2^{2+}$ concentration (Figure 3.4).

Figure 3.3: Oxidation of 10 µmol Pu$^{4+}$ in 1 M HNO$_3$ (black dotted line) to PuO$_2^{2+}$ (blue) by incremental addition of Cu$^{3+}$ periodate (6.0 µmol Cu$^{3+}$ periodate = red, 12.0 µmol = orange, 18.0 = µmol, 25 µmol = blue). Inset of baselined 623 nm PuO$_2^{2+}$ peak used to determine PuO$_2^{2+}$ concentration.
The precipitate formed after Cu$^{3+}$ periodate addition to the Pu solution is thought to contain all the Pu$^{4+}$ remaining after oxidation and this assumption was used in data interpretation. No Pu$^{4+}$ peaks were observed in the aqueous supernatant after the Cu$^{3+}$ periodate addition and reports of other tetravalent metal periodate precipitates are common in the literature.\textsuperscript{71,76,85} A lanthanide surrogate for plutonium, Ce$^{4+}$, has been shown to form a precipitate with periodate as CeHIO$_6$.\textsuperscript{76} Given the similar chemistry between Pu$^{4+}$ and Ce$^{4+}$, it is thought that Pu$^{4+}$ also precipitated as PuHIO$_6$.

Three sequential additions of Cu$^{3+}$ periodate (6.0 µmol each) to the Pu$^{4+}$ solution (10.2 µmol total) in 1 M HNO$_3$ resulted in 1.8 µmol (60% efficiency), 1.9 (63% efficiency) and 2.2 µmol (73% efficiency) of PuO$_2^{2+}$ being formed. The results show that 2.0 ± 0.2 µmol Pu$^{4+}$ is oxidized by 6.0 µmol Cu$^{3+}$ periodate in 1 M HNO$_3$ which approximates to a 1:3 mole ratio (Pu$^{4+}$:Cu$^{3+}$). Similar to NpO$_2^{+}$, the oxidation efficiency seems impacted by Cu$^{3+}$ periodate reduction in the molar nitric acid media.\textsuperscript{85} Similar observation was made by Sinkov et. al who used a 1:10 mole ratio to oxidize Pu$^{4+}$.
Am$^{3+}$ to AmO$_2^{2+}$ with Cu$^{3+}$ periodate.\textsuperscript{36} Furthermore, the study showed that while >99% oxidation was achieved below 2 M HNO$_3$, the efficiency decreased to 77% at 3.5 M HNO$_3$. Collectively, the results show increased mole ratio (actinide:oxidant) is necessary when going from a one electron oxidation (1:1.2, NpO$_2^+$) to two electron (1:3, Pu$^{4+}$) and three electron (1:10, Am$^{3+}$).

### 3.5 Solvent Extraction Results and Discussion

The determination of Np oxidation state speciation by UV-Vis spectroscopy during solvent extraction is problematic due to the lack of distinguishable peaks in the UV-Vis. Consequently, a NIR 900 to 1300 nm detector was used to measure NpO$_2^{2+}$ species and any possible formation of NpO$_2^+$. In the initial sample, a peak at 975 nm indicated some NpO$_2^+$ was present in the solution (Figure 3.5). After Cu$^{3+}$ periodate was added to the solution the residual NpO$_2^+$ was oxidized to NpO$_2^{2+}$. Addition of Cu$^{3+}$ periodate caused a broad peak to appear between the 900 and 1300 nm range due to presence of Cu$^{2+}$. To remove the Cu$^{2+}$ interference, the Np spectra was baselined by removing the Cu$^{2+}$ using a polynomial fit in order to accurately calculate NpO$_2^+$ and NpO$_2^{2+}$ species, shown in Figure 3.5. The NpO$_2^+$ 975 nm and NpO$_2^{2+}$ 1219 nm molar extinction coefficients were calculated as 293 M$^{-1}$cm$^{-1}$ and 44.5 M$^{-1}$cm$^{-1}$, respectively.\textsuperscript{87,90,91}

![Figure 3.5: Left, Near-IR spectra of 14 mM Np in 2 M HNO$_3$ before Cu$^{3+}$ periodate addition (purple) and after (red). Right, Near-IR spectra of baseline corrected NpO$_2^{2+}$ before (black) and after mixing aqueous phase with 1 M DAAP n-dodecane in 5 second increments (right).](image-url)
After contacting the aqueous and organic phases for 5 seconds, the aqueous NpO$_2^{2+}$ concentration dropped from 14.00 mM to 0.30 ± 1 mM corresponding to a distribution value of 47 ± 2. The distribution value increased to 52 ± 2 after the phases were contacted for 10 seconds. The distribution values increased slightly over extended contact times, but values remained within experimental error of each other (Figure 3.6); therefore, the data suggests NpO$_2^{2+}$ extraction reaches equilibrium after a 10 second contact time. The organic phase spectrum, Figure 3.7, displays two NpO$_2^{2+}$ peaks at 1110 and 1206 nm. Based on transfer of 13.7 mM NpO$_2^{2+}$ from aqueous to the organic phase, the molar extinction coefficient was calculated as 4.1 M$^{-1}$cm$^{-1}$ for 1110 nm and 2.6 M$^{-1}$cm$^{-1}$ for 1206 nm. A small peak at 975 nm is also present in the organic phase spectrum. After recontacting the phases, the 975 nm organic phase peak decreased and a peak at 975 nm appeared in the aqueous phase spectrum. This corresponded to the presence of 0.016 mM NpO$_2^{+}$ (Figure 3.5). Due to the changes of the 975 nm peak in the aqueous and organic phases the organic phase 975 nm peak was assigned to NpO$_2^{+}$. By letting the organic phase NpO$_2^{+}$ concentration increase over 7 days and measuring the changes in 975 nm aqueous and organic absorbances upon phase mixing the organic phase NpO$_2^{+}$ 975 nm molar extinction coefficient was calculated as 72 M$^{-1}$cm$^{-1}$.

Although NpO$_2^{+}$ and NpO$_2^{2+}$ are both linear dioxo cations, the effective charge on the hexavalent neptunyl cation is 3.10 while pentavalent neptunyl cation is 2.35. The lower pentavalent effective charge induces a weaker interaction between the ion and the phosphoryl group on DAAP causing NpO$_2^{+}$ to partition mostly into the aqueous phase. The reduction and redistribution cycle was observed over the course of 1 month. The NpO$_2^{2+}$ slowly reduced in the organic and aqueous phases. Upon recontacting, residual NpO$_2^{2+}$ in the aqueous phase was recovered to the organic phase, and the NpO$_2^{+}$ was back extracted into the aqueous phase. After
47 days, 1 mM NpO$_2^+$ was generated and 13 mM NpO$_2^{2+}$ remained where 12.89 mM was in the organic phase and 0.11 mM was in the aqueous phase. The mass balance throughout the duration of the experiment was 100 ± 1%. It has been noted that periodate’s oxidation capacity is not strong enough to oxidize Am$^{3+}$. However, reduction of periodate to IO$_3^-$ is strong enough to oxidize NpO$_2^+$ to NpO$_2^{2+}$. Reduction of Cu$^{3+}$ periodate in solution produces H$_5$IO$_6$ which remains stable for long durations in acidic media. The presence of NpO$_2^+$ in the aqueous phase indicated the presence of periodate was not enough to oxidize NpO$_2^+$; however, heating the vial to 60°C resulted in a decrease of the 975 nm NpO$_2^+$ aqueous phase peak and increase in the 1219 nm NpO$_2^{2+}$ peak.

![Figure 3.6: Extraction kinetics of NpO$_2^{2+}$ (blue circles) and PuO$_2^{2+}$ (red squares) determined by UV-Vis-NIR spectroscopy from 2 M HNO$_3$ by 1 M DAAP in n-dodecane. Standard deviations are less than 10% for NpO$_2^{2+}$ and less than 3% for PuO$_2^{2+}$ based off quadruple measurements.](image-url)
Due to the Pu$^{4+}$-periodate complexation previously mentioned, the PuO$_2^{2+}$ extraction experiments were studied in the absence of Cu$^{3+}$ periodate. The aqueous phase PuO$_2^{2+}$ concentration was determined using Beer’s Law with the 832 nm peak and a calculated $341.4 \text{ M}^{-1}\text{cm}^{-1}$ molar absorptivity value, Figure 3.8. After contacting the aqueous and organic phases for 5 seconds the aqueous PuO$_2^{2+}$ concentration decreased from 3.13 mM to $0.185 \pm 0.004 \text{ mM}$. This decrease in PuO$_2^{2+}$ concentration in the aqueous phase equated to a $15.9 \pm 0.4$ distribution value, Figure 3.6. The distribution value increased to $23.0 \pm 0.4$ after the phases were contacted for 10 seconds and did not change with longer mixing times. Therefore, PuO$_2^{2+}$ extraction reaches equilibrium after mixing the phases for 10 seconds. The organic phase displays several peaks.
between 350 and 900 nm, Figure 3.9. The most dominant feature is the peak at 844 nm and has a molar absorptivity of 47.1 M⁻¹cm⁻¹. In the same region, several peaks are observed between 780 and 835 nm. Additionally, more peaks appear below 675 nm. Compared to aqueous phase PuO$_2$$^{2+}$ UV-Vis, the organic phase shows more fine structure peaks because of plutonium’s less symmetric coordination environment with, presumably, the 2 DAAP ligands and four nitrates in the organic phase.

![Figure 3.8](image)

Figure 3.8: Left, UV-Vis of 3.1 M PuO$_2$$^{2+}$ in 2 M HNO$_3$ before (black) and after contacting aqueous phase with 1 M DAAP n-dodecane in 5 second increments. Right, zoom in of 823 nm peak used to calculated PuO$_2$$^{2+}$ distribution values.

Both NpO$_2$$^{2+}$ and PuO$_2$$^{2+}$ reached extraction equilibrium after 10 second phase mixing times. The fast extraction kinetics are favorable when considering AmO$_2$$^{2+}$ extraction. Previous study showed Cu$^{3+}$ periodate oxidized Am extraction by DAAP decreased rapidly over increased contact time.\textsuperscript{85} UV-Vis spectroscopy was used to monitor the oxidation state of Am species in the aqueous and organic phases. In 1 M HNO$_3$, 100% Am$^{3+}$ was oxidized to AmO$_2$$^{2+}$ (Figure 3.10) from the addition of Cu$^{3+}$ periodate to the aqueous phase. After mixing the aqueous phase with 1 M DAAP in n-dodecane, the aqueous phase spectrum indicated the presence of Am$^{3+}$, AmO$_2$$^{+}$, and AmO$_2$$^{2+}$ by the presence of their respective peaks at 503, 513, and 666 nm. The conditional molar
Absorptivities were established to be 326.0 M\(^{-1}\)cm\(^{-1}\) for Am\(^{3+}\) at 503 nm, 45.9 M\(^{-1}\)cm\(^{-1}\) for AmO\(^{2+}\) at 513 nm and 21.9 M\(^{-1}\)cm\(^{-1}\) for AmO\(^{2+}\) at 666 nm. The values are similar to molar absorptivities previously recorded in nitric acid media, and were found to vary slightly between nitric acid concentrations due to nitrate complexation, Table 3.1.\(^{11,34,95}\)

![UV-Vis spectrum of PuO\(^{2+}\) in 1 M DAAP n-dodecane extracted from a 2 M HNO\(_3\) aqueous phase.](image)

**Figure 3.9:** UV-Vis spectrum of PuO\(^{2+}\) in 1 M DAAP n-dodecane extracted from a 2 M HNO\(_3\) aqueous phase.

**Table 3.1:** Calculated Am Molar Absorptivities

<table>
<thead>
<tr>
<th>HNO(_3) (M)</th>
<th>Am(^{3+}), 503 nm (M(^{-1})cm(^{-1}))</th>
<th>AmO(^{2+}), 513 nm (M(^{-1})cm(^{-1}))</th>
<th>AmO(^{2+}), 666 nm (M(^{-1})cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>326.0</td>
<td>45.9</td>
<td>21.9</td>
</tr>
<tr>
<td>2</td>
<td>309.5</td>
<td>46.0</td>
<td>23.4</td>
</tr>
<tr>
<td>3</td>
<td>292.6</td>
<td>46.2</td>
<td>23.4</td>
</tr>
<tr>
<td>4</td>
<td>267.6</td>
<td>46.4</td>
<td>24.0</td>
</tr>
</tbody>
</table>
Figure 3.10: Oxidation of 3.0 mM $^{243}$Am by 20 mg Cu$^{3+}$ periodate in 1 (blue), 2 (green), 3 (orange), and 4 (red) M HNO$_3$. Spectra were taken during oxidation step. Remnants of Cu$^{3+}$ periodate are visible by the broad peaks below 600 nm while Cu$^{2+}$ has a broad peak above 600 nm. The peak at 666 nm indicates AmO$_2^{2+}$ is present. Absence of peaks at 503 nm for 1, 2, and 3, M HNO$_3$ indicates all Am$^{3+}$ had been oxidized while 78% Am$^{3+}$ was oxidized in 4 M HNO$_3$.

Distribution values, shown in Table 3.2 were assessed by calculating the initial Am$^{3+}$ concentration and final Am species concentration in the aqueous phase UV-Vis spectra, Figure 3.11. The distribution values calculated in this study are similar to those previously reported by gamma spectroscopy and show the distribution value decreases between 3 and 4 M HNO$_3$ from 2.1 ± 0.1 to 1.6 ± 0.1. These are the first distribution values assessed using macroscopic amounts of americium in a solvent extraction system using Cu$^{3+}$ periodate or sodium bismuthate with the DAAP extractant. The comparability of the macroscopic measurements to radiotracer studies is an...
encouraging validation of radiotracer techniques to effectively model more applicable fuel cycle conditions where millimolar amounts of americium will be present.

Table 3.2: Distribution values calculated using UV-Vis spectroscopy for Cu\(^{3+}\) periodate oxidized Am in various nitric acid solutions with 1 M DAAP n-dodecane. *Organic phase was not pre-equilibrated with HNO\(_3\) prior to extraction

<table>
<thead>
<tr>
<th>HNO(_3)</th>
<th>Am Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.9 ± 0.2</td>
</tr>
<tr>
<td>*1</td>
<td>1.72 ± 0.06</td>
</tr>
<tr>
<td>2</td>
<td>1.93 ± 0.08</td>
</tr>
<tr>
<td>3</td>
<td>2.1 ± 0.1</td>
</tr>
<tr>
<td>4</td>
<td>1.6 ± 0.1</td>
</tr>
</tbody>
</table>

The decreasing distribution values correlate to a drop in the Cu\(^{3+}\) periodate oxidation efficiency prior to mixing the aqueous and organic phases. While 1, 2, and 3 M HNO\(_3\) solutions resulted in 100% oxidation, the oxidation efficiency dropped to 78% in 4 M HNO\(_3\). For solvating ligands, actinide extraction decreases with a decrease in effective charge for An\(^{4+}\) > AnO\(_{2}^{2+}\) > An\(^{3+}\) > AnO\(_{2}^{+}\). The incomplete oxidation results in less AmO\(_{2}^{2+}\) being available for extraction. Since Am\(^{3+}\) or AmO\(_{2}^{+}\) is extracted to a lesser extent than AmO\(_{2}^{2+}\) the distribution value decreases. The 1.6 ± 0.1 distribution value in this study is slightly higher than 0.96 ± 0.05 value previously reported for radiotracer conditions.\(^{85}\) Considering presence of 100% AmO\(_{2}^{2+}\) in 1 – 3 M HNO\(_3\), one would expect the distribution values to increase as the nitric acid concentration increase. However, the distribution values decrease from 1 to 2 M HNO\(_3\). The decreased distribution value could be due to the increased rate of reduction (AmO\(_{2}^{2+}\) to AmO\(_{2}^{+}\)) at higher nitric acid concentrations.\(^{96}\) Since americium was oxidized in HNO\(_3\) and then 1 M DAAP was added, more AmO\(_{2}^{2+}\) could’ve reduced in 2 and 3 M HNO\(_3\) than 1 M HNO\(_3\) during the approximately 60
seconds between oxidation and organic phase addition/mixing. It should be noted that the 2.9 ± 0.2 distribution value at 1 M HNO₃ is higher than the 1.9 ± 0.1 value previously reported under similar conditions.⁸⁵ A distribution value of 1.72 ± 0.06 was achieved in a repeat experiment without pre-equilibrating the 1 M DAAP/n-dodecane phase with 1 M HNO₃.

The organic phase also shows the presence of the three americium oxidation states - Am³⁺, AmO₂⁺, and AmO₂²⁺. The organic phase contacted with 1 M HNO₃, shown in Figure 3.12 (page 73), has a large shoulder peak at lower wavelengths. At higher wavelengths, a peak is observed at 675 nm and broad peaks between 700 and 780 nm. After allowing the solution to sit overnight, the 675 nm shoulder peak and broad 765 nm peak decreased while peaks at 506, 511, 647, 711, and a broad 815 nm peak increased. The reduction of AmO₂²⁺ would give rise to AmO₂⁺ and Am³⁺ species; therefore, the shoulder peak, 675, and 765 nm peaks were assigned to AmO₂²⁺. To determine the remaining peaks, the aqueous and organic phases were recontacted. The new spectra showed a decrease in all peaks, but most notably the 511, 647, and 711 nm peaks experienced a large drop in intensity. Recalling that AmO₂⁺ species are extracted to a lesser extent than Am³⁺, the 511, 647, and 711 nm peaks were assigned to AmO₂⁺, while 506 and 815 nm peaks were assigned to Am³⁺. By comparing the change in intensity of the 711 nm peak to the change in aqueous AmO₂⁺ concentration after recontacting phases, the 711 nm organic phase peak was calculated to have a molar absorptivity of 56.8 M⁻¹cm⁻¹. The 511 nm molar absorptivity could not be calculated because of its overlap with the Am³⁺ 506 nm peak. To elucidate the Am³⁺ peaks, a spectrum was collected on unoxidized Am³⁺ extracted by 1 M DAAP, and confirmed that 506 and 815 nm peaks are indicative of the Am³⁺ species. From the Am³⁺ extraction, the 506 nm molar absorptivity was calculated as 380.2 M⁻¹cm⁻¹. To account for Am³⁺/AmO₂⁺ impact on each component peaks at 506 and 511 nm, a pure AmO₂⁺ spectra is required and was not able to be
obtained in this current study. The inability to obtain a pure organic phase AmO$_2^+$ spectra prevented assessment of Am$^{3+}$/AmO$_2^+$ concentrations in the organic phase. Furthermore, the molar absorptivity of AmO$_2^{2+}$ at its primary 675 nm peak could not be calculated because Am$^{3+}$ and AmO$_2^+$ concentrations could not be accounted for when considering AmO$_2^{2+}$ concentration in the organic phase. Consequently, qualitative observations were made when completing extractions at higher nitric acid concentrations.

Figure 3.12: Organic phase UV-Vis spectra of Cu$^{3+}$ periodate oxidized Am extracted by 1 M DAAP n-dodecane from 1 M HNO$_3$ immediately after extraction (blue), 24 hours (green), after recontacting aqueous and organic phases (orange).
Figure 3.11: (Top) UV-Vis spectrum of Cu$^{3+}$ periodate oxidized Am in 3 M HNO$_3$ showing presence of Am$^{3+}$ (503 nm), AmO$_2^{2+}$ (513 nm), and AmO$_2^{2+}$ (666 nm). (Middle) Baseline subtracted UV-Vis spectrum to determine Am$^{3+}$ concentration (orange), and Am$^{3+}$ peak subtracted to determine AmO$_2^{2+}$ concentration (blue). (Bottom) Polynomial fit to remove Cu$^{2+}$ UV-Vis spectral peak to determine AmO$_2^{2+}$ concentration.
Figure 3.13: (A) Organic phase UV-Vis spectra of Cu\textsuperscript{3+} periodate oxidized \textsuperscript{243}Am extracted by 1 M DAAP in n-dodecane from various nitric acid concentrations. (B) Organic phase UV-Vis spectra of Cu\textsuperscript{3+} periodate oxidized \textsuperscript{243}Am extracted by 1 M DAAP in n-dodecane from various nitric acid concentrations after sitting overnight. (C) Organic phase UV-Vis spectra of Cu\textsuperscript{3+} periodate oxidized \textsuperscript{243}Am extracted by 1 M DAAP in n-dodecane after recontacting aqueous and organic phases.
In all acid concentrations the low wavelength shoulder peak, 506 nm, 675 nm, and broad peaks from 700 to 780 nm were present after contacting two phases (Figure 3.13). Differences in the spectra were observed after the solutions sat for 24 hours. Prominent AmO$_2^{2+}$ peaks are observed at 511 and 711 nm in 1 M HNO$_3$. In 2 M HNO$_3$, the AmO$_2^{2+}$ peaks are not as prevalent, and even less so in 3 and 4 M HNO$_3$. This trend suggests AmO$_2^{2+}$ undergoes a three electron reduction to Am$^{3+}$ under higher nitric acid extraction conditions. Alternatively, AmO$_2^{2+}$ could undergo a one electron reduction to AmO$_2^{+}$ and the two electron reduction of AmO$_2^{+}$ to Am$^{3+}$ or AmO$_2^{+}$ disproportionation proceeds rapidly. After recontacting the two phases 503 and 815 nm Am$^{3+}$ peaks remained as well as the shoulder AmO$_2^{2+}$ peak. The AmO$_2^{2+}$ intensity is higher under the 3 and 4 M HNO$_3$ conditions, and corresponds to the presence of the 675 nm AmO$_2^{2+}$ peak after recontact. The presence of AmO$_2^{2+}$ suggests AmO$_2^{+}$ disproportionation occurs more readily in the organic phase under higher nitric acid extraction conditions. A time controlled UV-Vis experiment is needed to elucidate the reduction pathways, and such an experiment is not currently feasible with the spectrophotometers available at our facilities.

3.6 Conclusion

The oxidation of NpO$_2^{+}$ and Pu$^{4+}$ to the hexavalent state by Cu$^{3+}$ periodate was assessed using UV-Vis spectroscopy for application in a group hexavalent actinide separation. Quantitative oxidation was accomplished using a 1:1.2 and 1:3 metal:oxidant ratio was required for NpO$_2^{+}$ and Pu$^{4+}$, respectively. The oxidation efficiency decreases as one moves across actinides as Np > Pu > Am. Distribution values of hexavalent Np, Pu and Am extracted by DAAP were determined using UV-Vis spectroscopy. The extraction as found to reach equilibrium after 10 second phase mixing time for Np and Pu. A short contact time is preferable when considering AmO$_2^{2+}$ extraction as it quickly reduces to the less extracted AmO$_2^{2+}$ and Am$^{3+}$ species. The reduction of AmO$_2^{2+}$ in the
organic phase is a limiting factor for development of a hexavalent based actinide extraction. Future research should focus on stabilizing AmO$_2^{2+}$ in the organic phase. Distribution values determined by UV-Vis with macro amounts of Am were comparable to previously reported values which used tracer amounts. The ability to determine actinide concentrations is beneficial for online monitoring of solvent extraction systems and nuclear nonproliferation applications. The organic phase absorption spectra of NpO$_2^{2+}$ (near IR), PuO$_2^{2+}$ (visible), and Am species (visible) in 1 M DAAP solution were presented and molar absorptivities were calculated for characteristic 1110 and 1206 nm NpO$_2^{2+}$ and 844 nm PuO$_2^{2+}$ peaks. Peak positions for Am$^{3+}$, AmO$_2^+$, and AmO$_2^{2+}$ were determined, but low signal to noise ratio prevented molar absorptivity determination of AmO$_2^{2+}$. Furthermore, peak overlap of 506 nm Am$^{3+}$ and 511 nm AmO$_2^+$ inhibited species concentration determination. A spectrum of AmO$_2^+$ only species will need to be collected to determine the extent of overlap and accurately determine species concentration.
CHAPTER 4

COMPARING BRANCHED VERSUS STRAIGHT-CHAIN MONOAMIDE EXTRACTANTS FOR ACTINIDE RECOVERY

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The following chapter was reproduced with permission from the review paper published by Taylor & Francis as: Comparing Branched versus Straight-chain Monoamide Extractants for Actinide Recovery, Separation & Purification Reviews, 1-17, 2017. The sections on metal extraction by branched and straight chain monoamides from the review are included. Not included are monoamide synthesis, as that is covered in Chapter 5, and the sections that reviewed fission product and radiolytic degradation studies since that is not a major focus of this dissertation.

4.1 Abstract

Separations of used nuclear fuel at the engineered scale have generally been completed using the Plutonium Uranium Redox Extraction (PUREX) process. The PUREX process uses tributyl phosphate (TBP) as an extractant to recover uranium and plutonium. While the TBP extractant has proven effective at recovering U and Pu at the engineered scale, TBP is potentially vulnerable to third phase formation and TBP degradation products (monobutyl and dibutyl phosphoric acids) which can complicate recovery of extracted metals from the organic phase. An alternative class of extractants, monoamides, has been considered for applications in thorium and uranium fuel cycles. When compared to TBP, monoamides tend to have higher separation factors for U or Pu from fission products, structural materials, and Th. This review summarizes the literature that explores actinide separations using monoamides by assessing the physiochemical
properties between a broader library of branched and straight-chain monoamides than considered in previous reviews. An emphasis is placed on fine-tuning the selectivity of branched monoamides.

4.2 Introduction

The push to limit greenhouse gas emissions while meeting the world’s energy demand has increased interest in advancing nuclear power technology. Currently, pressurized water reactors (PWR) and boiling water reactors (BWR) in the United States are operating in an open, single throughput fuel cycle. A partially closed fuel cycle extends the useable lifetime of nuclear fuel by recovering uranium and plutonium from irradiated fuel for reprocessing into mixed oxide (MOX) fuel components. Reactors that convert thorium into fissile uranium are another option for increasing fuel economy. The recovery of U and Pu from irradiated U and Th fuels has been realized through the PUREX (Plutonium Uranium Redox EXtraction) and THOREX (THORium EXtraction) processes, respectively. These processes utilize tributyl phosphate (TBP) and a hydrocarbon diluent, such as kerosene or n-dodecane, to remove the desired metal. The use of TBP in nuclear fuel separation processes, while demonstrated as effective and viable, has several adverse effects, including: the inability to incinerate used solvent leading to large volumes of secondary low-level radioactive waste, generation of radiolytic degradation products that decreases the stripping efficiency of TBP, and third phase formation at high metal loading that impedes phase disengagement. The development of alternative extractants that overcome these limitations would potentially decrease the amount of low level waste associated with nuclear fuel recycle.

First explored by Siddall, the N,N-dialkyl aliphatic amide class of extractants has been reported to have several favorable features over organophosphorous ligands. Following the CHON principle (reagents composed exclusively of carbon, hydrogen, oxygen, and nitrogen), the
incinerable nature of N,N-dialkyl amides decreases secondary waste volumes. Furthermore, the formation of innocuous degradation products (aqueous soluble carboxylic acids and amines) does not hinder stripping efficiency. This decreases the need for scrubbing steps that remove degradation products in engineered scale separations leading to a more simplified process. In optimizing phase interaction and metal extraction, the synthetic tunability of dialkyl amides allows for systematic evaluations of their chemical and physical properties. For example, Siddall’s work suggests the interaction between the metal cation and monoamide ligand occurs at the acyl oxygen.48 Furthermore research by Siddall and others have shown the identity of the acyl group has a profound effect on the monoamide’s extraction capabilities.48–52,97

This review summarizes the research focused on utilizing monoamides as alternative extractants to TBP for recycling used nuclear fuel. While recent reviews have focused on metal extraction properties of straight chain monoamides, namely N,N-dihexyloctanamide (DHOA), this review systematically assesses the physio-chemical properties of monoamides with emphasis on tuning the selectivity of branched monoamides towards hexavalent actinides.51,52

4.3 Extraction Mechanism

Neutral, solvating ligands are preferential for used nuclear fuel recycle due to their rapid kinetics and ability to recover metal ions from higher acid concentrations that are closer to those the used for nuclear fuel dissolution. High acid concentrations provide counter ions that neutralize the metal’s charge and encourage partitioning to the organic phase. Usually nuclear fuel dissolution, for recycling purposes, is completed using nitric acid and the counter ion supporting metal recovery is nitrate.

Monoamides can be integrated into engineered processes designed for tributyl phosphate since they, like TBP, behave as solvating extractants. Several reports have examined concentration
dependent distribution studies (e.g. log D vs log[monoamide]) to assess the stoichiometry of the metal to ligand complex.\textsuperscript{97-103} A slope dependence of 1.8 on the log-log scale was observed for UO$_2^{2+}$ recovery with the extractant N$_2$N-dibutyloctanamide (DBOA) in mesitylene from 3 M HNO$_3$ while a slope of 2.5 was observed for Pu$^{4+}$.\textsuperscript{97} Results such as this can be indicative of non-ideality impacts in the organic phase or a mixture of 1:2 and 1:3 metal:extractant species present in an organic phase at the same time.\textsuperscript{104}

### 4.3.1 Acid Uptake

The interaction between nitric acid and the monoamide occurs through hydrogen bonding between the nitric acid’s proton and the monoamide’s carbonyl oxygen. The interaction has been studied by using infrared spectroscopy and monitoring the appearance of the O-N-O nitric acid stretch at 1595 cm$^{-1}$ in the presence of the monoamide.\textsuperscript{105} Preliminary studies by Pathak and Gupta found a 1:1 acid to ligand species, and was represented by the expression

$$H^+ + NO_3^- + 1L \leftrightarrow HNO_3 \cdot L$$

where a bar denotes species in the organic phase, L the monoamide ligand and $K_H$ is the acid uptake constant.\textsuperscript{100,101,103} The uptake of acid by N,N-di-(2-ethylhexyl)butyramide (D2EHBA) and N,N-di-(2-ethylhexyl)isobutyramide (D2EHiBA) in tetrahydrogenated propylene (TPH, a commercial mixture of branched dodecanes) was studied by Condamines et. al. over varied nitric acid concentrations (0.30 M to 1.70 M).\textsuperscript{105} The $K_H$ values for this study, 0.135 and 0.086 for D2EHBA and D2EHiBA, respectively, and various nitric acid:monoamide equilibrium constant values are presented in Table 4.1. A larger $K_H$ was reported for D2EHBA over D2EHiBA and
implies that acid uptake decreases when the substitution at the alpha carbon (carbon closest to the carbonyl group) increases.

Table 4.1: Acid uptake constant of various monoamides

<table>
<thead>
<tr>
<th>Monoamide</th>
<th>Pathak 1:1</th>
<th>Condamines 1:1</th>
<th>Condamines 1:2</th>
<th>Condamines 2:1</th>
<th>Musikas 1:1</th>
<th>Musikas 2:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDoA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.217</td>
<td>0.0930</td>
</tr>
<tr>
<td>D2EHAA</td>
<td>0.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D2EHPA</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D2EHBBA</td>
<td>0.135</td>
<td>0.043</td>
<td></td>
<td>5.7 x 10^-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D2EHiBA</td>
<td>0.15</td>
<td>0.086</td>
<td>0.053</td>
<td>1.35 x 10^-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D2EHPVA</td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

The uptake of nitric acid was studied as a function of substitution near the carbonyl group using 1 M N,N-di-(2-ethylhexyl)acetamide (D2EHAA), N,N-di-(2-ethylhexyl)propanamide (D2EHPA), D2EHiBA, and N,N-di-(2-ethylhexyl)pivalamide (D2EHPVA) in n-dodecane. The $K_H$ values, also shown in Table 4.1, were found to be 0.28 ± 0.03, 0.20 ± 0.01, 0.15 ± 0.04, and 0.06 ± 0.002 respectively. The results of this study are consistent with Condamines’ D2EHBBA and D2EHiBA values that indicate the uptake of acid decreases when the substitution near the carbonyl increases. Comparable $K_H$ values for D2EHiBA in the presence of two different diluents were reported in the two manuscripts. The more ordered alkyl chains in n-dodecane may promote increased solubility of nitric acid monoamide complexes while the variability in alkyl chain length of the TPH diluent and subsequent overall increased disorder leads to decreased solubility in the organic phase.

Condamines generated a speciation diagram that proposed the presence of additional nitric acid-monoamide species. The speciation diagram, presented in Figure 4.1, shows free amide and the monosolvated species are the main products, however, low amounts of a 1:2 nitric acid:amide species forms between 1 and 8 M HNO₃. At even higher acid concentrations, the 1:2 species decreases and a 2:1 HNO₃:amide species arises. The 2:1 species is unlikely to be present.
at the 3 – 4 M HNO₃ concentrations typically used in the PUREX process, but the 1:1 and 1:2 are species relevant under these conditions.

![Figure 4.1: N,N-di-(2-ethylhexyl)isobutyramide (D2EHiBA) speciation diagram with nitric acid concentrations.](image)

The Kᵢ values for nitric acid extracted by 0.3 M N,N-diethyldodecanamide (DEDoA) in toluene were also established for the three species system over a 0.1 M to 6 M HNO₃ acid concentration range. The three Kᵢ constants were found to be K₁:₁ = 2.17E-1 ± 1.22E-2, K₁:₂ = 9.30E-2 ± 8.61E-2, and K₂:₁ = 1.28E-4 ± 1.10E-4. The values follow the same trend observed in Condamines’ D2EHBA and D2EHiBA study. While a 1:1 acid:amide complex is the primary species, higher acidities encourage the formation of the 1:2 or 2:1 species. These findings are comparable to the industrial standard, TBP.

4.3.2 Metal Extraction Mechanism

Actinide metal-monoamide coordination was found to occur through the carbonyl group by measuring a shift in the carbonyl stretching vibration to lower wavenumbers in the infrared spectrum of D2EHBA coordinated with UO₂²⁺, Pu⁴⁺, and Th⁴⁺. When the monoamide is
coordinated to UO$_2^{2+}$ and Pu$^{4+}$, a new single carbonyl stretch appears indicating one metal-amide species forms. In contrast, when coordinated to Th$^{4+}$ a shoulder peak appears on D2EHBA’s carbonyl stretch. The shoulder, instead of the presence of clear, separate peaks, has been interpreted as monoamide-Th$^{4+}$ species with different stoichiometries. Therefore, 1:2 and 1:3 M:L stoichiometries were assigned to Th$^{4+}$-monoamide species. Considering the variable extraction mechanisms, a generalized equilibrium expression for metal cation-monoamide complexation can be expressed as

$$xM^{n+} + n\text{NO}_3^- + y\text{Amide} \rightleftharpoons M_x(\text{NO}_3)_n(\text{Amide})_y$$

(3)

$$K_{ex} = \frac{[M_x(\text{NO}_3)_n(\text{Amide})_y]}{[M^{n+}]^x [\text{NO}_3]^n [\text{Amide}]^y}$$

(4)

where amide represents the monoamide ligand, the bar denotes species in the organic phase, and $K_{ex}$ is the equilibrium constant for the metal extraction. Taking into account the metal-nitrate speciation in the aqueous phase, the overall generalized equilibrium expression can be written as

$$K_{ex} = \frac{D_M (1 + \sum \beta [\text{NO}_3]^{z})}{[\text{NO}_3]^n [\text{Amide}]^y}$$

(5)

where $\beta$ is the overall stability constant of metal:nitrate species formed in the aqueous phase, and $D_M$ is the concentration of metal species in organic phase divided by concentration of the metal in the aqueous (distribution value).

To observe the primary solvating species, IR spectra were collected for UO$_2^{2+}$ and Pu$^{4+}$ complexes extracted by 1 M D2EHBA and D2EHiBA from 0.5 M HNO$_3$. The complexed D2EHBA-UO$_2^{2+}$ spectrum shows a shift in carbonyl C=O vibration from 1650 cm$^{-1}$ to 1565 cm$^{-1}$. The shift to lower wavenumbers corresponds to a shift in lower energy, and confirms the metal-
amide complex is generated through interaction with the monoamide carbonyl group. A similar shift to lower energy was observed in the D2EHBA-Pu\(^{4+}\) complex with a shift from 1650 cm\(^{-1}\) to 1551 cm\(^{-1}\). The Th\(^{4+}\) carbonyl vibration shifted from 1650 cm\(^{-1}\) to a broad peak between 1566-1548 cm\(^{-1}\), which was attributed to the presence of more than one Th\(^{4+}\)-amide species.

To determine the number of ligands associated with an extracted species under high metal loading, 1 M D2EHBA in TPH was saturated with UO\(^{2+}\), Pu\(^{4+}\), and Th\(^{4+}\) from 1 M LiNO\(_3\), 1 M HNO\(_3\), and 5 M LiNO\(_3\) respectively.\(^{99}\) Using lithium nitrate may drive increased metal extraction (due to decreased competitive acid extraction) and comparisons between media may indicate if the extracted complex stoichiometry is sensitive to variations in aqueous nitrate/acid ratios.\(^{109,110}\) The ratio of ligand concentration over metal concentration in organic phase produced a stoichiometry of 2.05 for UO\(^{2+}\) and 1.95 for Pu\(^{4+}\). The proximity of these values to a whole integer number indicates UO\(^{2+}\) and Pu\(^{4+}\) extracted species are coordinated to 2 straight chained, monoamide ligands under high metal loading conditions. Thorium had a stoichiometry of 2.44 and supports the presence of two and three extractants associated with a Th\(^{4+}\)- monoamide species. The same ratios were observed by Musikas when UO\(^{2+}\), Pu\(^{4+}\), and Th\(^{4+}\) were extracted by DEDoA in toluene from 2 M HNO\(_3\).\(^{111}\) A log-log plot of the distribution coefficient vs. DEDoA concentration resulted in a slope of 2.25, 2.01, and 2.66 for UO\(^{2+}\), Pu\(^{4+}\), and Th\(^{4+}\), respectively. These results corroborate the conclusion in Condamines’ IR studies that extracted species are UO\(_2\)(NO\(_3\))\(_2\)Amide\(_2\), Pu(NO\(_3\))\(_4\)Amide\(_2\) and Th\(^{4+}\) is recovered as both Th(NO\(_3\))\(_4\)Amide\(_2\) or Th(NO\(_3\))\(_4\)Amide\(_3\).\(^{105}\)

### 4.4 Straight Chain Monoamides

Straight-chain monoamides are the most considered replacements to TBP for reprocessing MOX and fast reactor fuels.\(^{51,52,102,103,107,112–116}\) Preliminary studies focused on chemical and thermodynamic properties of varying acyl groups.\(^{52,112,116}\) Three monoamides N,N-
dihexylhexanamide (DHHA), N,N-dihexyloctanamide (DHOA), and N,N-dihexyldecanamide (DHDA), were selected for studies due to their solubility in n-dodecane and their resistance to third phase formation when contacted with molar nitric acid. After contacting with 3.5 M HNO₃, the acid uptake values (Kₗ) increased in the order DHHA (0.17) < DHOA (0.18) < DHDA (0.20). For reference, TBP has a Kₗ of 0.16. Demonstrated in equations 6 and 7, the conditional metal extraction equilibrium constants, based on equation (3) and (4), are expressed as:

\[
K_U = \frac{D_U}{[NO_3]^2[Amide]^2} \left(1 + \sum \beta_{\gamma} [NO_3]^z \right)
\]

(6)

\[
K_{Pu} = \frac{D_{Pu}}{[NO_3]^4[Amide]^2} \left(1 + \sum \beta_{\gamma} [NO_3]^z \right)
\]

(7)

From the equilibrium constants, the Gibbs free energy change, ΔG, can be calculated using the equation

\[
\Delta G = -RT \ln(K_M)
\]

(8)

where R is the universal gas constant in J/mol-K and T is temperature in Kelvin. The enthalpy change, ΔH, is calculated using the van’t Hoff method expressed as the equation:

\[
\ln(K_M) = \left(\frac{-\Delta H}{R}\right) \times \frac{1}{T} + \left(\frac{\Delta S}{R}\right)
\]

(9)

\[
\Delta G = \Delta H - T\Delta S
\]

(10)

Knowing the enthalpy and Gibb’s free energy, the entropy, ΔS, can be calculated using the free energy relationship, shown in equation 10. Gupta calculated the monoamide-metal ΔG, ΔH, and ΔS values for 0.5 M DHHA, DHOA, and DHDA in n-dodecane with 3.5 M HNO₃ between
For all ligands, the extraction of UO\(^{2+}\) and Pu\(^{4+}\) have negative ΔG values (roughly -8 kJ/mol for UO\(^{2+}\) and -20 kJ/mol for Pu\(^{4+}\)) meaning the process is spontaneous. The ΔH values were found to be -20.59, -21.60 and -17.66 kJ/mol for UO\(^{2+}\) with DHHA, DHOA, and DHDA respectively; similarly, the ΔS values were -0.042, -0.044, and -0.031 kJ/mol•K. The large, negative ΔH values compared to the ΔS values indicates the process is enthalpically driven. As the metal cation complexes with the ligand, water from the hydration sphere is displaced and metal-ligand bonds form resulting in small negative ΔS values for DHHA, DHOA with both metals, and DHDA with UO\(^{2+}\). Tetravalent plutonium extraction was also found to be enthalpically driven with -30.85, -28.21, and -18.46 kJ/mol ΔH values and -0.034, -0.026, and 0.053 kJ/mol•K ΔS values for DHHA, DHOA, and DHDA respectively. The small positive ΔS value (0.053 kJ/mol•K) for DHDA-Pu\(^{4+}\) extraction indicates the contribution of metal-ligand bond forming is not as favorable as hydration sphere bond breaking. Across the varying acyl chain lengths, an enthalpy/entropy balance is maintained as observed by relatively constant equilibrium constants for both cations. Between the two metals studied, the most favorable metal extraction thermodynamics are observed with DHOA for uranium, while DHHA and DHOA present comparable thermodynamics regarding plutonium recovery. The favorability for uranium recovery by DHOA, might be a reason why DHOA has been studied to a greater extent than other monoamides for processing MOX fuels.

The effect nitric acid concentration has on the extraction of UO\(^{2+}\) and Pu\(^{4+}\) by 0.5 M DHOA was studied by Gupta.\(^{112}\) For all acidities, the D\(_{\text{Pu(IV)}}\) values were higher than UO\(^{2+}\) (Figure 4.2). The D\(_{U}\) was found to increase steadily to a maximum value of about 6 at 6 M HNO\(_3\). Due to nitric acid competition with uranyl nitrate, the D\(_{U(VI)}\) steadily decreases at higher acid concentrations. Conversely, D\(_{\text{Pu(IV)}}\) plateaus around 23 above 6 M HNO\(_3\). The Pu\(^{4+}\) results have
been interpreted to suggest a change in the extraction mechanism brought about by Pu\(^{4+}\) forming an anionic hexanitrate species above 5 M HNO\(_3\).\(^{99,117}\) At higher acidities the amide undergoes protonation, behaving as a cationic extractant, and causes the $D_{Pu(IV)}$ to increase and level off.

![Figure 4.2: Uranium and plutonium distribution constants changes with nitric acid concentration with 0.5 M N,N-dihexyloctanamide (DHOA) extractant in dodecane.](image)

Extraction of tracer level UO\(_2^{2+}\) and Pu\(^{4+}\) by DHOA and TBP were compared under various natural uranium concentrations from 0 to 300 g/L.\(^{118}\) In the 1.1 M DHOA system, a third phase formed around 98 g/L UO\(_2^{2+}\) loading. For this reason, at 200 g/L and 300 g/L U the ratios of the organic to aqueous phases were 3 and 3.5 respectively to prevent third phase formation. The DHOA and TBP $D_{U(VI)}$ values, shown in Figure 4.3 A and B, decrease when the concentration of uranium in the aqueous phase increases. In certain systems consistent $D_{U(VI)}$ partitioning patterns are observed even in the presence of increasing uranium content (Figure 4.3 B and C). An explanation for this was not provided in the relevant report, but is an interesting finding. At all uranium and nitric acid concentrations, uranium distribution values were higher for TBP than DHOA. However, the low distribution of uranium at low acidities with DHOA is more favorable.
for stripping. Figure 4.3 (C and D) shows a different result for Pu$^{4+}$ extraction compared to uranium loaded nitric acid. The $D_{Pu(IV)}$ values were higher for DHOA than TBP at 3 and 4 M HNO$_3$. Conversely, at 0.5 M HNO$_3$, the $D_{Pu(IV)}$ values were lower for DHOA than TBP. These results show DHOA can extract Pu$^{4+}$ more effectively than TBP at 4M HNO$_3$, and Pu will strip more favorably at low acid concentrations.

![Figure 4.3: (A and B) Uranium and (C and D) Plutonium distribution constants under different nitric acid and uranium concentrations with (A and C) dihexyloctanamide (DHOA), or (B and D) tributyl phosphate (TBP) extractant.](image)

4.5 Branched Monoamides: Branching on the Nitrogen Alkyl Chain

The solubility of the extracted metal species, UO$_2$(NO$_3$)$_2$(Amide)$_2$, into an aliphatic hydrocarbon diluent greatly effects the distribution values. Low solubility will lead to low extraction efficiency and thus an increase in secondary waste volumes and extraction cycles. For
a solution of 1 M N,N-dibutyldecanamide (DBDoA) in hyfrane 120 (branched dodecane) the solubility of uranyl nitrate was 80 g/L and decreased to 64 g/L for N,N-di-sec-butyldodecanamide (DsBDoA). However, the solubility increased to greater than 120 g/L for N,N-diisobutyldecanamide (DiBDoA), where branching occurs at the beta carbon from nitrogen. This shows branching at the alpha carbon from the nitrogen is undesirable while branching at the beta position increases the solubility of uranyl nitrate into the branched hydrocarbon diluent.

The position of branched chains also influences third phase formation. The study by Gasparini noted higher initial uranium concentration encouraged earlier third phase formation. An exception was found for long, straight chain amides, such as DBOA, which formed no third phase. The nitrogen alkyl branched monoamide N,N-di-sec-butylhexanamide (DsBHA) took 3.5 months for a third phase to arise. Additionally, when 1 M N,N-dibutyl-2-ethylhexanamide (DB2EHA), containing a branched acyl group, was contacted with 0.10 M UO$_2$$^{2+}$ in 3 M HNO$_3$ a third phase formed after 3 hours. This study identified a general trend that third phase formation did not arise with long, straight chain monoamides, and was less likely to form when branching occurred at the nitrogen alkyl chains than at the acyl group.

The limiting organic concentration (LOC) often coincides with third phase formation. Conversely, a high interfacial tension (IFT) value between immiscible species promotes phase disengagement. Vidyalakshmi studied both uranium LOC and interfacial tension parameters as a function of monoamide structure by varying the alkyl nitrogen chain, acyl chain, and branching. The LOC varied when alkyl nitrogen chain lengths were compared between 0.5 M N,N-dibutylhexanamide (DBHA), N,N-dihexylhexanamide (DHHA), and N,N-dioctylhexanamide (DOHA) in n-dodecane. N,N-dioctylhexanamide had the highest LOC values ranging from 61 to 47.5 mg/mL uranium between “neutral” and 5.6 M nitric acid. The LOC values
ranged from 45 to approximately 20 mg/mL uranium from neutral to 4.5 M HNO₃ for DHHA, and DBHA had the lowest with <0.5 mg/mL U over the same acid range. Therefore, increasing the alkyl nitrogen chain length increases the LOC value.  

Similarly, increasing the alkyl nitrogen chain length also increased the IFT. The IFT, and LOC, also increased when the acyl chain length increased for 1 M N,N-dibutylhexanamide, N,N-dibutyloctanamide, and N,N-dibutyldecanamide in n-dodecane vs. water. This trend was observed by Gupta et. al. when they found that at 3 M HNO₃ a 1 M N,N-dihexyloctanamide (DHOA) n-dodecane solution had a uranium LOC of 98 g/L while 1 M N,N-dihexylhexanamide (DHHA) LOC value was 67 g/L. In fact, the LOC values for DHOA at 1 M concentrations in n-dodecane were all higher than DHHA over the 1 to 7 M HNO₃ range studied. Increasing the monoamide chain length at either the alkyl or acyl chain leads to increases in LOC and interfacial tension.

The LOC was also affected by branching on either the nitrogen or alkyl chains. When compared to N,N-dioctylbutyramide, the LOC increased for N,N-diisooctylbutyramide which has branching on the nitrogen alkyl chain. The LOC was completely suppressed with branching on the acyl chain for N,N-dioctylisobutyramide. This suggests branching on the nitrogen alkyl chain is more favorable than branching on the acyl chain to inhibit third phase formation. However, branching effects the LOC to lesser degree than chain length. A 1.1 M DHOA solution at an LOC of 34.0 g/L for Th⁴⁺ at 4 M HNO₃ while 1.0 M N,N-di(2-ethyl)hexylisobutyramide (D2EHiBA) had an LOC value of 11 g/L. When the D2EHiBA concentration was increased to 1.25 M the LOC value increased to 25 g/L Th⁴⁺, but the value is still lower than that observed with 1.1 M DHOA. Hexavalent actinide values appear to be less effected by structural differences as 1.1 M DHOA in n-dodecane was found to have a UO₂⁺ LOC value of 90 g/L at 4 M HNO₃ and D2EHiBA
had a 93 g/L UO$_2^{2+}$ LOC value at 4 M HNO$_3$.$^{122,123}$ Limiting organic concentration values have not been assessed for branching acyl monoamides with longer acyl chains or branching on the nitrogen alkyl chains. Furthermore, it is of interest to see if position and length of branching would further increase the LOC and IFT values.

The type of diluent is also known to affect the LOC in TBP systems. For aliphatic diluents, the LOC increases as the chain length decreases. Aromatic, alcohol, and branched alkyl diluents have also been shown to increase the LOC.$^{124}$ Only one study has compared the effect of diluent on third phase formation between TBP and the monoamide N,N-dihexyloctanamide.$^{125}$ The study generated a third-phase for each system by contacting 0.862 M Th$^{4+}$ in 4 M HNO$_3$ with 1.1 M TBP or 1.1 M DHOA in n-dodecane. The study noted the DHOA third phase volume was nearly twice than the 1.1 M TBP system. Small-angle neutron scattering analysis using the Baxter’s Sticky Sphere model revealed the attractive potential energy ($k_B T$) in the third phase is higher for DHOA (-2.13) than the TBP system (-1.36). When benzene and chloroform were used as the diluent under the same Th$^{4+}$ contact conditions no third phase was formed for either system. The study concluded that chloroform and benzene effectively solubilized the extracted species and prevented intermicellar attraction of micelles from reaching the energy level required to form third phases. Further diluent studies should focus on how alkyl chain length and branched diluents affect the LOC and third phase formation.

4.6 Branched Monoamides: Branching on the Acyl Group

Branching at the alpha carbon on the acyl group also has a considerable impact on actinide cation extraction.$^{48–53,97,99,100,105,119,126–136}$ The impact of methyl substitution on the alpha acyl carbon is shown in Table 4.2. When the acyl group has an adjacent, alpha, primary carbon the distribution of UO$_2^{2+}$ is 9.9 for a 0.5 M N,N-dibutylacetamide (DBAA) in toluene and 3 M HNO$_3$
system. Distribution of N,N-dibutylbutyramide (DBBA), containing a secondary alpha carbon, decreases to 5.3. The distribution further decreases to 2.4 for N,N-dibutylisobutyramide (DBiBA), containing a tertiary alpha carbon. Lastly, the quaternary alpha carbon monoamide N,N-dibutylpivalamide (DBPVA) resulted in a 0.60 \( \text{UO}^{2+} \) distribution. Similarly, the distribution of \( \text{Pu}^{4+} \) decreases in the order 21, 4.0, 0.080, and 0.0009 for DBAA, DBBA, DBiBA, DBPVA respectively. Although the distributions decreased, the substantial \( D_{\text{Pu(IV)}} \) decrease compared to \( D_{\text{U(VI)}} \) coincides with an increase in the separation factors (S.F., \( D_{\text{U(VI)}}/D_{\text{Pu(IV)}} \)) of 0.47 < 1.3 < 30 < 667 for DBAA, DBBA, DBiBA, and DBPVA respectively. At a higher nitric acid concentration, 6 M \( \text{HNO}_3 \), the same trend was observed, but resulted in lower separation factors (S.F.) compared to 3 M \( \text{HNO}_3 \). In general, increased separation factors for hexavalent actinides over tetravalent actinides are accompanied by decreases in recovery of both oxidation states.

Table 4.2: Impact of methyl substitution on the \( \alpha \)-acyl carbon of various straight-chain monoamides

<table>
<thead>
<tr>
<th>Monoamide</th>
<th>( D_{M+} ) 3M HNO(_3)</th>
<th>( D_{M+} ) 6M HNO(_3)</th>
<th>SF 3M HNO(_3)</th>
<th>SF 6M HNO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{UO}^{2+} )</td>
<td>( \text{Pu}^{4+} )</td>
<td>( \text{UO}^{2+} )</td>
<td>( \text{Pu}^{4+} )</td>
</tr>
<tr>
<td>DBAA</td>
<td>9.9</td>
<td>21</td>
<td>0.47</td>
<td>6.4</td>
</tr>
<tr>
<td>DBBA</td>
<td>5.3</td>
<td>4.0</td>
<td>1.3</td>
<td>4.7</td>
</tr>
<tr>
<td>DiBBA</td>
<td>5.1</td>
<td>3.5</td>
<td>1.5</td>
<td>4.8</td>
</tr>
<tr>
<td>DBiBA</td>
<td>2.4</td>
<td>0.080</td>
<td>30</td>
<td>3.3</td>
</tr>
<tr>
<td>DiBiBA</td>
<td>2.0</td>
<td>0.057</td>
<td>35</td>
<td>3.1</td>
</tr>
<tr>
<td>DBPVA</td>
<td>0.60</td>
<td>0.0009</td>
<td>667</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The effect of methylation on the alpha carbon on the acyl group was considered by Pathak for monoamides with branched nitrogen alkyl chains in an aliphatic diluent. Similar to straight nitrogen alkyl chains, distribution of uranium was highest for the monoamide with a primary alpha acyl carbon, 1 M N,N-di-(2-ethylhexyl)acetamide (D2EHAA), in n-dodecane over the range of 0.01 – 6 M nitric acid. Distribution of \( \text{UO}^{2+} \) and \( \text{Th}^{4+} \) decreases as the substitution of the alpha acyl carbon increases from a primary to quaternary carbon in the order of D2EHAA > D2EHPA >
D2EHiBA > D2EHPVA, respectively. Although the metal distribution decreases, the separation factor \((D_{U}/D_{Th})\) increases with increased alpha acyl substitution. In a similar study, Pathak also showed the extraction of UO\(_{2}^{2+}\) from a 4 M HNO\(_{3}\) solution by 1 M D2EHBA, which contains a secondary acyl alpha carbon, in n-dodecane resulted in a distribution value of 8.36\(^{127}\). The distribution of D\(_{U(VI)}\) using D2EHiBA, a monoamide with a tertiary alpha acyl carbon, decreased to 3.70. Similarly, the distribution of Th\(^{4+}\) decreases by a factor of 6, from \(6.01 \times 10^{-2}\) to \(1.0 \times 10^{-2}\) when substitution increased. The significant decrease in D\(_{Th(IV)}\) values results in a higher S.F. \((D_{U}/D_{Th})\) for D2EHiBA compared to D2EHBA. For monoamides with the same acyl chain, isobutyramide, the S.F. further increases when nitrogen alkyl chains were straight for N,N-dioctylisobutyramide (DOIba). Although DOIba had promising results over D2EHiBA, few studies have focused on straight chained monoamides with branched acyl groups\(^{133,134}\).

The few studies on straight chained monoamides with branched acyl groups, like DOIba, could be due to third phase formation under higher metal loadings. Solutions of 1 M monoamide N,N-dihexyl(2-ethyl)hexanamide (DH2EHA) in n-dodecane will provide a distribution ratio of 1.63 for 0.5 M UO\(_{2}^{2+}\) in 3 M HNO\(_{3}\). However; third phase formation occurred when 1.5 M UO\(_{2}^{2+}\) was used under the same conditions with DH2EHA\(^{53}\). Under the same metal loadings, the monoamides containing branched nitrogen alkyl chains (D2EHBA, D2EHiBA, and D2EHPVA) did not show signs of third phase formation. Under tracer conditions in 3 M HNO\(_{3}\) and 1 M monoamide in n-dodecane, DH2EHA had higher \(D_{U(VI)}/D_{Pu(IV)}\) and \(D_{U(VI)}/D_{Np(IV)}\) separation factors than the straight acyl chain D2EHBA. Shown in Table 4.3, the distribution of UO\(_{2}^{2+}\) and Pu\(^{4+}\) decreased with increased alpha acyl substitution, similar to the UO\(_{2}^{2+}\) and Th\(^{4+}\) extraction results studied by Pathak. Furthermore, the decreased distribution was more pronounced for Pu\(^{4+}\), resulting in higher S.F. \((D_{U(VI)}/D_{Pu(IV)})\) with increased alpha acyl substitution.
Table 4.3: Impact of methyl substitution on the α-acyl carbon of various branched-chain monoamides

<table>
<thead>
<tr>
<th>Monoamide</th>
<th>$D_{U(VI)}$</th>
<th>$D_{Np(VI)}$</th>
<th>$D_{Pad(V)}$</th>
<th>S.F. $(D_{U(VI)}/D_{Np(VI)})$</th>
<th>S.F. $(D_{U(VI)}/D_{Pad(V)})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DH2EHA</td>
<td>1.82</td>
<td>&lt;0.01</td>
<td>0.27</td>
<td>&gt;182</td>
<td>6.74</td>
</tr>
<tr>
<td>D2EHPA</td>
<td>8.85</td>
<td>0.26</td>
<td>1.93</td>
<td>34.04</td>
<td>4.59</td>
</tr>
<tr>
<td>D2EHiba</td>
<td>2.73</td>
<td>&lt;0.01</td>
<td>0.034</td>
<td>&gt;273</td>
<td>80.29</td>
</tr>
<tr>
<td>D2EHPVA</td>
<td>1.50</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&gt;150</td>
<td>&gt;150</td>
</tr>
</tbody>
</table>

The impact on the complexation thermodynamics as a result of the increased substitution at the alpha acyl carbon was studied on the extraction of $\text{UO}_2^{2+}$ from 3 M HNO$_3$ by 1 M D2EHAA, D2EHPA, D2EHiba, and D2EHPVA.$^{135}$ The $K_M$ was used to calculate $\Delta G$, the van’t Hoff method was used to establish $\Delta H$, and $\Delta S$ was calculated using the Gibb’s free energy equation. The results showed $\text{UO}_2^{2+}$ extraction becomes less exothermic as the substitution on the alpha acyl carbon increases (-8.80, -4.51, -1.31, 1.48 kJ/mol for D2EHAA, D2EHPA, D2EHiba, D2EHPVA respectively). For the most substituted monoamide, D2EHPVA, the Gibb’s free energy becomes positive. Increased branching on the alpha acyl carbon leads to an overall decrease in complex stability, and results in a positive Gibbs free energy value.

Unlike observations for the straight chained monoamides, no apparent enthalpy compensation exists when branching at the alpha acyl carbon is varied. Thus, there is a decrease in the log $K$ for metal extraction with an increase in branching. The positive $\Delta G$ for D2EHPVA means $\text{UO}_2^{2+}$ extraction is thermodynamically unfavorable, and $\text{UO}_2^{2+}$ extraction becomes more favorable when the acyl alpha carbon is less substituted. Using the van’t Hoff and calorimetric methods, $\Delta H$ and $\Delta S$ values were established by Rodrigues for the extraction of $\text{UO}_2^{2+}$ from 3 M LiNO$_3$ by 1 M D2EHiba.$^{108,136}$ Under these conditions $\Delta H$ was $-28.3 \pm 1.2$ kJ/mol while $\Delta S$ was $-0.097 \pm 0.004$ kJ/mol·K. Differences between Pathak and Rodrigues values can be attributed to the different aqueous phases of 3 M HNO$_3$ and 3 M LiNO$_3$, respectively. These results support the
aforementioned trend where increased substitution of the alpha acyl carbon decreases distribution values, and demonstrate the complexity of the extraction mechanism.\textsuperscript{101,135}

4.7 Branched Monoamides: Effect of Nitric Acid

The effect nitric acid has on the extraction of UO\textsubscript{2}\textsuperscript{2+} and Pu\textsuperscript{4+} by 1 M D2EHiBA was studied over 0.5 M to 10 M HNO\textsubscript{3}.\textsuperscript{126} Figure 4.4 shows D2EHiBA extracts UO\textsubscript{2}\textsuperscript{2+} favorably over Pu\textsuperscript{4+}. Extraction of UO\textsubscript{2}\textsuperscript{2+} increases rapidly with increased acid concentration, reaches a maximum D\textsubscript{U(VI)} value of about 4.5 at 8 M HNO\textsubscript{3} after which it begins to decrease. Conversely, distribution of Pu\textsuperscript{4+} remains below 0.5 over all acid conditions, but a gradual increase is observed. The cause of low D\textsubscript{Pu(IV)} values was recently elucidated by Acher et. al.\textsuperscript{54}

Acher’s study combined experimental and computational methods to determine the coordinate environments between UO\textsubscript{2}\textsuperscript{2+}, Pu\textsuperscript{4+}, and Ce\textsuperscript{4+} with straight chain and branched monoamides.\textsuperscript{54} N,N-dibutylbutyramide (DBBA) UO\textsubscript{2}\textsuperscript{2+} crystals were generated by slowly evaporating a 1:2.5 uranyl nitrate:DBBA molar ratio in diisopropyl ether. Single crystal XRD analysis revealed the uranyl cation is coordinated to two oxygens from the monoamide ligand and two bidentate nitrate anions in the equatorial plane. The 2.503 Å U-O\textsubscript{NO3} bond distances are longer than the 2.343 Å U-O\textsubscript{amide} bond distances. The equatorial position and oxygen bond distances created a distorted hexagonal bipyramidal coordination environment.

The Pu\textsuperscript{4+} (or Ce\textsuperscript{4+}) crystals were generated by extraction of a 0.25 M Pu\textsuperscript{4+} nitric acid solution containing 7 M lithium nitrate into 0.25 M DBBA toluene solution. The Pu\textsuperscript{4+} toluene solution was dried, causing crystal formation. Both Pu\textsuperscript{4+} and Ce\textsuperscript{4+} were found to be complexed to oxygen’s from two DBBA ligands and four bidentate nitrate anions. Two types of bond distances were observed for the nitrate ions on each metal which indicated nitrates were coordinating in an asymmetric bidentate fashion. The 2.26 Å Pu-O\textsubscript{amide} bond distance was found to be longer than the
2.24 Å Ce-\textit{O}_{\text{amide}} bond distance, and was attributed to steric constraints of the bidentate nitrate ligands brought about by the smaller atomic radii of Pu$^{4+}$ compared to Ce$^{4+}$. Aside from the slight variations in bond distances, Pu$^{4+}$ and Ce$^{4+}$ exhibited a distorted bicapped dodecahedron coordination environment.

![Figure 4.4: Distribution values as a function of nitric acid concentration on the extraction of tracer level uranium (circles) and plutonium (squares) with 1 M D2EHBA in n-dodecane.](image)

Extended X-ray absorption fine structure (EXAFS) was used to compare coordination environments of UO$_2^{2+}$ and Pu$^{4+}$ with the straight acyl chain monoamide N,N-di(2-ethylhexyl)butyramide and the branched N,N-di(2-ethylhexyl)isobutyramide in n-dodecane. The uranyl oxygen and equatorial bidentate nitrate anions bond distances were the same between D2EHBA and D2EHBA. Small variations were found between the U-\textit{O}_{\text{amide}} bond distances. The 2.40 Å D2EHBA U-O bond distance was longer than 2.38 Å D2EHBA U-O bond distance. The slight variation was attributed to the higher electronic donation of the branched, D2EHBA, acyl oxygen compared to the straight chain D2EHBA.
Elucidation of the Pu\textsuperscript{4+}-monoamide coordination environment required different Pu\textsuperscript{4+} monoamide complexes to be modeled against the EXAFS data. The straight chain, Pu\textsuperscript{4+}-D2EHBA coordination environment matched the bicapped dodecahedron complex that was observed for Pu\textsuperscript{4+}-DHHA. Poor agreement was found between the bicapped dodecahedron model complex (Pu(NO\textsubscript{3})\textsubscript{4}L\textsubscript{2}) and Pu\textsuperscript{4+}-D2EHiBA EXAFS data. Accounting for the protonation of monoamides at high nitric acid concentrations (> 6 M), a Pu(NO\textsubscript{3})\textsubscript{6}(HL)\textsubscript{2} complex was modeled where the protonated monoamides are hydrogen bonded to nitrate ions in an outer-coordination sphere. The Pu(NO\textsubscript{3})\textsubscript{6}(HL)\textsubscript{2} complex also did not match the experimental EXAFS data. However, a 50/50 mixture of the two complexes resulted in agreement between the calculated and experimental data.

![Figure 4.5: Extraction constants of uranium and thorium by 1 M N,N-di(2-ethylhexyl)isobutyramide (D2EHiBA) in dodecane.](image)

This suggested the possibility of a Pu(NO\textsubscript{3})\textsubscript{5}L(HL) complex that would compromise between the Pu(NO\textsubscript{3})\textsubscript{4}L\textsubscript{2} and Pu(NO\textsubscript{3})\textsubscript{6}(HL)\textsubscript{2} complexes. This Pu(NO\textsubscript{3})\textsubscript{5}L(HL) complex features one monoamide in the inner sphere and a protonated monoamide coordinated to a nitrate in the outer sphere. The computed results from the third complex also matched the experimental EXAFS data. The study was not able to ascertain if the Pu\textsuperscript{4+}-D2EHiBA complexes in solution were indeed a 50/50 mixture of the two species, or if the third complex is forming. Regardless, the data shows
the increase of steric hindrance from the branched monoamide causes an inner-sphere as well as an outer-sphere complex to form.

The effect of nitric acid was also compared for the extraction of Th$^{4+}$ and UO$_2^{2+}$ by D2EHiBA.\textsuperscript{100,127} Using tracer levels of U, the distribution of uranium increased with increased nitric acid, and matched the trend previously observed by Prabhu et. al.\textsuperscript{126} Similar to Pu$^{4+}$, Figure 4.5 shows Th$^{4+}$ is not extracted considerably by D2EHiBA. In the presence of 4 mM Th, the D$_U$ values did not change. However, at higher Th$^{4+}$ loading conditions (40 mM to 1 M), the D$_{U(VI)}$ increased due to a salting out effect caused by a large excess of Th.\textsuperscript{109,110} Pathak compared the UO$_2^{2+}$/Th$^{4+}$ separation factors (S.F.) between 1 M D2EHiBA and 30% TBP over a range of 1 to 6 M HNO$_3$.\textsuperscript{100} Table 4.4 shows the S.F.’s for D2EHiBA are an order of magnitude greater than those found for TBP. These studies show that the selectivity of D2EHiBA for dioxo-cations is not dependent on the size of the bare metal cation (Pu$^{4+}$ and Th$^{4+}$) and that D2EHiBA can selectively extract UO$_2^{2+}$ over Pu$^{4+}$ and Th$^{4+}$.

<table>
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<tr>
<th>HNO$_3$ (M)</th>
<th>S.F. (D$<em>U$/D$</em>{Th}$)</th>
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<td>1</td>
<td>120</td>
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<td>2</td>
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4.8 Branched Monoamides: Effect of Pu Oxidation State

To further probe the ability for D2EHiBA to selectivity extract a dioxo-cation over a bare metal cation, the extraction of PuO$_2^{2+}$ in the presence of Th$^{4+}$ was compared to the Pu$^{4+}$ extraction by Pathak et. al.\textsuperscript{129,130} The first study assessed the efficacy of different oxidation agents to generate
and stabilize PuO$_2^{2+}$ long enough for extraction. The oxidants studied were potassium dichromate (K$_2$Cr$_2$O$_7$), ammonium cerium nitrate ((NH$_4$)$_2$Ce(NO$_3$)$_6$), and silver oxide (AgO). Of the three oxidizers, in the presence of 0.96 M Th$^{4+}$, 0.032 M AgO produced the highest PuO$_2^{2+}$ distribution value of 4.3 in 4 M HNO$_3$. Under the same acid and Th$^{4+}$ concentration, 0.1 M K$_2$Cr$_2$O$_7$ and 0.1 M (NH$_4$)$_2$Ce(NO$_3$)$_6$ had $D_{Pu}$ values of 0.8 and 3.8, respectively. An intense yellow color was observed in the K$_2$Cr$_2$O$_7$ and (NH$_4$)$_2$Ce(NO$_3$)$_6$ systems which suggested Cr$^{6+}$ and Ce$^{4+}$ were co-extracted with PuO$_2^{2+}$ by D2EHiBA. Further analysis of how much Cr$^{6+}$ or Ce$^{4+}$ was recovered using ICP-MS or ICP-OES would be interesting since a yellow color is not a quantifiable assessment of Cr$^{6+}$ or Ce$^{4+}$ presence. No evidence existed for Ag extraction and the recovery of Ag$^{2+}$ or Ag$^+$ would not be anticipated by these extractants. The high Pu$^{4+}$ distribution value and limited evidence of Ag co-recovery with Pu$^{4+}$ indicates AgO is currently the best oxidant compared to K$_2$Cr$_2$O$_7$ and (NH$_4$)$_2$Ce(NO$_3$)$_6$.

Due to AgO oxidation efficiency, Pathak compared the extraction of Pu$^{4+}$ to AgO oxidized PuO$_2^{2+}$ in the presence of 0.96 M Th$^{4+}$ at 4 M HNO$_3$ by 1.0 to 1.5 M D2EHiBA in n-dodecane. The study showed $D_{Th}$ and $D_{Pu}$ values increased from 0.030 to 0.076 and 1.2 to 2.9 for Th$^{4+}$ and Pu$^{4+}$, respectively, as the extractant concentration increased. For PuO$_2^{2+}$, the distribution value increased from 4.3 to 8.0 as D2EHiBA concentration increased. In all D2EHiBA concentrations, PuO$_2^{2+}$ distributions values were higher than Th$^{4+}$ and Pu$^{4+}$. Furthermore, PuO$_2^{2+}$/Th$^{4+}$ separation factors were much higher than Pu$^{4+}$/Th$^{4+}$ for all monoamide concentrations. This study complements the previous uranium study by showing that D2EHiBA is selective for PuO$_2^{2+}$ over Pu$^{4+}$. The different distribution values between Pu$^{4+}$ and Th$^{4+}$ indicates that while cation size is not the dominating factor for selectivity, it does play a slight role. These results also show the potential for D2EHiBA to be used in the group actinide extraction (GANEX) process which would be a
more proliferation resistant separation process due to the co-recovery of U, Pu and Np.\textsuperscript{51} For further consideration, the oxidation of Am\textsuperscript{3+} to AmO\textsuperscript{2+} and subsequent extraction by D2EHiBA should be investigated.

4.9 Conclusion

Monoamides have been shown as a viable candidate to replace TBP in nuclear fuel reprocessing. The straight chain monoamide, DHOA, outperformed TBP for recovery of Pu from a simulated used uranium fuel waste stream. This was a result of the higher distribution of Pu seen with DHOA at 4 M HNO\textsubscript{3} than TBP, and the stripping efficiency of Pu from a solution of DHOA with low concentrations of nitric acid. Branching of the alpha acyl chain allows for the selective extraction of dioxo-cation, hexavalent actinides from tetravalent actinides, but is accompanied with a general decrease in metal distribution. Separation factors between U/Th and Pu/Th were much higher for monoamides with alpha acyl branching than those observed with TBP, which may be preferential depending on future decisions regarding advanced nuclear fuel cycle implementation. Monoamides, like TBP, are able to form third phases. Future research should focus on why certain monoamide structures are susceptible to third phase formation. Results from third phase studies will advance an optimized monoamide structure for reprocessing purposes. When considering a group actinide extraction process, branched acyl chain monoamides should be studied; specifically, N,N-dioctylisobutyramide as an extracting ligand due to its higher D\textsubscript{U} values and U/Th separation factors compared to D2EHiBA. Advances in hexavalent actinide extraction will lead to further studies for group extraction of U, Np, Pu, and Am with branched monoamides.
CHAPTER 5

INNER VERSUS OUTER SPHERE METAL-MONOAMIDE COMPLEXATION:
RAMIFICATIONS FOR TETRAVALENT & HEXAVALENT ACTINIDE SELECTIVITY

Kevin McCann, Sergey I. Sinkov, Gregg J. Lumetta, Jenifer C. Shafer

5.1 Abstract

Oxidation of americium to the hexavalent state could streamline used nuclear fuel management through a group hexavalent actinide separation process. Monoamides, N, N-dialkyl amides, are being considered in this work due to their selectivity towards hexavalent, over tetravalent, actinides. Hexavalent selectivity arises when the monoamides contain a branched acyl chain. While this selectivity has been known since its preliminary studies by Siddall, structures of the extracted species have only recently been investigated. This study expands on other research efforts by examining the structure-extraction functionality of straight and branched monoamides with Pu$^{4+}$ and PuO$_2^{2+}$. In both Pu oxidations states, the effect of acyl chain length with N,N-dihexylbutyramide, N,N-dihexylvaleramide, N,N-dihexylhexanamide were compared to methyl branched N,N-dihexyl(2-methyl)butyramide and N,N-dihexyl(2-methyl)valeramide, as well as ethyl branched N,N-dihexyl(2-ethyl)butyramide and N,N-dihexyl(2-ethyl)hexanamide. These structure-extraction relationships were characterized by collecting UV-Vis spectra of the metal-monoamide extracted species and tracer distribution studies. The UV-Vis analysis was found to match distribution values collected under radiotracer conditions and indicated Pu was extracted as the tetra- and hexanitrato monoamide complex for Pu$^{4+}$ and the bis- or trisnitrato species for PuO$_2^{2+}$. The monoamides’ ability to recover Cu$^{3+}$ periodate oxidized Am was also studied using

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radiotracer methods. Initial efforts with nitric acid pretreated monoamides, salting agents, and synergistic studies with di-(2-ethylhexyl)phosphoric acid (HDEHP) were ineffective. Pretreatment with sodium bismuthate was found to improve Am recovery, and distributions above one were achieved with straight chain monoamides at 3 M HNO₃.

5.2 Introduction

Table 5.1: Structure, name, and abbreviation of straight (left column) and branched (middle and right column) of monoamides studied in this manuscript. Chain length increases moving down.
Used nuclear fuel arising from commercial nuclear power reactors can generally be managed by using open, partially closed, or fully closed nuclear fuel cycles. In an open nuclear fuel cycle, used nuclear fuel goes directly from the reactor to disposition into a geological repository without any chemical processing. Open nuclear fuel cycles have several limitations, including million year waste management timelines, lack of viable repository sites and limited demonstration of safe waste disposal, and only 5% energy consumption of the nuclear fuel originally placed in the reactor. A partially closed nuclear fuel cycle seeks to recover the remaining energy available in the nuclear fuel by separating deleterious fission products from U and Pu. The recovered plutonium can be reprocessed into MOX (Mixed Oxide) fuel, which increases the energy recovered from the original nuclear material. More aggressive, fully closed, fuel cycles design strategies for the recovery and burnup of neptunium and americium to decrease the waste storage timelines and high level waste (HLW) repository capacity. While fully closed nuclear fuel cycle would have several waste management benefits, the separations technology necessary to enable implementation of a closed fuel cycle requires further development to decrease costs and increase proliferation resistance.

Industrial scale separations of use nuclear fuel necessary to enable closed nuclear fuel cycles have, by in large, remained unchanged since 1954. In this year, the Plutonium Uranium Reduction Extraction (PUREX) solvent extraction process was launched at the Hanford site in south central Washington state. The PUREX process uses tributyl phosphate (TBP) dissolved in an organic diluent to recover hexavalent uranium, UO$_2^{2+}$, and tetravalent plutonium, Pu$^{4+}$, from nitric acid solution containing fission products and cladding materials. In a partially closed fuel cycle, the PUREX process, or a comparable commercial derivative, is the only separation step. In a fully closed fuel cycle, the selective recovery of americium and neptunium is necessary to enable
their transmutation to shorter lived isotopes. This transmutation process significantly shortens nuclear waste management timelines and typically requires one or two additional separation steps beyond the PUREX process to complete Am and Np recovery.

Since neptunium’s chemistry readily parallels that of uranium or plutonium, the PUREX process can be adjusted to recover neptunium. Recovery of americium is non-trivial due to the similar chemistry americium shares with lanthanide fission products. Both americium and the lanthanides share a common trivalent oxidation state, have similar atomic radii, and tend towards ionic interactions due to the contraction of the 4f and 5f orbitals with the 6s and 7s valence shells. Americium – lanthanide separation methods under development use soft donor, such as nitrogen, ligands to selectively complex Am over the lanthanides since actinides participate in limited covalent interactions with soft donor ligands.\textsuperscript{25,82,84,138} These approaches are non-ideal since they require the removal of U, Np, and Pu, via a PUREX derivative prior to the Am – lanthanide separation. This increases the cost associated with used nuclear fuel management largely due to the cost of constructing a second reprocessing facility for the Am-lanthanide separation. A more streamlined process, where Am is co-recovered with U, Np, and Pu, would be preferred to minimize reprocessing cost.

A potential means of achieving the selective group recovery U, Np, Pu, and Am centers on the common availability of the hexavalent oxidation state. Actinides readily form the unique linear dioco cation geometry upon oxidation to the pentavalent (AnO\textsubscript{2}\textsuperscript{+}) or hexavalent (AnO\textsubscript{2}\textsuperscript{2+}) oxidation state.\textsuperscript{29,33,40,85} Uranium generally forms the linear dioxo cation under the PUREX operating conditions, and neptunium and plutonium can be readily oxidized to the hexavalent state.\textsuperscript{42} Americium, on the other hand, requires the use of strong oxidants, such a sodium bismuthate or Cu\textsuperscript{3+} periodate, that can overcome the AmO\textsubscript{2}\textsuperscript{2+}/Am\textsuperscript{3+} 1.68 V standard reduction potential.\textsuperscript{36} Recent
studies have demonstrated the oxidation of Am to the hexavalent state and recovery by phosphorous based ligand, TBP or diamyl amylphosphonate.\textsuperscript{33,41,85} The over sixty years of operational precedent associated with the PUREX process have demonstrated the viability of TBP as an actinide extractant, however, the use of TBP has two major drawbacks. As a phosphorous based ligand, TBP cannot be incinerated which leads to large volumes of secondary low-level radioactive waste. Secondly, the radiolytic degradation products of TBP decrease metal stripping efficiency. To circumvent TBP’s shortcomings, monoamides (Table 5.1) have been studied due to their innocuous degradation products and incinerability as a CHON (carbon, hydrogen, oxygen, nitrogen) based ligand.\textsuperscript{139}

Extraction studies of UO\textsubscript{2}\textsuperscript{2+} and Pu\textsuperscript{4+} using monoamides have shown the chemistry of the acyl group effects the monoamide’s extraction capabilities. Namely, straight chain monoamides will effectively extract tetravalent and hexavalent actinides. When the alpha carbon off the acyl oxygen group becomes more substituted the monoamide becomes more selective for hexavalent actinides over tetravalent actinides.\textsuperscript{53,100,139} Selective recovery of the hexavalent state, over the tetravalent state, is unusual since the favorability of actinide recovery usually trends as An\textsuperscript{4+} > AnO\textsubscript{2}\textsuperscript{2+} >> An\textsuperscript{3+} > AnO\textsubscript{2}\textsuperscript{2+} due to the decrease in charge density.\textsuperscript{37,93} While previously reported literature compared the structural effects to hexavalent U to tetravalent Pu and Th, this manuscript uses the same metal, Pu, to study structural effects of synthesized straight chained N,N-dihexylhexanamide, N,N-dihexylvaleramide, N,N-dihexylhexanamide and branched N,N-dihexyl(2-methyl)butyramide, N,N-dihexyl(2-ethyl)butyramide, N,N-dihexyl(2-methyl)valeramide, and N,N-dihexyl(2-ethyl)hexanamide (Table 5.1).

Hexavalent selectivity of branched monoamides is advantageous when considering a hexavalent group actinide separation process. Oxidation of Am\textsuperscript{3+} to the hexavalent state (1.68 V
vs. SCE)\(^{2-26}\) and extraction by solvating ligands from molar nitric acid has been demonstrated using strong oxidants such as sodium bismuthate\(^{40}\) and Cu\(^{3+}\) periodate.\(^{85}\) The strong oxidants are capable of oxidizing other metals encountered in the back end nuclear fuel cycle, i.e. Ce\(^{3+}\) to Ce\(^{4+}\). Oxidation of Ce\(^{3+}\) to the tetravalent state would cause Ce to be extracted by phosphorous type solvating ligands, such as diamyl amylphosonate or tri-butylphosphate, instead of remaining with the trivalent lanthanides.\(^{41}\) Straight chain and hexavalent selective branched monoamides have been shown to extract AmO\(_2\)\(^{2+}\) oxidized by sodium bismuthate.\(^{86}\) The sodium bismuthate study demonstrated that group hexavalent actinides can be extracted by straight or branched monoamides, but branched are preferred when considering the presence of Ce\(^{4+}\). The manuscript also showed hexavalent U and Np had different solvation number (~1.5) compared to Pu and Am (~2.0). This manuscript assesses the ability for monoamides to extract AmO\(_2\)\(^{2+}\) using Cu\(^{3+}\) periodate as an oxidant. Furthermore, UV-Vis spectra of Pu\(^{4+}\) and PuO\(_2\)\(^{2+}\) monoamide species are presented, and provide insight into the structure of the extracted species based off variations in the monoamides structure and plutonium’s oxidation state.

5.3 Experimental: Monoamide Synthesis

All monoamides were synthesized using nucleophilic attack of dialkylamines with acyl chlorides.\(^{98}\) To make N,N-dihexylbutyramide, 0.131 moles dihexylamine (Acros Organics, 99+%) was diluted with 45.00 mL chloroform (Sigma-Aldrich, HPLC Plus) and 17.00 mL triethylamine (Alfa Aesar, 99+%) in a 250 mL round bottom flask with a stirbar, reflux condenser and addition funnel attached. In the addition funnel, 0.150 moles butyryl chloride (Alfa Aesar, 98%) were diluted with 18.40 mL chloroform. The reaction apparatus was purged with nitrogen gas. The round bottom flask was chilled in an ice bath to prevent the reaction from exceeding 10\(^\circ\) C during dropwise addition of butyrl chloride to the dihexylamine solution. The addition funnel was
replaced with a stopper after addition of solutions, and flask was purged with nitrogen. The solution was heated to 60° C, the boiling point of chloroform, and refluxed for 2 hours. The product was filtered, and the filtrate was washed with 10 weight percent Na₂CO₃, 1 M HCl, and distilled water to remove triethylamine chloride and unreacted triethylamine. The solution was dried with sodium sulfate overnight. To purify the product, chloroform was removed using a rotovap and finally purified via vacuum distillation. The final product was determined to be 99% pure via ¹H NMR and had a 71% yield. In total, N,N-dihexylvaleramide, N,N-Diheylhexanamide, N,N-dihexyl(2-methyl)butyramide, N,N-dihexyl(2-ethyl)butyramide, N,N-dihexyl(2-methyl)valeramide, and N,N-dihexyl(2-ethyl)hexanamide were synthesized by following the same procedure with the desired acyl chloride substituent. All products were 99% pure by ¹H NMR (JEOL 500MHz) and percent yield ranged from 53% to 77%. Monoamides were also characterized using Bruker Alpha (ATR) FTIR, Figure 5.1 and 5.2.

¹H NMR Results:

N,N-dihexylbutyramide: (CDCl₃, 500 MHz), δ = 0.69 – 0.91 (9H, m, CH₃), 1.1 – 1.3 (12 H, br, CH₂), 1.33 – 1.50 (4H, br, CH₂), 1.50 – 1.64 (2H, m, CH₂), 2.15 (2H, t, OCH-CH₂), 3.01 – 3.26 (4H, 2 t, N-CH₂)

N,N-dihexylvaleramide: (CDCl₃, 500 MHz), δ = 0.74 – 0.92 (9H, m, CH₃), 1.13 – 1.37 (14H, m, CH₂), 1.37 – 1.63 (6H, m, CH₂), 2.22 (2H, t, CH₂), 3.08 – 3.29 (4H, 2 t, N-CH₂)

N,N-dihexylhexanamide: (CDCl₃, 500 MHz), δ = 0.76 – 0.93 (9H, m, CH₃), 1.15 – 1.35 (16H, br, CH₂), 1.39 – 1.68 (6H, m, CH₂), 2.22 (2H, t, CH₂), 3.06 – 3.33 (4H, 2 t, N-CH₂)

N,N-dihexyl(2-methyl)butyramide: (CDCl₃, 500 MHz), δ = 0.71 – 0.88 (9H, br, CH₃), 0.95 – 1.06 (3H, m, CH₃), 1.1 – 1.7 (18H, m, CH₂), 2.44 (1H, m, CH), 3.02 – 3.34 (4H, m, N-CH₂)
N,N-dihexyl(2-ethyl)butyramide: (CDCl₃, 500 MHz), δ = 0.75 – 0.91 (12H, m, CH₃), 1.16 – 1.34 (12H, br, CH₂), 1.34 – 1.67 (8H, m, CH₂), 2.31 – 2.39 (1H, m, CH), 3.14 – 3.32 (4H, 2 t, N-CH₂)

N,N-dihexyl(2-methyl)valeramide: (CDCl₃, 500 MHz), δ = 0.73 – 0.90 (9H, m, CH₃), 0.96 – 1.06 (3H, d, CH₃), 1.12 – 1.66 (20H, m, CH₂), 2.47 – 2.62 (1H, m, CH), 3.04 – 3.36 (4H, m, N-CH₂)

N,N-dihexyl(2-ethyl)hexanamide: (CDCl₃, 500 MHz), δ = 0.72 – 0.90 (12H, m, CH₃), 1.0 – 1.64 (24H, m, CH₂), 2.31 – 2.45 (1H, m, CH), 3.08 – 3.33 (4H, m, N-CH₂)

Figure 5.1: FT-IR of synthesized straight chain monoamides N,N-dihexylhexanamide DHHA (blue), N,N-dihexylvaleramide DHVA (black), and N,N-dihexylbutyramide DHBA (green).
5.4 Experimental: Extraction Studies

Extraction studies were completed on $^{239}\text{Pu}^{4+}$ and $^{239}\text{PuO}_2^{2+}$ in HNO$_3$ (Fisher, optima grade) with 1.0 M monoamide in n-dodecane (Sigma-Aldrich). The organic phase was pre-equilibrated with nitric acid prior to Pu extraction. The $^{239}$Pu stocks were prepared by adding 30% H$_2$O$_2$ dropwise to 25 mM Pu 2 M HNO$_3$ solution to reduce any oxidized species and generate pure Pu$^{4+}$ solution as measured using UV-Vis spectroscopy on a Spectral 420 CCD Array UV-Vis Spectrophotometer. The PuO$_2^{2+}$ solution was generated by addition of HClO$_4$ to oxidize Pu mixed
species to PuO$_2^{2+}$. The solution was slowly evaporated until wet PuO$_2^{2+}$ crystals formed, diluted with 0.5 M HNO$_3$, and repeated two more times. The final concentration was 48 mM PuO$_2^{2+}$ in 0.5 M HNO$_3$, and was determined to be 100% PuO$_2^{2+}$ by visible absorbance spectroscopy. To complete tracer level extractions, Pu was added to 2 M HNO$_3$ for a final concentration of 0.21 mM Pu$^{4+}$ or 0.40 mM PuO$_2^{2+}$. Extractions were completed by contacting 1 – 5 M HNO$_3$ Pu containing solutions with an equal volume of pre-equilibrated 1 M monoamide. The solutions were mixed by hand for 30 seconds, and centrifuged to disengage the two phases. Each phase was subsampled and added to LSC cocktail (PerkinElmer, Ultima Gold AB) and quantified using PerkinElmer LSC Tri-Carb 3110 TR. Organic phase visible absorbance spectra were also collected after contacting 1.0 M monoamide (pre-equilibrated) with 4.0 mM Pu$^{4+}$ and 3.0 mM PuO$_2^{2+}$ in 4.5 and 4.7 M HNO$_3$, respectively.

Americium extractions were done using $^{241}$Am (Eckert & Ziegler, 1 M HCl). The stock was diluted in 2 M HNO$_3$, and was slowly evaporated until dry and redissolved in 4 M HNO$_3$. The solution was evaporated until almost dry and diluted with 0.1 M HNO$_3$. The process was repeated a third time, and final $^{241}$Am solution was in 0.1 M HNO$_3$. The organic phase was pre-equilibrated with the corresponding nitric acid prior to Am extraction. To oxidize Am, 20 mg of Cu$^{3+}$ periodate (synthesized as previously reported) was added to 2 mL vial and 500 µL $^{241}$Am in respective nitric acid was added to the vial. An equal volume of nitric acid pre-equilibrated 1.0 M monoamide was added, and was shaken by hand for 5 seconds and centrifuged to disengage the two phases. Each phase was subsampled and added to LSC cocktail (PerkinElmer, Ultima Gold AB) and quantified using PerkinElmer LSC Tri-Carb 3110 TR.
5.5 Tetravalent and Hexavalent Pu-Monoamide Extraction Results and Discussion

Distribution values of Pu$^{4+}$ with DHBA, DHVA, and DHHA were collected to determine the effect of acyl chain length on extraction efficiency. As shown in Figure 5.3, the Pu$^{4+}$ distribution values are above 1 at 2 M HNO$_3$ and increase up to the 5 M HNO$_3$ measurement. The distribution increases as a function of acid concentration because monoamides are solvating ligands that extract charge neutral species.$^{99,105}$ The charge neutral species for Pu$^{4+}$ takes on the form Pu(NO$_3$)$_4$ where the nitrates bind in a bidentate fashion to Pu$^{4+}$. As the concentration of nitric acid increases the partitioning of Pu(NO$_3$)$_4$ into the organic phase by 2 monoamide ligands increases.$^{139}$ The extraction by monoamide ligands with increased acyl chain length from 4 carbons (DHBA) to 6 carbons (DHHA) does not show an overall trend. At 5 M HNO$_3$ the Pu$^{4+}$ distribution value is 25 ± 3 while DHVA is 15.1 ± 0.5 and DHHA is 20 ± 2. While the DHBA extracts Pu$^{4+}$ more efficiently than the longer acyl chain monoamides, DHVA shows lower distribution values in general than the six carbon DHHA. It should be noted the range in distribution values differs from roughly 96.2% DHBA extraction to 93.8% with DHVA, a difference of 2.4%.

When the carbon adjacent to the carbonyl group is changed from a secondary (straight chain) to tertiary carbon (branched) the distribution values of Pu$^{4+}$ drop significantly across all acid ranges as shown in Figure 5.3. The type of branching, i.e. methyl versus ethyl, resulted in a specific grouping across all acid ranges as well. The methyl branched DH2MBA and DH2MVA molecules show nearly identical distribution values of 1.09 ± 0.03 and 1.0 ± 0.1, respectively, at 5 M HNO$_3$. Similarly, the DH2EBA and DH2EHA molecules produced distribution values of 0.81 ± 0.06 and 0.77 ± 0.04. The proximity of the distribution values indicates the length of the primary alkyl chain does not greatly affect the distribution values. On the other hand, when comparing DH2MBA vs. DH2EBA, where the primary alkyl chain lengths are equivalent, the distribution
values drop from 1.09 to 0.81 for methyl vs. ethyl branching and equates to a 7.4% change in extraction efficiency. To better understand changes in the extracted species visible absorbance spectra were collected on Pu$_{4}^{+}$ extracted by the various monoamides.

Figure 5.3: Distribution values of Pu$_{4}^{+}$ at various HNO$_3$ concentrations for straight chain monoamides (sky blue) DHBA (circle), DHVA (square), DHHA (diamond). Distribution with methyl branched monoamides (navy blue) DH2MBA (circle) and DH2MVA (diamond) as well as ethyl branched monoamides (green) DH2EBA (square) and DH2EHA (triangle).
The visible absorbance spectrum of Pu$^{4+}$ extracted by DHBA from 4.5 M HNO$_3$, Figure 5.4, bears a striking resemblance to plutonium hexanitrate, Pu(NO$_3$)$_6$, absorbance spectrum. A spectrum of Pu$^{4+}$ in 10 M HNO$_3$, producing Pu(NO$_3$)$_6^{2-}$ species, was overlayed on the Pu$^{4+}$-DHBA spectrum (Figure 5.5). The two spectra have identical spectral signatures, and show only slight variation in peak intensity at 609, 445, and 405 nm as well as a slight blue shift with 10 M HNO$_3$ Pu$^{4+}$ spectrum around 492 nm. Acher et. al. made a similar observation at elevated nitric acid concentrations, and used EXAFS to determine plutonium hexanitrate was being extracted by two protonated N,N-di(2-ethyl)hexylbutyramide ligands via an outer-sphere coordination as Pu(NO$_3$)$_6$(HL)$_2$. The results presented here support the extraction of plutonium hexanitrate...
species by the straight chain monoamides. The reason why the three peaks between 580 and 730 nm are prominent in this work at 4.5 M HNO$_3$ compared to Acher’s spectra in which the three peaks are present but less defined at 5 M HNO$_3$ is not obvious. Nonetheless, in Figure 5.4 the 609 nm peak has a lower intensity than the 650 and 746 nm peaks for all three monoamides. A more intense 609 nm peak relative to 650 and 746 nm would indicate a pure plutonium hexanitrate species is present (Figure 5.5).$^{143}$ Therefore, the spectra indicate another species, plutonium tetranitrate, is present.

![Absorbance spectrum of Pu$^{4+}$](image)

**Figure 5.5:** Absorbance spectrum of Pu$^{4+}$ in 10 M HNO$_3$ which takes the form of plutonium hexanitrate species, Pu(NO$_3$)$_6^{2-}$ (dark blue) and spectrum of Pu$^{4+}$ extracted by 1 M DHBA in n-dodecane from 4.5 M HNO$_3$ (light blue).

In the Pu$^{4+}$ 1 M DHBA spectrum (Figure 5.4), the 650 nm peak is more intense than 609 and 746 nm. This peak intensity pattern indicates some inner-sphere Pu(NO$_3$)$_4$L$_2$ species are present in solution or a dual inner/outer species, Pu(NO$_3$)$_5$L(HL).$^{54,142}$ Similarly, the most
prominent peak for DH2MBA and DH2EBA between 580 – 730 nm spectral region occurs at 649 nm. All three peaks are broadened in both branched monoamides with DH2EBA peaks being the broadest. The broadening is an indication that Pu$^{4+}$ extracted species is more characteristic of inner-sphere species, Pu(NO$_3$)$_4$L$_2$. Furthermore, the peak intensity at 746 nm decreases relative to the 580 – 730 nm peaks, and the 495 nm peak broadens when moving from the straight to methyl to ethyl branched monoamide. The spectra reveal that the branched monoamides show an increase in inner-sphere species, such as Pu(NO$_3$)$_4$L$_2$ or the dual inner/outer species, Pu(NO$_3$)$_5$L(HL). An increase of inner-sphere extracted species for branched monoamides is peculiar as the branching on monoamides induces an increase in steric hindrance and has been ascribed as the reason tetravalent actinide extraction decreases.

The Pu$^{4+}$ distribution values were calculated by measuring the Pu$^{4+}$ concentration at the 476 nm aqueous phase peak before and after extraction, Figure 5.6. For 1 M DHBA, the Pu$^{4+}$ concentration was below limit of quantitation after mixing owing to its 96% extraction efficiency measured in Figure 5.3 by LSC. The 1 M DH2MBA and DH2EBA distribution values were 1.12 ± 0.05 and 0.79 ± 0.04 respectively and match the values measured in Figure 5.3. The decrease in distribution values correlates to a decrease in outer-sphere extraction character as DHBA > DH2MBA > DH2EBA. Intuitively, the branched monoamide would experience less steric hindrance with an outer-sphere species since the extractant is sitting further from the metal center. The decrease in monoamide protonated outer-sphere species, Pu(NO$_3$)$_6$(HL)$_2$, with branched monoamides for Pu$^{4+}$ extraction under similar HNO$_3$ concentration suggests branched monoamides are less apt to protonation than their straight chain homologues. Therefore, steric hindrance as well as availability of protonated monoamides could be contributing to the decreased distribution values observed with branched monoamides.
Figure 5.6: UV-Vis spectrum of Pu$^{4+}$ in 4.5 M HNO$_3$ before (black) and after (red) vortexing with 1 M N,N-dihexyl(2-ethyl)butyramide.

Distribution value was calculated as 0.79 ± 0.04 by calculating the concentration of Pu$^{4+}$ before and after contact with the organic phase. Concentrations were calculated using molar absorptivity of 89.5 M$^{-1}$cm$^{-1}$ at 476 nm. Distribution = $\frac{[Pu^{4+}]_{org}}{[Pu^{4+}]_{aq}} = \frac{(Pu^{4+}_{initial} - Pu^{4+}_{final})}{Pu^{4+}_{final}}$

Extraction of hexavalent plutonium, PuO$_2$$^{2+}$, by straight chain monoamides displayed a trend across all acid concentrations with increasing acyl chains. Shown in Figure 5.7, the distribution values decrease with increased acyl chain length as 7.9 ± 0.3 > 6.1 ± 0.1 > 5.4 ± 0.1 for DHBA > DHVA > DHHA from 5 M HNO$_3$. The extraction efficiency is approximately 88.8% for DHBA and decreases to 84.4% for DHHA. The extraction efficiency is lower than that observed with Pu$^{4+}$, but is to be expected due to Pu$^{4+}$ having a higher charge density than PuO$_2$$^{2+}$.

Conversely, branched monoamides extract PuO$_2$$^{2+}$ to a greater extent than Pu$^{4+}$, Figure 5.7. All PuO$_2$$^{2+}$ distribution values approach 1 at 3 M HNO$_3$ with branched monoamides, while Pu$^{4+}$ values approach 1 at 5 M HNO$_3$ with the same ligands. At 5 M HNO$_3$, the PuO$_2$$^{2+}$ distribution values
reach $2.27 \pm 0.01$, $2.5 \pm 0.3$, $2.8 \pm 0.1$, and $2.60 \pm 0.07$ for DH2MBA, DH2EBA, DH2MVA, and DH2EHA respectively. The values fall within experimental uncertainty of each other; therefore, no overall trend could be deduced.

The organic phase absorbance spectra of PuO$_2^{2+}$ extraction from 4.7 M HNO$_3$ shows a multitude of peaks compared to the PuO$_2^{2+}$ HNO$_3$ spectrum, Figure 5.8. Several peaks are present between 450 and 670 nm, and five distinct peaks are observed at 789, broad 801, 809, broad 824, and 849 nm. The monoamide spectra bear a stark resemblance to UV-Vis collected by Keder et. al. of 4 M HNO$_3$ PuO$_2^{2+}$ extraction by tri-n-octylamine in o-xylene, particularly in the 450 – 670 nm region and with 789 – 824 nm peaks. Keder et. al. deduced PuO$_2^{2+}$ was extracted as a
trinitrate species, $\text{PuO}_2(\text{NO}_3)_3^{-}$, by comparing the $\text{PuO}_2^{2+}$ tri-n-octylamine spectrum to a tetraethylammonium trinitratodioxoplutonate(VI) spectrum. Both spectra are consistent with the aforementioned peaks observed in this work with one exception, the 849 nm peak. Absence of the 849 nm peak in the tetraethylammonium trinitratodioxoplutonate(VI) spectrum indicates another species is being extracted by the monoamides. Correlating with Keder’s research, one species is the plutonyl trinitrate species which would be extracted by a protonated monoamide as, $\text{PuO}_2(\text{NO}_3)_3\cdot\text{HL}$.$^{86,99}$ The second is the charge neutral dinitrate plutonyl species, $\text{PuO}_2(\text{NO}_3)_2(\text{L})_2$, that gives rise to the 849 nm peak.$^{144}$

![Absorbance spectra of PuO$_2^{2+}$ extracted from 4.7 M HNO$_3$ by 1 M DHBA (dashed), DH2MBA (dark green), DH2MVA (light green), DH2EBA (navy blue), and DH2EHA (light blue) in n-dodecane.](image)

Figure 5.8: Absorbance spectra of PuO$_2^{2+}$ extracted from 4.7 M HNO$_3$ by 1 M DHBA (dashed), DH2MBA (dark green), DH2MVA (light green), DH2EBA (navy blue), and DH2EHA (light blue) in n-dodecane.

The presence of two species contradicts 1:2 metal:ligand ratio previously reported for monoamide extraction from 6.5 M HNO$_3$.$^{86}$ However, the slope analysis method used to determine the metal:ligand ratio was lower than 2. A slope of 2 would be indicative of ideal conditions where
only one extracted species exists, but the less than 2 value indicates a 1:1 species can exist which absorption spectra in this study indicate. Changes of Pu concentration in the aqueous phase were measured before and after extraction, and showed 2.2 mM PuO$_2$$^{2+}$ was extracted into the organic phase for all branched monoamides. Given the same PuO$_2$$^{2+}$ concentrations in each monoamide study, the spectra are distinct from each other based off the type of branching. The methyl branched monoamides exhibit similar relative peak intensities compared to the ethyl branched monoamides between 450 and 670 nm. In the 780 – 860 nm range the 789, 801, and 809 peaks are similar. The 824 nm peak, however, shows a broader intensity for the methyl branched while the ethyl branched come to more of a point around 821 nm. The reason for slight differences in the 824 nm spectral region is not obvious. Future studies, using EXAFS, could explicate the type of extracted species and the fine structure differences observed in the UV-Vis.

5.6 Hexavalent Americium Extraction Results and Discussion

Extraction efficiency decreases as one moves across the actinides due to the decrease in charge density for the same oxidation states.$^{86}$ Therefore, it was interest to see if the synthesized monoamides were strong enough to effectively extract hexavalent americium, AmO$_2$$^{2+}$. Prior to studying AmO$_2$$^{2+}$ the extraction of Am$^{3+}$ by 1 M DHBA was measured for 1 – 5 M HNO$_3$ solutions. Trivalent americium was not extracted by DHBA in quantifiable amounts from any acid concentration. This is a favorable result as it indicates trivalent lanthanides will not be extracted in appreciable amounts by monoamides if employed in fuel reprocessing. The Cu$^{3+}$ oxidized Am did show extraction, Figure 5.9, with 1 M DHBA, DHVA, and DHHA, however, the distribution values are below 1, or less than 50% was extracted. The distribution values increased from 1 to 3 M HNO$_3$, but decreased at higher nitric acid concentrations. The trend is similar to that observed with DAAP, and further studies have revealed the decreased values are a result of incomplete Am$^{3+}$
oxidation as well as reduction of AmO$_2^{2+}$ in higher nitric acid concentrations.$^{85}$ Reduction of AmO$_2^{2+}$ also occurs in the organic phase and produces AmO$_2^+$ and Am$^{3+}$ species which are poorly extracted by monoamides.$^{86}$ Comparing the monoamide chain length, DHBA shows the highest distribution while DHVA and DHHA extract comparatively. Considering PuO$_2^{2+}$ had similar distribution values for all three straight chain monoamides it is thought that AmO$_2^{2+}$ experienced a higher degree of reduction with DHVA and DHHA due to the presence of trace reducing agents.

Several parameters were adjusted in attempts to obtain greater than 50% extraction efficiency for AmO$_2^{2+}$ with straight chain monoamides. Salting agents can be used to increase the ionic strength of aqueous phase and promote metal extraction. Using the acid concentration with highest distribution, 3 M HNO$_3$, distribution values were determined with the addition of 0.1 to 1.0 M LiNO$_3$ and Al(NO$_3$)$_3$ (Figure 5.10). In the absence of LiNO$_3$ distribution value was 0.75 ±
0.02. In the presence of 0.1 M LiNO$_3$, the distribution value increased slightly to 0.81 ± 0.08 and steadily decreased to 0.71 ± 0.03 at 1 M HNO$_3$. All distribution values fell within experimental uncertainty of each other; therefore, LiNO$_3$ had no effect on the distribution values. A small effect was observed when Al(NO$_3$)$_3$ was added to 3 M HNO$_3$ solutions. The distribution increased from 0.69 ± 0.09 in absence of Al(NO$_3$)$_3$ to 0.86 ± 0.04 with 0.30 M Al(NO$_3$)$_3$. The distribution values then fell to 0.75 ± 0.8 at 1 M Al(NO$_3$)$_3$. The addition of 1 M Al(NO$_3$) results in a 3 mole equivalent addition of NO$_3^-$ . The increased NO$_3^-$ concentration would promote formation of the charge neutral AmO$_2$(NO$_3$)$_2$ extracted species, but the high concentration of NO$_3^-$ at 1 M Al(NO$_3$)$_3$ could promote formation of anionic species which are only extracted by protonated monoamides that exist at high molar acid concentrations.$^{86,142}$ Although Al(NO$_3$)$_3$ showed some improvement the distribution values did not increase in appreciable amounts.

![Figure 5.10: Distribution values of Cu$^{3+}$ periodate oxidized Am with varied concentrations of salting agents LiNO$_3$ (light blue circle) and Al(NO$_3$)$_3$ (navy blue square).](image)

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Mixed ligand separations such as a neutral extractant, diglycolamide (T2EHDGA), and the acidic extractant 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (HEH[EHP]) in the ALSEP system promote higher metal extraction than when the extractants are used individually. The increased extraction is referred to as a synergistic effect. It was of interest to see if the neutral monoamide extractants would experience synergism with the acidic extractant di-(2-ethylhexyl)phosphoric acid, HDEHP. On its own, HDEHP does not extract Am$^{3+}$ at high nitric acid concentrations (Figure 5.11). Extraction of Cu$^{3+}$ periodate oxidized Am resulted in distribution values as high as 3.43 ± 0.03 at 2 M HNO$_3$ with 0.5 M HDEHP in n-dodecane, Figure 5.11. Since the highest monoamide distribution value occurred at 3 M HNO$_3$, the distribution of oxidized Am was measured at 3 M HNO$_3$ by maintaining an extractant concentration of 1 M while...
changing the ratio of DHBA and HDEHP. The results are shown as a Job’s plot in Figure 5.12. When no HDEHP is present the distribution is $0.66 \pm 0.03$ and the distribution increases with the inclusion of 0.1 and 0.3 M HDEHP. At 0.5 M HDEHP/0.5 M DHBA the distribution value is $1.7 \pm 0.4$, which matches the $2.0 \pm 0.7$ distribution value obtained with 0.5 M HDEHP individually. The similar distribution value indicates no synergistic effect is observed for HDEHP with DHBA. Based on comparisons with other solvating reagents,$^{145-147}$ the inability for monoamide reagents to participate in a synergistic metal extraction mechanism with HDEHP was unanticipated. In other synergistic systems the extractants can orient to have a polar head (oxygen donor) and nonpolar tails, akin to a shuttlecock. The monoamide extractants do not share a similar ability, and the acyl group’s vicinity to the nonpolar nitrogen alkyl chains could be inhibiting the synergistic coordination.

The presence of trace reducing species in the organic phase was considered as contributing to the low extraction since $\text{AmO}_2^{2+}$ would be readily reduced to poorly extracted $\text{AmO}_2^+$ and $\text{Am}^{3+}$ species. To decrease the amount of reducing species, $\text{NaBiO}_3$ was added to $\text{HNO}_3$ during the pre-equilibration step. Although $\text{Cu}^{3+}$ periodate is used to oxidize $\text{Am}^{3+}$ in the actual extractions, $\text{Cu}^{3+}$ periodate quickly reduces in the presence of organic phase.$^85$ Due to $\text{Cu}^{3+}$ periodate’s short lifetime, $\text{NaBiO}_3$ was used during pre-equilibration because it persists for the longer time durations used to pre-equilibrate the solutions (2 hours) and has been used elsewhere in literature.$^86$ The results, shown in Figure 5.13, show the same trend observed with $\text{Am}^{3+}$ where the distribution values increase between 1 and 3 M $\text{HNO}_3$ but decrease at 4 and 5 M $\text{HNO}_3$. Although the same trend occurs, the distribution values are higher compared to non-oxidative pre-treatment samples. The distributions are noticeably higher between 3 and 5 M $\text{HNO}_3$. This suggests the $\text{NaBiO}_3$ did behave as a scavenger to eliminate reducing agents in the organic phase.
Figure 5.12: Distribution values of Cu\(^{3+}\) periodate oxidized Am in 3 M HNO\(_3\) extracted by varying the ratio of HDEHP and DHBA. Extractant concentration was maintain at 1 M in n-dodecane while the amount of DHBA decreased from 1 M DHBA (ratio value of 0) to 0.5 M with 0.5 M HDEHP (ratio value of 1). Distribution of oxidized Am in 3 M HNO\(_3\) extracted by 0.5 M HDEHP n-dodecane is included for comparison (green square).

Less of a difference between pre-treatments with and without NaBiO\(_3\) is observed at 1 and 2 M HNO\(_3\) solutions since less Am recovery occurs in the presence of lower nitric acid concentrations. Higher nitric acid concentrations increase the concentration of AmO\(_2\)(NO\(_3\))\(_2\) species causing the increase in distribution values. The sensitivity of AmO\(_2^{2+}\) towards reduction prevented deduction of an observable trend in distribution values for the increasing monoamide acyl chain. Distribution values were within close proximity to each other at 3 M HNO\(_3\) as 1.03 ± 0.02, 1.16 ± 0.03, and 1.08 ± 0.07 with DHBA, DHVA, and DHHA respectively. At other acid concentrations, the values were not statistically different. As seen with PuO\(_2^{2+}\), distribution values with branched monoamides are lower than straight chained for hexavalent actinides. Although NaBiO\(_3\) was used to pretreat 1 M DH2MBA and DH2EBA solutions, the extraction efficiency did
not exceed 50%. Previous research has shown that distribution values with monoamides increase up to 6.5 M HNO$_3$ for NaBiO$_3$ oxidized Am$^{3+}$. If more efficient oxidation, with less reduction could be achieved at 4 and 5 M HNO$_3$ with Cu$^{3+}$ periodate, the distribution values should also increase above 3 M HNO$_3$ concentrations.

Figure 5.13: Distribution values of Cu$^{3+}$ periodate oxidized Am over 1 – 5 M HNO$_3$ acid range. The 1 M monoamide in n-dodecane solution were pre-equilibrated with 60 mg/mL NaBiO$_3$ in the respective acid concentration. Oxidized americium extraction by straight chain monoamides (light blue) 1 M DHBA (circle), DHVA (square), and DHHA (diamond) are compared to branch chain DH2MBA (navy blue circle) and DH2EBA (green triangle).
5.7 Conclusion

Extraction of Pu$^{4+}$ and PuO$_2^{2+}$ with synthesized straight and branched monoamides was demonstrated. As expected, Pu$^{4+}$ and PuO$_2^{2+}$ was efficiently extracted (96% and 89% respectively) by straight monoamides. No trend was observed over increasing acyl chain length for Pu$^{4+}$ extractions, but PuO$_2^{2+}$ extractions decreased with increasing acyl chain length from butyramide to hexanamide. Branched monoamides demonstrated the selective extraction of PuO$_2^{2+}$ over Pu$^{4+}$. No trend was observed with PuO$_2^{2+}$ extractions, but Pu$^{4+}$ extraction was grouped based off the branch being either methyl or ethyl branched monoamide. The monoamide UV-Vis spectra showed a decrease in the outer-sphere extracted species, Pu(NO$_3$)$_6$(HL)$_2$, in the order of straight $>$ methyl branched $>$ ethyl branched and indicated Pu(NO$_3$)$_4$(L)$_2$ or Pu(NO$_3$)$_5$L(HL) was also extracted. The PuO$_2^{2+}$ monoamide UV-Vis spectra indicated a plutonyl trinitrate species, mostly likely as PuO$_2$(NO$_3$)$_3$(HL), was extracted as well as PuO$_2$(NO$_3$)$_2$(2L). Slight variations were observed in the Pu(NO$_3$)$_3$(HL) region between methyl and ethyl branched monoamides indicating fine structural effects which should be investigated in future studies. Oxidized americium distribution values were below one for acid pretreated monoamide solutions. Salting agents LiNO$_3$ and Al(NO$_3$)$_3$ did not significantly improve extraction, and no synergistic extracted effect was observed with addition of HDEHP. Distribution values above one were achieved in 3 M HNO$_3$ when straight chain monoamide solutions were pretreated with NaBiO$_3$ to remove reducing species, but values decreased at 4 and 5 M HNO$_3$ due to incomplete Am$^{3+}$ oxidation and rapid AmO$_2^{2+}$ reduction. Future studies should focus on determining the structure of hexavalent monoamide species, which could provide further insight on the branched monoamide selectivity.
CHAPTER 6
CONCLUDING STATEMENTS

6.1  Group Hexavalent Actinide Extraction

An effective group hexavalent actinide separation process is limited by the ability to oxidize Am$^{3+}$ to AmO$_2^{2+}$ due to its high reduction potential. This research has demonstrated that Am$^{3+}$ oxidation in molar nitric acid and subsequent extraction by extractant ligands such as DAAP, straight monoamides, and HDEHP can be achieved. Reduction of AmO$_2^{2+}$ is an uphill battle whether it’s in the acidic aqueous media or organic phase. The AmO$_2^{2+}$ reduction limited phase contact times to as short as 5 seconds. In order to implement a large scale, chemically robust process the hexavalent state would need to be stabilized or ability to continuously re-oxidize Am$^{3+}$ and AmO$_2^{+}$ will need to be demonstrated. Extraction of UO$_2^{2+}$, NpO$_2^{2+}$, and PuO$_2^{2+}$ by DAAP were demonstrated individually, and implied a group hexavalent actinide extraction can be achieved. Future studies will need to demonstrate quantitative oxidation by Cu$^{3+}$ periodate and extraction of all four actinides in the same solution with concentrations similar to that experienced in the nuclear fuel cycle. Furthermore, the chemistry of Cu$^{3+}$ periodate and other strong oxidants with the remaining metals found in used nuclear fuel will need to be examined. The advantages and limitations of Cu$^{3+}$ periodate based hexavalent actinide separation encountered in this body of work are highlighted in the following sections, and the need for future research efforts are suggested towards the goal of creating a hexavalent group actinide separation process.

6.2  Americium Oxidation by Cu$^{3+}$ periodate in Molar Acid:

Americium oxidation is in competition with the reduction of Cu$^{3+}$ periodate by HNO$_3$. The results suggested that orthoperiodate decomplexes with Cu$^{3+}$ and becomes protonated in acidic media. The Cu$^{3+}$ is left to oxidize H$_2$O, other metal species, and americium. A saturation effect
was observed for Cu$^{3+}$ periodate reduction by HNO$_3$, and means reduction rate is not affected by higher acid concentrations. The acid reduction saturation effect and demonstration that Am could be oxidized by Cu$^{3+}$ periodate meant hexavalent solvent extractions could be attempted. It was shown in Chapter 2 that a distribution value of 2 could be achieved using diamyl amylphosphonate between 1 and 3 M HNO$_3$. Above 3 M HNO$_3$ the distribution values dropped below 1. In Chapter 2, UV-Vis spectra showed that quantitative oxidation of Am$^{3+}$ to AmO$_2^{2+}$ is not achieved at 4 M HNO$_3$. The decreased amount of AmO$_2^{2+}$ contributed to the lower distribution values since Am$^{3+}$ is less extracted at those acid concentrations. Chapter 2 also showed that AmO$_2^{2+}$ is reduced upon contact with the organic phase. However, the UV-Vis spectra showed AmO$_2^{2+}$ was present as well as Am$^{3+}$ and AmO$_2^{+}$. Due to the reduction of AmO$_2^{2+}$ by the organic phase species, longer contact times decrease the distribution values because Am$^{3+}$ and AmO$_2^{+}$ are poorly extracted by diamyl amylphosphonate. Therefore, short contact times are necessary when conducting AmO$_2^{2+}$ extractions using Cu$^{3+}$ periodate.

Low AmO$_2^{2+}$ species concentration is the driving force behind lower distribution values either by incomplete oxidation above 3 M HNO$_3$ or reduction in the organic phase. This work used diamyl amylphosphonate as is, and pretreated the 1 M DAAP n-dodecane extractant solution only with HNO$_3$ prior to use. Two different batches of DAAP were used and provided different results. According to Eichrom, different purification processes were used and effected the reduction of AmO$_2^{2+}$. The type of impurities present in DAAP was not investigated, and the type of reduced species generated by AmO$_2^{2+}$ reduction was not determined. A scaled up extraction system using the DAAP material would need to pay close attention to the purification process prior to use for hexavalent americium extraction. Although not attempted in this study, pretreatment of the DAAP material with a strong oxidizer prior to use could potentially remove the reductive species and
improve AmO$_2^{2+}$ extraction. However, due to AmO$_2^{2+}$ high reduction potential the organic phase will be oxidized by AmO$_2^{2+}$.

The incomplete oxidation of AmO$_2^{2+}$ in acid concentrations above 3 M HNO$_3$ is of particular quandary and interest for future studies. Sinkov, in his study, suggested addition of more Cu$^{3+}$ periodate would result in increased oxidation of Am$^{3+}$. In the UV-Vis studies, the Am$^{3+}$:Cu$^{3+}$ ratio was roughly 1:20, which is the preferred amount for complete oxidation. However, the tracer studies had a molar ratio of 1:10$^7$. Even with the high molar excess the same distribution values were achieved, and thus points to incomplete oxidation of Am$^{3+}$ (which couldn’t be measured by UV-Vis due to the low concentrations). Furthermore, in the 4 M HNO$_3$ UV-Vis experiments Cu$^{3+}$ periodate was visibly present in solution, but was not able to further oxidize the remaining Am$^{3+}$. Future experiments should focus on the oxidation mechanism. Insight into the mechanism could promote the design of other Cu$^{3+}$ based oxidants or other oxidants with high reduction potentials such as Ag$^{3+}$, Co$^{3+}$, or Bi$^{5+}$.

6.3 **Cu$^{3+}$ periodate reactions with Pu, Np, and metals in the nuclear fuel cycle:**

The addition of Cu$^{3+}$ periodate to the extraction system will oxidize nearly everything in the solution. Principally, oxidation of the metal species is desirable to achieve a hexavalent group actinide extraction. Uranium predominantly exists in the hexavalent state in nitric acid while Np and Pu display different oxidation states. The studies presented in Chapter 3 showed Np and Pu are oxidized by Cu$^{3+}$ periodate to the hexavalent state, and are not further oxidized to the heptavalent state. The study also showed that the metal to oxidant molar ratio needed to achieve the hexavalent state increased from one electron oxidation (1:1.2 for NpO$_2^{2+}$) to two electron (1:3 for Pu$^{4+}$) and three electron (1:20 for Am$^{3+}$). The reduction of Cu$^{3+}$ periodate by nitric acid and
water can account for some of the molar excess required, but as previously mentioned the oxidation mechanism should be studied in order to improve oxidation efficiency.

One problem encountered with Pu⁴⁺ was the formation of a precipitate upon addition of Cu³⁺ periodate to the Pu⁴⁺ solution. The precipitate dissipated with the addition of more oxidant and indicated Pu⁴⁺ was precipitating out with periodate. A precipitate also formed with the addition of sodium periodate to a Ce⁴⁺ solution, and a literature search revealed Ce⁴⁺ is precipitated as CeHIO₆. Due to the similar chemistries between Ce⁴⁺ and Pu⁴⁺, it was deduced that the Pu⁴⁺ precipitate is most likely PuHIO₆. Further studies are needed to determine if the precipitate is indeed PuHIO₆.

Several other metals were also found to form a precipitate with periodate. Using a “post-PUREX” process simulant it was determined that Zr, Sn, Ru, Ce, Mo, and Sm all precipitated with the addition of Cu³⁺ periodate. Since the various transition metals can be oxidized, they will be in competition with Cu³⁺ periodate along with Np, Pu, and Am. An oxidized Am extraction with the post-PUREX simulant showed Am distribution values decreased substantially, but were higher than unoxidized Am³⁺. Furthermore, the mass balance showed 20% of Am was missing from the aqueous and organic phase. A third phase was not observed and therefore was postulated that Am was intercalated into a precipitate as well.

The precipitate formation is of concern as it will create problems from an engineering standpoint and safety in regard to build-up of a Pu precipitate. These preliminary studies show how periodate can complicate the process, and has even more implications not considered in this work. For example, by lightly heating NpO₂⁺ in the studies in Chapter 3, periodate became redox active and oxidized residual NpO₂⁺ to NpO₂²⁺. The experiments in this dissertation were all performed at room temperature. In practice, the solvent extraction process experiences higher
temperatures which would cause periodate to be redox active. The redox active periodate reduces to iodate, IO₃⁻. The iodate ion is known to form precipitates with trivalent actinides and lanthanides. In order to move towards a hexavalent group actinide solvent separation, the use of periodate based oxidizers should be avoided.

6.4 Hexavalent Actinide Extraction with Monoamides

Branched monoamides were considered for a group hexavalent actinide extraction due to their selectivity towards hexavalent over tetravalent actinides. The selectivity was noted since they were first studied for actinide separation, but the effect of monoamide structure on the type of species extracted has only recently been studied. Using radiotracer methods, no trend was observed when the acyl chain length increased from four to six carbons for Pu⁴⁺ and PuO₂²⁺ separations. It was confirmed that branched monoamides were selective for PuO₂²⁺ extraction over Pu⁴⁺. In the radiotracer studies, no trend in PuO₂²⁺ extraction was observed between methyl and ethyl branched monoamides. On the hand, Pu⁴⁺ extraction studies showed distribution values were grouped based off the methyl or ethyl branching of the monoamides. Differences between straight, methyl branched, and ethyl branched monoamide extracted species were identified by the UV-Vis spectral measurements.

For Pu⁴⁺ extractions, the organic phase UV-Vis showed Pu⁴⁺ is extracted as an anionic hexanitrato species by protonated monoamides, Pu(NO₃)₆(HL)₂, denoted as an outer-sphere species. Inner-sphere character as Pu(NO₃)₄(L)₂ was also observed in the UV-Vis spectra. The amount of outer vs. inner sphere character decreased in the order of straight > methyl branched > ethyl branched. The decrease in outer sphere character correlated with the decrease in Pu⁴⁺ distribution values. It is possible that a species with both inner and outer sphere character could also be forming as Pu(NO₃)₅L(HL). Inner and outer sphere species were also observed for PuO₂²⁺.
in the form of \( \text{PuO}_2(\text{NO}_3)_3(\text{HL}) \) outer and \( \text{PuO}_2(\text{NO}_3)_2(\text{L})_2 \) inner. Small variations in the \( \text{PuO}_2(\text{NO}_3)_3(\text{HL}) \) spectral region between straight, methyl branched, and ethyl branched monoamides were observed. An EXAFS study on \( \text{PuO}_{22^+} \) extracted species could reveal structural differences between monoamides, and possibly provide insight as to why hexavalent over tetravalent selectivity occurs in branched monoamides. This study considered only one nitric acid concentration. Measuring organic phase UV-Vis spectra at different acid concentrations will improve species identification and how the spectra changes depending on type of species present.

Although the type of extracted species are identified, the reason why monoamides form outer-sphere species remains unanswered. Furthermore, is the monoamide truly protonated, or is it a monoamide complexed to nitric acid? Organic phase UV-Vis spectra and EXAFS should be collected on U, Np, and Am to help identify what is driving the formation of inner vs. outer sphere complexation. The size and charge density of hexavalent actinides decreases across the series. The suggested studies across the series could reveal what drives the inner vs. outer sphere complexes. Stability constants and speciation diagrams should be studied for the varied monoamide structures to aid in identifying the type of species being extracted.

Extraction of \( \text{AmO}_2^{2+} \) followed the same pattern observed in studies with diamyl amylphosphonate extractant. The distribution increased in 1 to 3 M HNO\(_3\), but decreased for 4 and 5 M HNO\(_3\). Initial studies with the straight chain monoamides achieved distribution values lower than one. Addition of LiNO\(_3\) and Al(NO\(_3\))\(_3\) as a salting agent did not improve the distribution values. Surprisingly, a synergistic effect whereby the distribution values increased did not occur when HDEHP and DHBA were used as an extractant mixture. Determining the structure of the monoamide extracted species could explain why synergy doesn’t occur in this system but works with other extractant mixtures. Although a synergistic effect was not observed, HDEHP itself
displayed high distribution values proving it as a viable candidate for recovering hexavalent actinides from molar nitric acid.

To achieve AmO$_2^{2+}$ distribution values above 1, the monoamides required pretreatment with an oxidant, NaBiO$_3$, while pre-equilibrating the organic phase with nitric acid. The improved distribution values for oxidant pre-treated monoamides suggests AmO$_2^{2+}$ was reduced in prior attempts during phase contact which lead to the low distribution values. Branched monoamides did not achieve distribution values above one even when pretreated with the oxidant. As seen in PuO$_2^{2+}$ extractions, the branched monoamides display lower distribution values than their straight chained counterparts so the low AmO$_2^{2+}$ branched monoamides values were expected. In order to improve branched monoamide distribution values N,N-dihexylisobutyramide should be considered. Also, quantitative oxidation and/or re-oxidation of Am$^{3+}$ in 4 and 5 M HNO$_3$ could result in desirable distribution values. Of particular interest would be UV-Vis-NIR studies to determine which species are present in the organic phase, and if the same mixed species observed with PuO$_2^{2+}$ also appear in AmO$_2^{2+}$ extraction.
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