USING *N,N*-DIALKYLAMIDES TO PARTITION ACTINIDES FOR SPACE POWER APPLICATIONS

by:

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ABSTRACT

Plutonium-238 (^{238}Pu) has been the preferred heat source for radioisotope thermoelectric generators (RTGs), which have been used to power spacecraft for decades. The primary method to produce ^{238}Pu is to transmute neptunium-237 (^{237}Np). Short irradiation times of the ^{237}Np targets are necessary to not have heavier actinides form, such as ^{239}Pu. This results in a mixture of ^{237}Np, ^{238}Pu, and fission products. Efficient separation of ^{238}Pu and ^{237}Np is necessary to reuse unreacted ^{237}Np and produce pure $^{238}PuO_2$ pellets to be used as the heat source in RTGs.

The current extractant used to separate Np and Pu is tributylphosphate (TBP). A major consequence of using TBP is that its degradation products result in phosphorus contamination in both radionuclide products. The excess phosphorus has to be removed, a process that is costly and time-consuming. A workaround for this issue is to use an extractant that does not contain phosphorus, a *N,N*-dialkylamide. *N,N*-Dialkylamides (monoamides) are a class of metal extractants that have been considered as replacements for TBP for actinide separation for decades. Four *N,N*-dialkylamides: *N,N*-dihexylhexanamide (DHHA), *N,N*-dihexyloctanamide (DHOA), *N,N*-diethylhexylbutanamide (DEHBA), and *N,N*-diethylhexylisobutanamide (DEHiBA) have been selected for study based on their solubility in an aliphatic solvent and promising extraction capabilities for actinide +IV and +VI cations. These prerequisites are part of the current conditions being used at Oak Ridge National Lab (ORNL) for their $^{237}Np(VI)/^{238}Pu(IV)$ separation.

The focus for this research was to ascertain which synthesized *N,N*-dialkylamide would be ideal to separate Np from Pu so that TBP can be replaced without changing other conditions of the separation (Monoamide Plutonium Neptunium Extraction-MAPNEX). The first area of study was the extraction efficiency of trace and semi-macro quantities of $^{237}Np(IV,V, VI)$. The favorable *N,N*-dialkylamides for Np(VI) extraction and Np(V) stripping were DHHA, DHOA, and DEHBA.

Also, after studying the extraction of Pu(III, IV, VI) in trace quantities, the same *N,N*-dialkylamides extract Pu(IV) well and can strip Pu(III) at low acidities. DHHA, which exhibited the best tetravalent and hexavalent actinide extraction overall, was used to successfully coextract Np(VI)/Pu(IV). Separately, these studies additionally showed that DHHA, DHOA, and DEHBA can be used to preferentially extract Np(IV) or Pu(VI) if desired.

This study also investigated using a *N,N*-dialkylamide instead of di-(2-ethylhexyl) phosphoric acid (HDEHP) to purify the initial $^{237}NpO_2$ targets. The ^{237}Np, which has Th(IV) contaminants, is first procured from Np stockpiles. The purification process using HDEHP results in phosphorus contamination as well. DEHiBA, which can extract Np(VI) decently well and tetravalent actinides poorly, has proven to be a suitable alternative to HDEHP in a simulated study using trace concentrations of Np and semi-macro concentrations of Th.

The last area of focus was to understand some of the behavior of the redox agent nitrous acid in *N,N*-dialkylamide extraction systems. Nitrous acid is used by ORNL to reduce Np(VI) to Np(V) so that the Np can be removed from the Pu. This study found at higher concentrations of nitric acid, nitrous acid will react with *N,N*-dialkylamides. Fortunately, the process conditions employed at ORNL use nitrous acid to reduce Np(VI) in low concentrations of nitric acid where the adverse effect from nitrous acid was not observed.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

Typed words express an infinitesimal amount of my appreciation for all that have helped me lay this cornerstone for my professional career. Occasionally, I wished this moment had been realized much sooner but a quote by Thales (the ‘father of science’) comes to mind, “time is the wisest of all things that are; for it brings everything to light.” I feel that the unrelenting guidance by my advisor, Mark Jensen, as helped make me into one of the best researchers that I can be. While my family and friends supported me throughout my Ph.D., they also made sure that I made time for enjoying non-work activities, an essential life balance. Dziękuję!

For Kendra Gogolski

CHAPTER 1

INTRODUCTION

1.1 Background

Spacecraft and satellites can be powered by chemical, solar, or nuclear energy. While chemical energy is currently used for rocket propulsion from the Earth's surface, spacecraft planning for multi-year missions would require continuous refueling because of the poor energy density obtained from chemical reactions. Energy from the sun, solar power, can be used to power spacecraft and satellites as long as the solar cells are not damaged. However, the current efficiency of solar cells limits their functionality to just past Mars. A 1 m^2 solar array orbiting Earth can provide 400 W but a 25 m^2 solar array would be needed for a satellite orbiting Jupiter because of the decrease in usable energy over that distance [1]. In contrast, nuclear energy is a dense form of power that would allow spacecraft to have an efficient compact design, provide electricity to its instruments, and travel anywhere in the solar system and beyond [2].

The two current main sources of nuclear energy that produce electricity are a result of the heat generated by fission events and radioactive decay. Common nuclear reactors enable the controlled fission of fissile material, usually uranium-235 (^{235}U), to produce electricity. Even though there are plans for constructing nuclear reactors for space travel, current logistics have hampered deployment of space nuclear reactors [2]. To date, the United States has launched only one nuclear reactor into space as part of the Systems for Nuclear Auxiliary Power (SNAP) program.

An alternative to nuclear fission for space power is to use the radioactive decay of specific radionuclides as a source of heat in radioisotope thermoelectric generators (RTGs). Radionuclides that have been used or studied for application in RTGs include polonium (^{208}Po, $t_{1/2}$ = 2.9 years and ^{210}Po, $t_{1/2}$ = 138 days), strontium-90 (^{90}Sr, $t_{1/2}$ = 28.8 years), plutonium-238 (^{238}Pu, $t_{1/2}$ = 88 years), americium-241 (^{241}Am, $t_{1/2}$ = 433 years) [2], cerium-144 (^{144}Ce, $t_{1/2}$ = 284 days), and curium (^{242}Cm, $t_{1/2}$ = 162.8 days, and ^{244}Cm, $t_{1/2}$ = 18 years) [3]. The requirements of a compact and long-range space mission can narrow these choices to an optimal radionuclide. Converting the decay heat into electricity using a passive system (i.e. without movable parts) such as the thermoelectric effect (Seebeck effect) works well to provide power for the spacecraft, but an ideal radionuclide would need to have a high power density and multi-year half-life ($t_{1/2}$). Other design considerations occur because the radioactive decay of any nuclide will require appropriate shielding and will increase the impurities over time, these concerns will impact the size of the spacecraft and the electrical resistivity [4].

The polonium isotopes have a substantial power density and decay into stable isotopes of lead, which would ease disposal or reuse of the spacecraft. However, both ^{208}Po and ^{210}Po have a short half-life so they are only ideal for space missions of short duration. Even though the curium isotopes are attractive possibilities because of their power density, production is costly and their gamma decay and spontaneous fission events incur shielding issues. The radionuclides ^{144}Ce and particularly ^{90}Sr have substantial shielding issues from their gamma energies as well. In contrast, the almost pure alpha decay and decades long half-life of ^{238}Pu makes the radionuclide ideal for long space missions. The United States has exclusively used ^{238}Pu to power its long-range spacecraft: Voyager, Pioneer, and New Horizons [5]. The European Space Agency is considering ^{241}Am as a possible replacement for ^{238}Pu because isotopically pure ^{241}Am is abundant in used nuclear fuel [2]. Even though ^{241}Am can potentially power a spacecraft for a thousand years due to its long half-life, it is less energy dense than ^{238}Pu and requires more shielding as a consequence of its gamma emission [2]. These design requirements impede the implementation of ^{241}Am based RTGs, whereas the design for ^{238}Pu is well understood [4].

Even though the designs that implement ^{238}Pu based RTGs have evolved over the years, from SNAP to the current General Purpose Heat Source (GPHS) model and soon to a Multi-Mission RTG (MMRTG), the fundamental aspects have not really changed such as the size of the $^{238}PuO_2$ pellets or the thermoelectric converter designs shown in Figure 1.1 [6]. The electron acceptor (N) and donor (P) usually use phosphorus and boron, respectively, as dopants. The hot shoe side has the heat source (^{238}Pu) and the cold side completes the pathway so that the electricity can be generated. While the lack of a moving parts for a thermoelectric assembly is an attractive design, the low efficiency (ca. 6 %) is a major drawback [6].

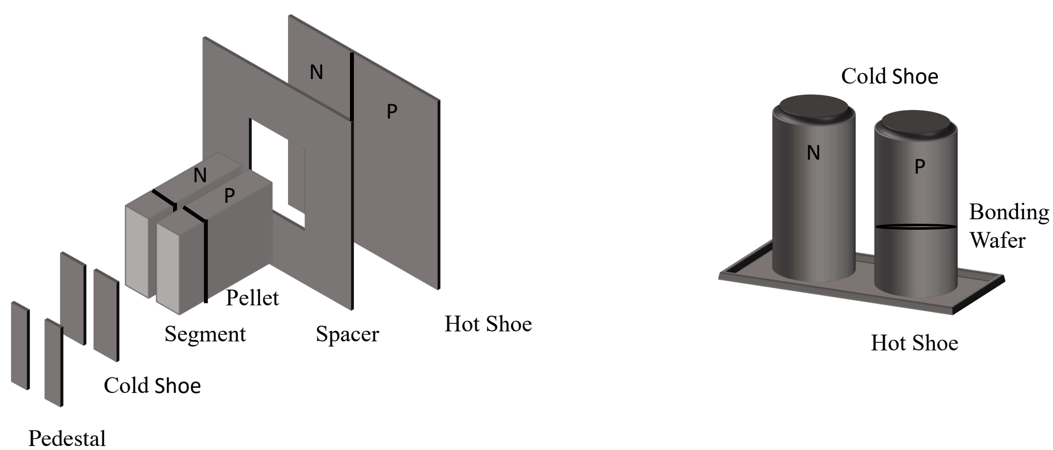


Figure 1.1: Schematic of a thermoelectric pre-assembly for GPHS (left) [7] and for MMRTG (right) [8].

The Advanced Stirling Radioisotope Generator (ASRG) design, that is currently being developed would dramatically improve the energy efficiency (ca. 4 times) [6]. It is technically not an RTG because the heat conversion to electricity occurs via the Stirling cycle instead of the Seebeck effect. The ^{238}Pu heat powers reciprocating pistons, Figure 1.2, that spin an alternator to produce electricity for the spacecraft.

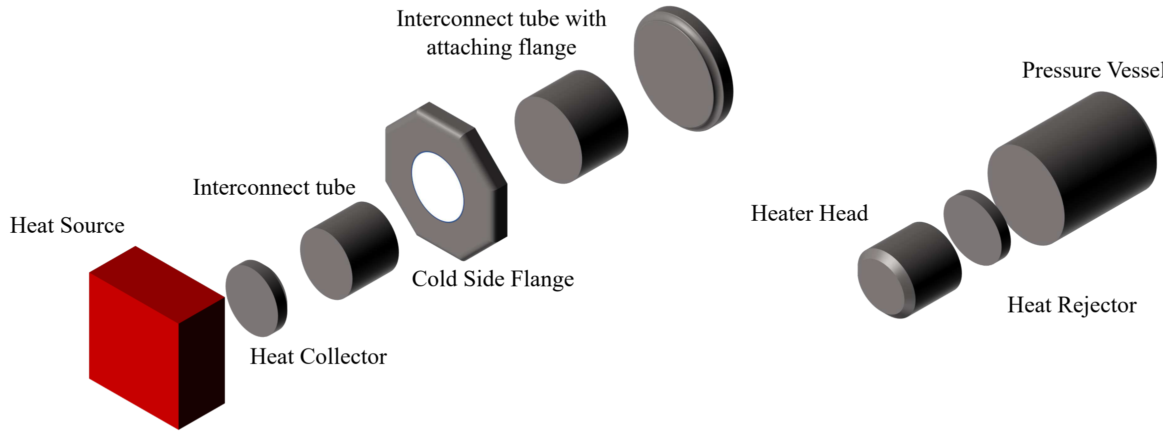


Figure 1.2: Schematic of an ASRG interface (left) and advanced Stirling convertor or piston (right) [9].

Since the commonality between the mentioned designs for electricity generation is that they all use ^{238}Pu. The paramount concern for terrestrial launches of these spacecraft is the radiological containment of ca. 0.6 kg $^{238}PuO_2$, for GPHS and MMRTG, and 0.2 kg $^{238}PuO_2$, for ASRG [6]. Therefore, the $^{238}PuO_2$ is encapsulated in graphite impact shell (GIS), design shown in Figure 1.3. The floating membrane allows release of alpha particles and the iridium cladding with the carbon-carbon shell preserves the fuel integrity throughout the spacecraft's interplanetary mission or abrupt destruction [6, 7].

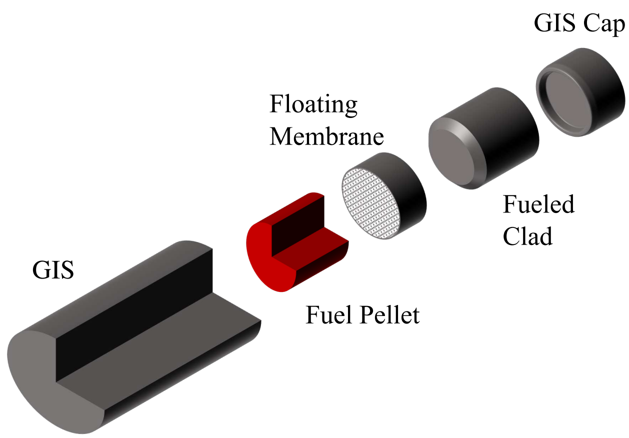


Figure 1.3: Schematic of GIS module [7].

The purity of $^{238}PuO_2$ pellets directly impacts the efficiency of generating electrical energy. To allow for alpha particle release and have the desired heat transfer characteristics, the ^{238}Pu pellets are fabricated to have a uniform density and certain porosity. The current method to make the pellets is as follows: fine PuO_2 powder dissolved in nitric acid reacts with oxalic acid, this precipitates Pu(III) oxalate; the precipitate is heated to drive off moisture and reform PuO_2, completely replacing ^{17}O and ^{18}O, which can be activated in (α, n) reactions, with ^{16}O. The PuO_2 powder is ball milled to shape the PuO_2 into a desired configuration [10, 11]. Failure to maintain the desired PuO_2 morphology can significantly decrease the heat output and most likely causes structural instability of the $^{238}PuO_2$ pellet.

The K-reactor at Savannah River Site (SRS) produced ^{238}Pu until 1988, when the site switched to solely processing ^{238}Pu produced by Russia [5]. Purchases of Russian ^{238}Pu no longer occur and the current stockpile of ^{238}Pu will soon be depleted. Recently, renewed interest in long-range space programs has caused a multi-national lab effort in the United States to restart ^{238}Pu production by irradiation of neptunium-237 (^{237}Np) targets [12].

1.2 Production of ^{238}Pu from ^{237}Np

Irradiated nuclear fuel contains most of the global supply of ^{237}Np since it has a half-life of 2.14 x 10^6 years and does not occur naturally. There are two main routes to ^{237}Np: the neutron capture of ^{235}U or the alpha decay of ^{241}Am, as shown in the following reactions.

$$^{235}U + {}^{1}n \rightarrow {}^{236}U + \gamma \tag{1.1a}$$

$$^{236}U + {}^{1}n \rightarrow {}^{237}U + \gamma \tag{1.1b}$$

$$^{237}U \rightarrow {}^{237}Np + {}_{-1}e \tag{1.1c}$$

$$^{241}Am \rightarrow {}^{237}Np + {}^{4}He \tag{1.2}$$

An (n, 2n) reaction with ^{238}U can also form ^{237}Np. Transmuting ^{237}Np into ^{238}Pu can be accomplished by bombarding ^{237}Np with neutrons, as shown in reaction 1.3. For reasons that are explained later, the ^{237}Np target and the product ^{238}Pu need to be selectively separated after irradiation.

$$^{237}Np + {}^{1}n \rightarrow {}^{238}Np \rightarrow {}^{238}Pu + {}_{-1}e \tag{1.3}$$

While production of ^{238}Pu from ^{237}Np is a straightforward process, other side reactions occur within the process that can complicate the purification of the target actinides. As ^{238}Np is generated by neutron capture, it then rapidly decays ($t_{1/2}$ = 2.1 days) to ^{238}Pu, shown in reaction 1.3. However, irradiating the ^{237}Np can also transmute the nuclide into undesired radionuclides and fission products, as shown in Figure 1.4. This leads to short irradiation cycles so that about 20% of ^{237}Np is converted to ^{238}Pu [13].

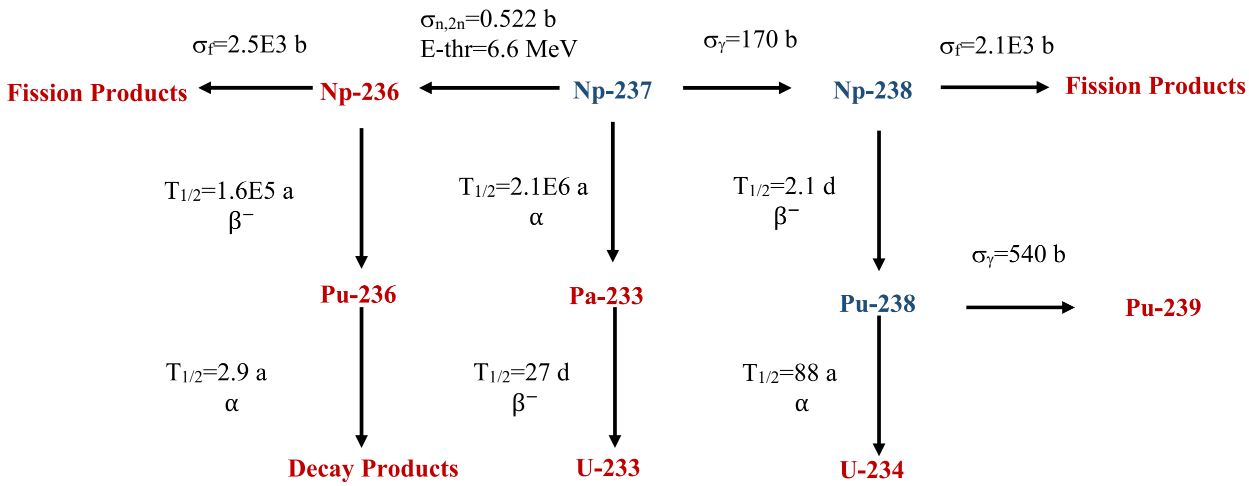


Figure 1.4: Irradiation scheme of ^{237}Np to make ^{238}Pu (blue), along with the formation of other radionuclides (red). The following are the thermal cross sections in barns (b): σ_f is fission, σ_γ is neutron capture with gamma emission, and $\sigma_{n,2n}$ is neutron capture with two neutron emissions. Half-lives-are expressed as a=years and d=days with the primary decay mode.

High purity $^{238}PuO_2$ is needed to power the RTG efficiently and even minor impurities can affect the material properties of the $^{238}PuO_2$ product. There are restrictions on the amount of each fission product or impurities in the $^{238}PuO_2$ the general purpose heat source (GPHS) design specifications will allow [14]. Therefore, the ^{238}Pu needs to be separated from any leftover ^{237}Np, other transuranic elements, and fission products that were produced during the irradiation. Note that ^{238}Pu and ^{238}Np can also fission with other heavy radionuclides during ^{238}Pu production, as illustrated in Figure 1.4.

1.3 Neptunium and Plutonium

Since the behavior of other elements in solution can cause complications in extraction, it is necessary to go into further detail for Np and Pu. A comprehensive analysis of Np and Pu would include the three main oxidation states of both elements: Np^{4+}, NpO_2^{+}, and NpO_2^{2+} for Np and Pu^{3+}, Pu^{4+}, and PuO_2^{2+} for Pu because each of these oxidation states have different binding affinities for an extractant. The oxidation states of Np and Pu can also change depending on the acidity of the aqueous environment. Redox agents that are primarily used to adjust the oxidation states of Pu and Np are sodium nitrite ($NaNO_2$), hydroxylamine nitrate (HAN), and hydrogen peroxide (H_2O_2). However, due to the complex redox chemistry of ^{237}Np and ^{238}Pu in solution, unintended changes in their valence states can interfere with the ^{237}Np separation and ^{238}Pu purification.

1.3.1 Common Valence States of Neptunium

Most neptunium separation schemes extract Np as Np(IV) or Np(VI) and then strip as Np(V). The most stable form of Np is Np(V) but solvent extraction studies often overlook the pentavalent state of Np. This is due to the effective charge of NpO_2^{+} (+2.2) being lower than either Np^{4+} (+4) or NpO_2^{2+} (+3.1) which causes Np(V) to not be efficiently extracted by most ligands [15]. On the other hand, in HNO_3 solutions, it is possible to disproportionate, reduce, or oxidize the stable Np(V) into an extractable oxidation state without adding any redox agents [16-19]. The mechanism for some of these reactions, along with the behavior of specific redox agents are explained further to emphasize the likelihood of Np changing oxidation states in a HNO_3 solution.

Neptunium(V) is generally stable at low acidities but at nitric acid concentrations higher than 3 M HNO_3, Np(V) will either oxidize to Np(VI) or disproportionate into Np(IV) and Np(VI) [16]. The oxidizing and reducing agents, nitrate (NO_3^-) and nitrite (NO_2^-), respectively, present in HNO_3 can create an equilibrium between Np(V) and Np(VI) [19-21]. As the HNO_3 is degraded by radiolysis, it will increase the concentration of NO_2^-, which will then form nitrous acid (HNO_2). The reducing agent $NaNO_2$ will also form HNO_2 which will reduce Np(VI) to Np(V) as shown in Equation 1.4. Although at less than 0.1 mM HNO_2 [22] , Np(V) is oxidized to Np(VI) [20, 23].

$$2NpO_2^{2+} + HNO_2 + H_2O \Leftrightarrow 2NpO_2^{+} + 3H^{+} + NO_3^{-} \tag{1.4}$$

Most of the neptunium in a concentrated HNO_3 solution will be oxidized to Np(VI), as the acidity increases the redox potential of NpO_2^{2+}/NpO_2^{+} correspondingly decreases [24, 25]. However, if the solution is continually irradiated then the Np will start to be reduced back to Np(V) at low acidities [17] but it has been seen separately that it is possible to have Np(VI) stabilized with an oxidizing agent, potassium bromate ($KBrO_3$) [23].

Although the disproportionation of Np(V) will produce Np(IV) in solution, Np(IV) is generally not formed otherwise. A strong reducing agent, such as ferrous sulfamate, will need to be used to reduce Np(V), as shown in reaction 1.5. Excess Fe(II) will also keep Np(IV) stable even in strong acid [26, 27]. As mentioned earlier, $NaNO_2$, will form HNO_2 which will also reduce Np(V), as shown in reaction 1.6. However, if there is insufficient reducing agent present then Np(IV) will be oxidized back to Np(V) in an acidic solution, greater than 2 M HNO_3 [27, 28].

Another pathway for Np(IV) oxidation is that at less than 1 M HNO_3, H_2O_2 can act as an oxidizing agent [29], shown in Equation 1.7. Albeit it is a kinetically slow oxidation [18]. To summarize, the oxidation state of Np can change depending on the acidity of the solution, the presence of redox agents, and the radiolysis of those reagents.

$$NpO_2^+ + Fe^{2+} + 4H^+ \Leftrightarrow Np^{4+} + Fe^{3+} + 2H_2O \quad (1.5)$$

$$2Np^{4+} + HNO_3 + 3H_2O \Leftrightarrow 2NpO_2^+ + HNO_2 + 6H^+ \quad (1.6)$$

$$2Np^{4+} + H_2O_2 + 2H_2O \Leftrightarrow 2NpO_2^+ + 6H^+ \quad (1.7)$$

1.3.2 Common Valence States of Plutonium

Plutonium can exist in four primary oxidation states (+3, +4, +5, +6) in solution. The most stable state, Pu(IV), can disproportionate into Pu(III) and Pu(VI) in most acids [30]. The pentavalent transdioxo Pu(V) ion (PuO_2^+) does exist in solution but this oxidation state is often unstable in acidic conditions and will quickly oxidize to PuO_2^{2+}. Since there are some similarities to how Pu behaves in an aqueous solution compared to Np, it is worthwhile to briefly describe some of the relevant redox mechanics.

Ferrous sulfamate can be used to reduce Pu(VI) to Pu(IV) and stabilize plutonium as Pu(IV), Equation 1.8. Care needs to be taken because the reducing agent can cause plutonium to be reduced further to Pu(III), in which case adding more Pu(VI) will cause Pu(III) to oxidize back to Pu(IV) [30]. Alternatively, removing the excess reducing agent or heating the solution can oxidize the Pu(III) back to Pu(IV) as well [31]. Although heating at higher acidities (greater than 2 M HNO_3), the Pu(IV) will be further oxidized to Pu(VI). Oxidation of Pu(III) can also occur if the HNO_2 concentration is less than the Pu concentration, Equation 1.9 [32, 33], a similar effect mentioned for Np(V) oxidation.

$$PuO_2^{2+} + 2Fe^{2+} + 4H^+ \Leftrightarrow Pu^{4+} + 2Fe^{3+} + 2H_2O \quad (1.8)$$

$$Pu^{3+} + HNO_2 + H^+ \Leftrightarrow Pu^{4+} + NO \quad + H_2O \quad (1.9)$$

Sodium nitrite can be used to reduce the Pu(IV) to Pu(III) under the right conditions but partly due to Equation 1.9, the Pu(III) is not as stable in solution. Another redox agent such as HAN can be used as a holding reductant to keep Pu(III) from oxidizing. HAN cannot be solely used as a reducing agent because even with a slight excess of HAN to Pu, it will reduce ca. 85 % Pu(IV) in 1 hour in 2.4 M HNO_3 [34], a slow reaction time. Determining how stable Pu(III) is at low acidities will help determine a working model for neptunium and plutonium separation and selective extraction. The extractable species Pu(IV) and the unextractable species Pu(III) are the focus for a plutonium and neptunium separation in solvent extraction [12] but it would also be beneficial to also understand the extraction potential of the other stable oxidation state, Pu(VI).

1.4 Solvent Extraction Process

The purification of ^{238}Pu from the irradiated $^{237}NpO_2$ targets at SRS was done using an anion exchange process [31]. Before being sent through the column, the targets were dissolved in concentrated HNO_3 (10 M), with Fe(II) to stabilize Np and Pu in their tetravalent states. Since Np(IV) and Pu(IV) are strongly absorbed onto the column, the column could be rinsed to remove the fission products. The actinides were then eluted with dilute HNO_3 (0.35 M) and sent through a fresh column in 8 M HNO_3. The second column was used to remove extra fission products by rinsing at the same acidity. A 5.5 M HNO_3 solution with Fe(II) and hydrazine was used to strip the Pu from the column as Pu(III). Pure Np was recovered using dilute HNO_3. The process at SRS had been reliably used for decades until the ^{238}Pu production ceased.

Oak Ridge National Lab (ORNL) was selected as the site to restart ^{238}Pu production using solvent extraction to purify the plutonium instead of anion exchange chromatography. Separation of neptunium and plutonium using solvent extraction can be accomplished using principles from the plutonium and uranium redox extraction process (PUREX). PUREX uses tributylphosphate (TBP), shown in Figure 1.5, as the extracting ligand to extract the actinide elements in their tetravalent and hexavalent oxidation states with the trivalent and pentavalent states being poorly extracted [35].

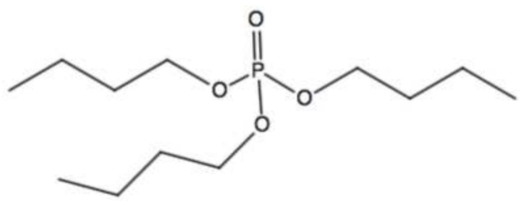


Figure 1.5: Tributylphosphate, the extracting ligand used for ^{238}Pu purification and ^{237}Np recovery at ORNL.

The main steps of PUREX are as follows: irradiated nuclear material is dissolved in ca. 8 M HNO_3, diluted to ca. 4 M HNO_3, and the U(VI) and Pu(IV) are extracted using 30 % TBP, along with some Np(IV) and Np(VI). The Pu(IV) is then reduced to Pu(III) using a reducing agent so that the Pu will partition from the U in the stream. In the last step, the leftover U is stripped from the TBP [35].

Separation of ^{237}Np and ^{238}Pu at ORNL is done similarly with TBP using solvent extraction, except the Np is stripped before the Pu is reduced [12]. This is counter-intuitive [36] because the bulk of the stream is unreacted ^{237}Np [12]. The process at ORNL is to dissolve the NpO_2 targets in concentrated HNO_3 and then use 30 % TBP to extract Np(VI) and Pu(IV) by stabilizing Np(VI) and Pu(IV) and oxidizing Np(V). The ^{237}Np is then stripped using $NaNO_2$ to reduce the Np(VI) to poorly extracted Np(V). Finally, HAN reduces Pu from Pu(IV) to be stripped as Pu(III). Figure 1.6 shows extraction profile of Pu(IV) and Np(VI) using TBP.

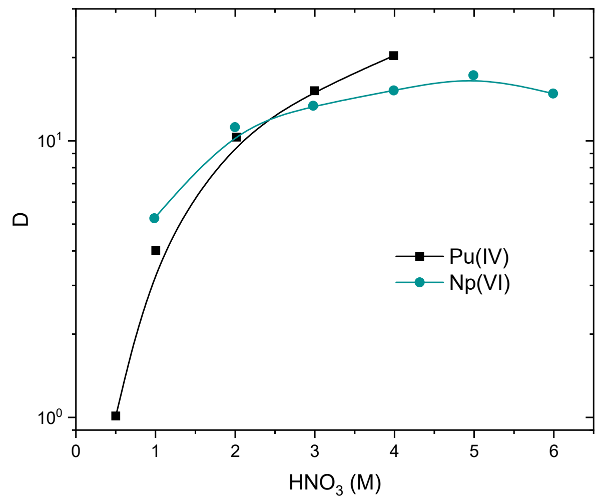


Figure 1.6: Distribution ratios of Pu(IV) and Np(VI) using 1.1 M TBP in dodecane as a function of HNO_3 concentration [37].

Unfortunately, switching from anion exchange chromatography separations to a solvent extraction separation has presented some issues. Resolving these issues is the primary reason for this work. Although TBP has been able to separate Np and Pu at the pilot scale, TBP-based separations have a few significant issues that need to be addressed before the process is scaled to produce ^{238}Pu in the quantities that NASA would require for its space missions [12]. The issues are a result of the radiolytic degradation products of TBP: dibutylphosphate, monobutylphosphate, and phosphate. These byproducts complicate the extraction and purification of ^{238}Pu and ^{237}Np [38]. The degradation products form insoluble salts and other compounds [39, 40] that prevent ^{238}Pu and ^{237}Np from being extracted efficiently. For instance, as ^{238}Pu is stripped from low acidities, dibutylphosphate will deprotonate and keep ^{238}Pu in the organic phase. While these issues can be significant, the critical issue is the phosphorus contamination that is prevalent after separating the actinides. The GPHS specification for the $^{238}PuO_2$ product the presence of less than 25 μg phosphorus per gram of product (μg/g), but the phosphorus levels of ^{238}Pu produced from TBP separations at ORNL have exceeded 1,100 μg/g [12]. In addition, phosphorus contamination can cause the rejection of recycled ^{237}Np targets.

Another instance of phosphorus contamination occurs when di-(2-ethylhexyl) phosphoric acid (HDEHP) is used to purify ^{237}Np by removing thorium and plutonium prior to its first irradiation cycle. However, the degradation of HDEHP is suspected to be contaminating the initial ^{237}Np targets with phosphorus, causing target rejection [12]. The $^{237}NpO_2$ targets also have strict design specifications. For instance, the current $^{237}NpO_2$ targets used in the High Flux Isotope Reactor (HFIR) at ORNL are more dense than the targets previously used for the K-reactor at SRS [5]. This design constraint increases the heat being produced from the extra fission events occurring per target so that the material characteristics of the target now need to withstand the increase in temperature [12] while remaining compatible with the target's aluminum cladding, which can only withstand temperatures up to 650°C.

Removing the excess phosphorus contamination is protracted and difficult. An alternative to TBP or HDEHP is to use an extractant that does not contain phosphorus but can still separate ^{237}Np and ^{238}Pu as efficiently. A possible candidate that could potentially be directly substituted for TBP or HDEHP in these processes is a *N,N*-dialkylamide (monoamide).

1.5 *N,N*-Dialkylamides

Monoamides have been considered as replacements for TBP for reprocessing used nuclear fuel for decades [41]. There are two main benefits that monoamides have over TBP. First, the volume of radioactive waste is diminished because monoamides can be completely incinerated because they comply with the CHON principle [42] and will not leave any residual phosphorus contamination. Since any extracting ligand will inevitably degrade from radiolysis, the second benefit is that the degradation products of monoamides consist of carboxylic acids [43] and imides [44], neither of which bind strongly to relevant metal ions under the acidic conditions used for the extraction. Although, the degradation products can buildup in the system over time and need to be removed by periodic solvent washing, an issue that is also seen with TBP [35]. This study focuses on a class of monoamides, *N,N*-dialkylamides.

Figure 1.7 shows the basic structure of the *N,N*-dialkylamides. While the variations of *N,N*-dialkylamides are not limitless, there are many that can be used for actinide extraction [42]. Fortunately, the selection can be narrowed considerably due to the requirements of the extraction process, mainly the solvents used for the aqueous (HNO_3 and water) and the organic (Exxsol D60) solution. Exxsol D60 is currently being used at ORNL [12] and is an industrial aliphatic solvent similar to dodecane. Another requirement for a potential monoamide is strong binding affinity with Pu(IV) and Np(VI) and weak binding with Np(V) and Pu(III).

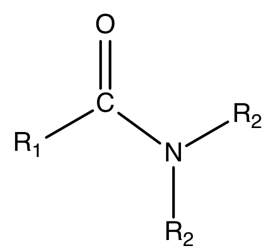


Figure 1.7: Base Structure of *N,N*-dialkylamides: R_1 are carbon chains of the dialkyl side and R_2 is a carbon chain on the acyl side.

The effectiveness of liquid-liquid extraction hinges on two immiscible liquids, so that after intensive mixing, the liquids can quickly separate into two distinct phases of different densities [36]. The structure of the extractant and organic solvent are usually similar to allow the extractant to fully dissolve. Therefore, it is likely that monoamides with aromatic or cycloalkane substituents will be less soluble in a solvent like Exxsol D60 than in an aromatic solvent such as toluene. Lengthening the hydrocarbon (R_2) chains on the monoamide will allow it to be soluble in a solvent like *n*-dodecane to some extent [45] and by extension, Exxsol D60. The arrangement of the chains off the carbonyl or the nitrogen side will also impact the *N,N*-dialkylamides solubility in organic solutions and their extraction potential of metals [46-49]. However, as a ligand extracts metal, acid, or other compounds, a new complex can be formed that is soluble in neither of the initial phases, thus creating a third phase. Monoamides are no exception [50]. As the monoamides form complexes with uranyl in aliphatic hydrocarbons, the new monoamide-uranyl complex can precipitate or cause third phase formation with high uranium concentrations and at high acidities [51]. Even though uranium is not the target metal, there might be issues with the similar monoamide-neptunyl complex that will need to be monitored.

However, there are a few other concerns that can significantly impact the application of monoamides. It has been observed that altering the alkyl groups can change a particular monoamide's preference for the tetravalent or the hexavalent actinides [42]. This allows the extractant to be tuned to favor either tetravalent actinide ions (An(IV)) or hexavalent actinide ions (An(VI)), which could selectively separate ^{237}Np and ^{238}Pu. Changing the monoamide structure can also impact the monoamides' overall extraction efficiency and the solubility of the monoamide-nitrate-metal complex in the organic phase. For the past few decades, the bulk of monoamide work has focused on the extraction potential of the actinides Th(IV), U(VI), or Pu(IV) [41, 52-54] with some recent studies of the extraction behavior of neptunium by monoamides [37, 49, 55] or the other common oxidation state of plutonium, Pu(VI) [55].

Separating ^{237}Np and ^{238}Pu so that ^{237}Np can either be recycled or removed from the ^{238}Pu product stream using a monoamide will require a thorough understanding of the separations behavior for the relevant oxidation states of neptunium and plutonium in these systems. As referenced earlier, the factors to consider are how each oxidation state is formed under process conditions, how they partition in the solvent extraction process, and how the oxidation states interconvert during the extraction process. Understanding how relevant reducing or oxidizing agents, along with nitric and nitrous acid, partition in the organic phase is also critical to understanding the mechanics of the overall system.

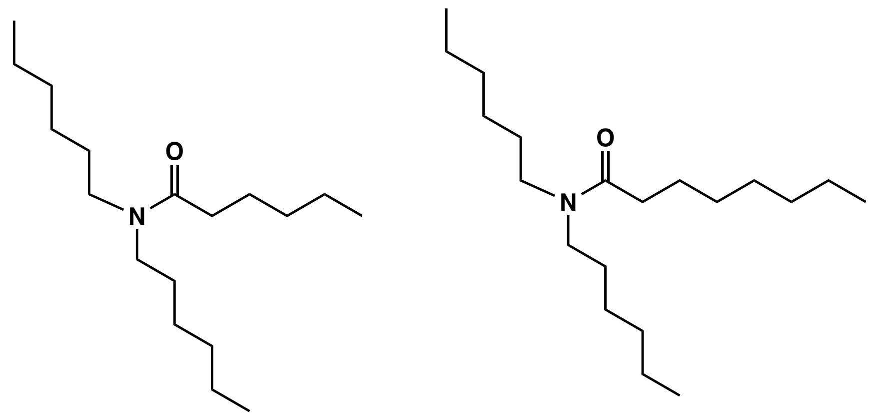
The extractant structure and actinide extraction potential both factor into choosing monoamides to examine. Several studies provide a broad overview for monoamide extraction of actinides [41, 42, 56, 57] but testing all of the possible monoamides over the range of conditions is impractical. Narrowing the variety of possible monoamides to study can be done by analyzing the monoamide structure and cross-comparing with the available literature.

Prior research of one class of monoamides, cycloalkane monoamides, was reported to yield unsatisfactory results when using mesitylene as the organic solvent [38]. Curiously, cycloalkane monoamides that were studied in toluene [41, 58, 59] suggested positive results. Perhaps a higher complexity due to the cycloalkane within the monoamide structures, comparatively to other monoamides, are conducive to binding actinides in certain solvents. Regardless, the dicyclohexyl amides that were a focus in those studies were excluded by the lack of available and conclusive detail on actinide extraction [42, 44]. Instead, monoamides without cycloalkane components were further researched for probable usage.

The previously mentioned third phase formation is a possibility that is dependent on the branching chains from the monoamide and the diluent, along with the metal concentration and the solution acidity. While it is reported that certain monoamides may not be soluble in an aliphatic diluent, such as Exxsol D60 [41], a specific length of the carbon chains can significantly improve their solubility. Actinide extraction studies of monoamides in *n*-dodecane were compared to determine an ideal extractant to pursue. Studies of monoamide extraction in toluene, or other aromatic solvents, were generally excluded from consideration unless to be used as a comparison for the final selected extractants.

The monoamides can be further subdivided into two groups, nonbranched (linear alkyl chains) and branched (alkyl groups branching off the linear alkyl chains). It was found that within the first group, a 4 to 10 carbon chain on either R_1 or R_2 (see Figure 1.7) were possibilities for further study. Shortening the carbon chain on the acyl side (R_1) to 4 could reduce the likelihood of third phase formation as observed for *N,N*-dihexylbutanamide (DHBA) and *N,N*-dihexylisobutanamide (DHiBA). Unfortunately, while it was seen that at 4 M HNO_3, the distribution ratios for Pu(IV) and U(VI) were greater than 1, the max distribution ratios were ~ 7 for Pu(IV)-DHBA and ~ 3 for the U(VI)-DHBA and both DHiBA actinide complexes [60]. A distribution ratio higher than 10 at 4 M HNO_3 is ideal for tetravalent or hexavalent actinide extraction because that indicates over 90 % of the metal is being extracted in each contact. Slightly lengthening the carbon chains for *N,N*-dioctylbutanamide (DOBA) and *N,N*-dioctylisobutanamide (DOiBA) had similar results, albeit the Pu(IV) extraction by DOBA is significantly higher with a distribution ratio of ~ 25 [61]. Since these results with a 4 carbon group chain on the acyl chloride side are not promising for actinide extraction, 6, 8, and 10 carbon chains of R_1 were evaluated next: *N,N*-dihexylhexanamide (DHHA), *N,N*-dihexyloctanamide (DHOA), and *N,N*-dihexyldecanamide (DHDA).

A previous study using 0.5 M DHHA in *n*-dodecane reported ~ 90% and ~ 75 % extraction of Pu(IV) and U(VI), respectively, in 4 M HNO_3. In addition to favorable actinide extraction, it was reported that third phase formation was not observed until 7 M nitric acid [62], above ORNL's operating parameters. A significant amount of research has been done with DHOA extraction of actinides [37, 48, 63]. Those studies indicate favorable actinide (U, Np, Pu) extraction, which will be discussed later. One study used 300 g/L of U and did not see a third phase form [37]. Other studies demonstrate the versatility of DHOA such as a performance increase with using ionic liquids [64] and use as a phase modifier with other extractants [65]. The last monoamide in this category considered, DHDA, had initial results showing that Pu(IV) extraction was lower and about the same for U(VI) extraction as DHHA and DHOA [66]. However, it has been noted that DHOA and DHHA are more thermodynamically favorable for Pu recovery than DHDA [42]. Due to the potential of DHOA and DHHA from these studies, these nonbranched monoamides were further evaluated experimentally. Figure 1.8 illustrates their structures.

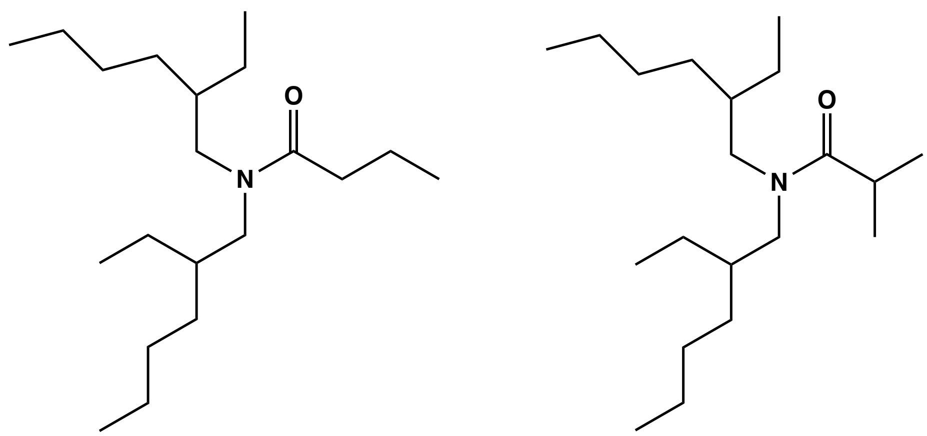


DHHA DHOA

Figure 1.8: Structure of the studied nonbranched monoamides

The other category, branched monoamides, have also been the focus of several studies because they have not been observed to form a third phase even at high metal concentrations. Even though branched monoamides have been observed to selectively extract hexavalent over tetravalent actinides, the overall distribution ratios of actinide extraction were lower compared to the nonbranched monoamides [42]. Regardless, several branched monoamides were considered to determine their feasibility and potential for extraction of neptunium and plutonium.

N,N-di(2-ethylhexyl)pivalamide (DEHPVA) in dodecane was found to significantly extract U over Np and Pu [67]. However, that study showed almost no extraction of the two target metals (Np and Pu). DEHPVA could be a useful monoamide to use as a substitute in the PUREX process but not for Pu/Np separations. Another study with a similar monoamide, *N,N*-di(2-ethylhexyl)-2,2-dimethylpropanamide (DEHDMPA) did not show encouraging results [68]. Even so, that study also compared DEHDMPA with *N,N*-diethylhexylbutanamide (DEHBA), with the observation that DEHBA had consistently better extraction over DEHDMPA for Np(VI) and that there was no observed third phase (up to 4.5 M HNO_3). Furthermore, another study found that DEHBA is more apt at extracting hexavalent actinides over DHOA [69]. The positive characteristics of DEHBA were reviewed along with its isomer, *N,N*-diethylhexylisobutanamide (DEHiBA). Figure 1.9 illustrates their structures. Recall that both DEHBA and DEHiBA are referred to as branched monoamides due to the ethylhexyl groups on the alkyl chains.



DEHBA DEHiBA

Figure 1.9: Structures of the studied branched monoamides

1.6 DHOA, DHHA, DEHBA, and DEHiBA

The previous section discussed various characteristics and behavior of multiple monoamides. The promising monoamides that were selected for this study are DHHA, DHOA, DEHBA, and DEHiBA. It is worthwhile to further quantify the behavior of these monoamides regarding their specific potential for extraction of Np(IV, V, VI) and Pu(III, IV, VI), third phase formation, radiolytic degradation, and other characteristics that are known from the literature.

1.6.1 Neptunium Extraction

Since neither the PUREX nor the thorium extraction (THOREX) processes use neptunium as part of their fuel cycles, there were few studies of the distribution behavior using monoamides as extractants for neptunium by itself and with other actinides until recently by Mahanty et al. [70, 71]. This work will later analyze and discuss neptunium extraction by the selected monoamides in Chapters 2 - 4. However, it is necessary to understand the trends of what has been observed in the literature and the possible mechanisms for those trends.

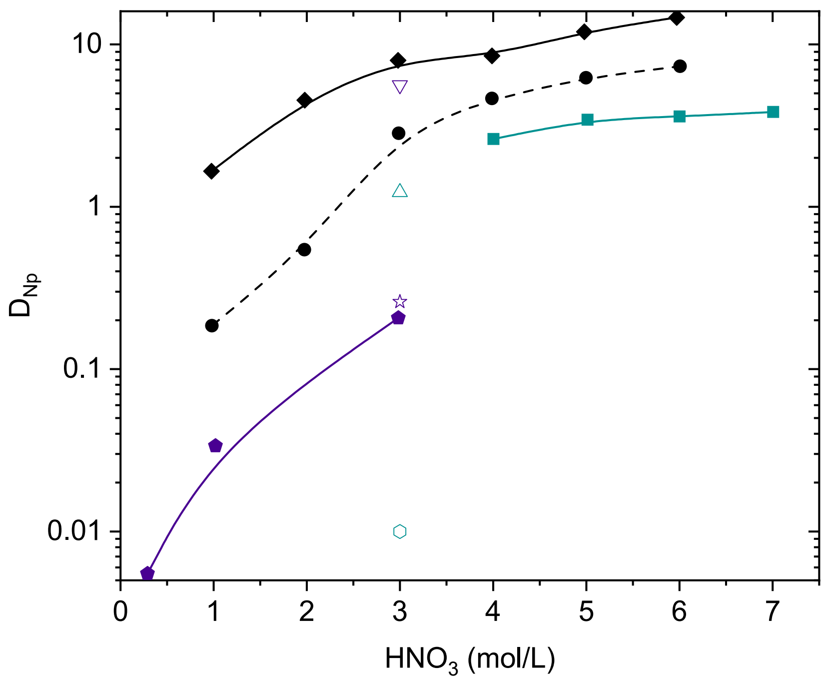


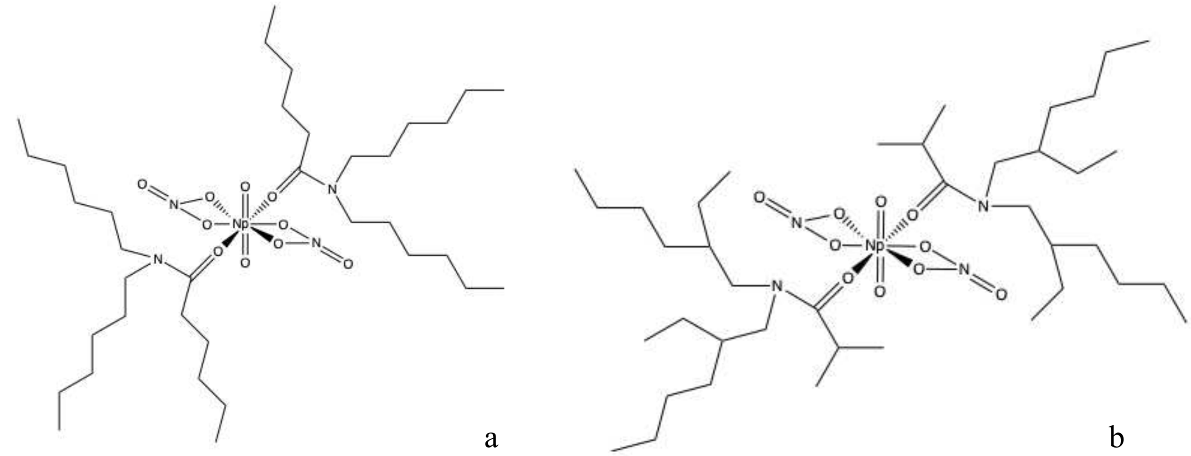
Figure 1.10: Distribution ratios of neptunium from the literature for several monoamides: 1.1 M DHOA: ( ) Np(VI) and ( ) Np(IV) [37], 1M DEHBA: upside-down triangle-Np(VI) and star-Np(IV) [49], ( ) 1.5 M DEHBA-Np(V), 1M DEHiBA: ( ) Np(VI) [69], triangle-Np(VI) and hexagon-Np(IV) [49]. Lines are a visual aid.

Figure 1.10 is a compilation from the existing literature for neptunium extraction by DEHBA, DEHiBA, and DHOA. Suzuki et al. only reported single data points for DEHBA and DEHiBA extracting Np(IV) and Np(VI) but in separate studies. Additional details from the literature indicate that the monoamides will extract Np(VI) better than Np(IV). It is likely that

Np(V) is not well extracted compared to other oxidation states but comparing the results from Ban et al. suggest that the branched monoamides may extract Np(IV) and Np(V) similarly.

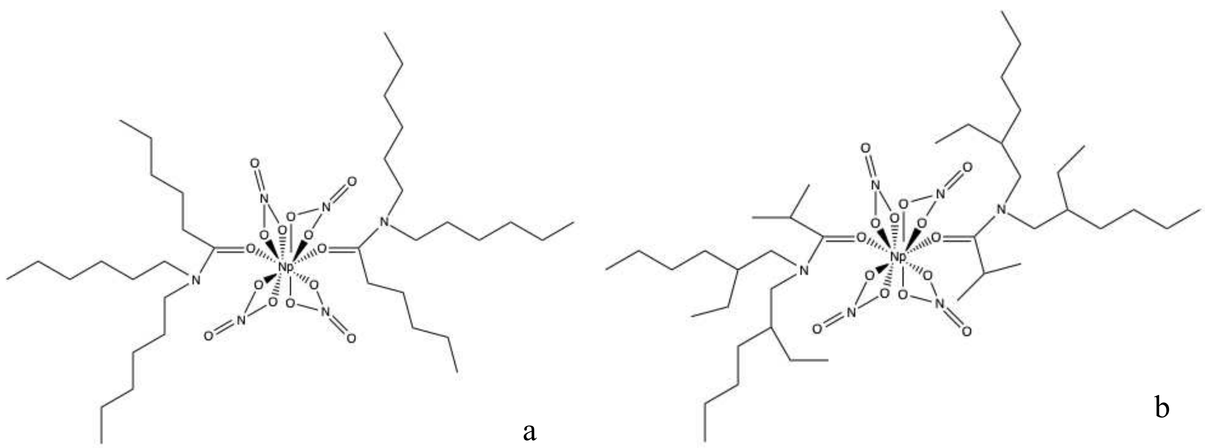
Even though there are no available data for DHHA extracting Np, Figure 1.10 implies that the nonbranched monoamides can extract Np(VI) better than branched monoamides. The reason for this can be elucidated by comparing the Np(VI)-DHHA and Np(VI)-DEHiBA complexes in Figure 1.11. These complexes, including the ones in Figure 1.12, are modeled from U(VI) and Pu(IV) complexes with monoamides since there has not been any structural analysis of Np-monoamide complexes. The carbon chain off of the carbonyl group (the acyl chain) on the branched monoamides can sterically hinder the formation of the AnO_2^{2+}-monoamide complexes for U [46, 47]and Np [49] because that is where the actinide ion binds to the monoamide [48]. As indicated in Figure 1.11b, metal ion access to the carbonyl group can be further obstructed depending if there is a branched carbon chain present near the carbonyl or the amide. On the other hand, nonbranched monoamides should not be as sterically hindered, as indicated in Figure 1.8. As expected, the isobutyl group limits metal binding to DEHiBA.

Further comparison of the Np(VI)-monoamide complexes with Np(IV)-monoamide complexes in Figure 1.12 may explain why Np(IV) is not as well extracted as Np(VI). The Np(IV)-monoamide complex forms with four bidentate nitrate groups, instead of two for Np(VI), to complete a dodecahedron structure with the monoamides, illustrated in Figure 1.12a for a nonbranched monoamide and Figure 1.12b for branched monoamide. While the Np(IV)-monoamide is a stable complex, the intricacy of the inner coordination sphere may prevent sufficient binding to the Np(IV) ion. The isobutyl group on DEHiBA seems to be effectively preventing the metal ion Np^{4+} from binding, as it did for NpO_2^{2+}, so it is likely that DEHiBA does not extract Np(IV) well.



a b

Figure 1.11: Possible 2D configurations of (a) $Np(VI)(NO_3)_2DHHA_2$ and (b) $Np(VI)(NO_3)_2DEHiBA_2$ based on U(VI)-monoamide complexes [72].



a b

Figure 1.12: Possible 2D configurations of (a) $Np(IV)(NO_3)_4DHHA_2$ and (b) $Np(IV)(NO_3)_4DEHiBA_2$ based on Pu(IV)-monoamide complexes [72].

However, it is important to be aware that there are other possible factors that could cause Np(IV) to not be as well extracted as Np(VI), such as the relative hydrophobicity of the Np-monoamide complex or the energy necessary to extract 4 vs. 2 nitrates. Rabbe et al. concluded that monoamide separation is controlled by three main factors: electron density of the coordination sphere (Figure 1.11 and Figure 1.12), steric effects, and the lipophilicity [59]. While the concern about the solubility of monoamide:U(VI) complexes in aromatic solvents such as mesitylene has been expressed elsewhere [52], the length of the hydrocarbon chains for the chosen monoamides are conducive to help monoamide:actinide complexes be soluble in aliphatic solvents (*n*-dodecane and Exxsol D60) [50]. Since there is little variation between the monoamide structures used in this study, the distribution coefficients are anticipated to be similar for monoamide:An(VI) complexes and slightly higher for monoamide:An(IV) complexes (An=Pu and Np) [52] .

1.6.2 Plutonium Extraction

This dissertation will also discuss the distribution behavior of plutonium's common oxidation states using the selected monoamides in Chapter 4. However, as with neptunium, a brief introduction of what is known from the literature will help ascertain the expectations of plutonium extraction. It has been shown elsewhere that TBP extracts Pu(IV) better than Pu(VI) and that Pu(III) is not well extracted [36]. There have been a number of studies for monoamides extracting Pu(IV) but relatively few for Pu(VI) and Pu(III). A compilation of these results are shown in Figure 1.13.

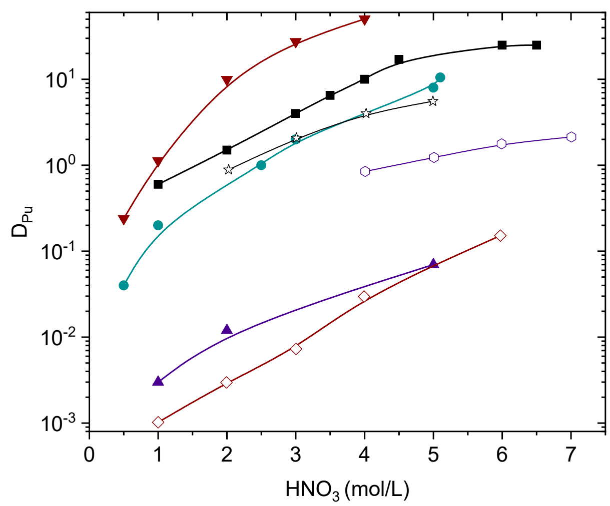


Figure 1.13: Distribution ratios of plutonium from the literature for several monoamides: 0.5 M DHHA: (—■—) Pu(IV), 1 M DHHA: (—☆—) Pu(VI) [62, 73], 1 M DEHBA: (—●—) Pu(IV) [46], 1 M DEHiBA: (—▲—) Pu(IV) and (—⬡—) Pu(VI) [46, 69], and 1.1 M DHOA: (—▼—) Pu(IV) and(—◇—) Pu(III) [37, 70]. Lines are a visual aid.

Nonbranched monoamides generally extract Pu(IV) better than the branched monoamides, as can be seen in Figure 1.13. However, there is little indication of how well Pu(VI) is extracted because DHHA extracts Pu(IV) better than Pu(VI). If the trends are otherwise consistent for the distribution ratios for the other monoamides, then it is likely that DHHA and DHOA will both be as ideal extractants for Pu(IV) and Pu(VI) as they are for Np. It is uncertain how well DEHBA will compare to DHOA and DHHA for extraction of Pu(IV) or Pu(VI).

It is worthwhile to note that DEHBA and DEHiBA have been previously investigated for the co-extraction of U(VI) and Pu(IV) at high acidities (~ 6 M) and selective stripping at low acidities [47]. While the possibility of using two extractants to partition actinides is not a new concept, the idea is still worth pursuing and will be referred to several times later. Further comparison of these two branched monoamides was also done with Pu(IV) and Np(IV). Although the Np(IV) and Np(VI) extraction was done in only 3 M HNO_3, it is indicative of but not conclusive for extraction preferences and trends [49].

1.6.3 Radiolytic Degradation

The energy from radioactive decay can degrade all aspects of the solvent extraction system. The degradation products that are formed can alter or otherwise affect the system in either unexpected ways or have counterproductive effects. The rate that degradation products are formed can substantially increase depending on the concentration of particular radionuclides. As an example, the main nuclide being extracted in the PUREX process, ^{238}U, has 79% of its alpha decays occur at an energy of 4198 keV. On the other hand, 70.91 % of the alpha decays from ^{238}Pu occur at 5499 keV, a significant increase [74]. The buildup of the degradation products increase in the presence of oxygen [44, 75]. This could indicate that without oxygen either the compounds are comparatively stable or the formed degradation products readily react with other compounds in solution. This study only considered the thermal decomposition products (up to 215°C) and not the effects of radiolysis. While any extractant being used to selectively extract the ^{238}Pu from ^{237}Np will degrade, an extractant that has essentially non-deleterious degradation products is ideal.

The central monoamide structure shown in Figure 1.7 can splinter at either the alkyl or acyl bond to form the major degradation products: bis-2-ethylhexylamine (DEHA) and mono-2-ethylhexyl-isobutanamide (EHiBA) for DEHiBA [75], DEHBA would form mono-2-ethylhexyl-butanamide (EHBA) instead of EHiBA, dihexylamine and dihexylketone for (DHOA), along with caprylic acid [63], and DHHA would probably have similar products as DHOA. Carboxylic acids are also major degradation products that are observed from monoamides [76, 77]. Previous studies indicate that monoamides used at the industrial scale do not have potentially harmful issues such as causing criticality incidents nor back extraction issues [63, 76, 77].

1.7 Goal

The objective of this project is to ascertain which monoamide will most efficiently extract and selectively separate Np and Pu. The suitable monoamide could then replace TBP in the current process conditions. Figure 1.14 shows the separation route for Np and Pu. The monoamide extracts Np(VI) and Pu(IV) in moderate to high acidic conditions. The reducing agents sodium nitrite ($NaNO_2$) and hydroxylamine nitrate (HAN) are then used to reduce Np(IV) to Np(V) and Pu(IV) to Pu(III) respectively. This proposed separation pathway is tentatively referred to as the MonoAmide Plutonium Neptunium EXtraction (MAPNEX) process. Based off an extensive review of the literature, the monoamides DHHA, DHOA, DEHBA, and DEHiBA, are the potential candidates to substitute for TBP in neptunium and plutonium separations in Exxsol D60.

Preliminary studies of MAPNEX described in the following chapter comprise the extraction of U(VI) and Np(IV, VI) for confirmation and comparison of existing studies with DEHiBA and DHOA. The second part of the preliminary studies also examined the utility of DHHA for Pu purification. Chapter 3 details higher than trace level conditions for Np(IV, V, VI) (0.001 – 0.006 M ^{237}Np) that were used to find extractant and nitric acid dependencies for each monoamide. Chapter 4 compares the extraction potential and possible extraction mechanisms of other actinides of interest; thorium, protactinium, and americium with uranium, neptunium and plutonium. This chapter also suggests potential extraction schemes for Np/Th and Np/Pu separations. A final component of these studies is the investigation of the effects of reducing agents, specifically nitrous acid, on monoamides.

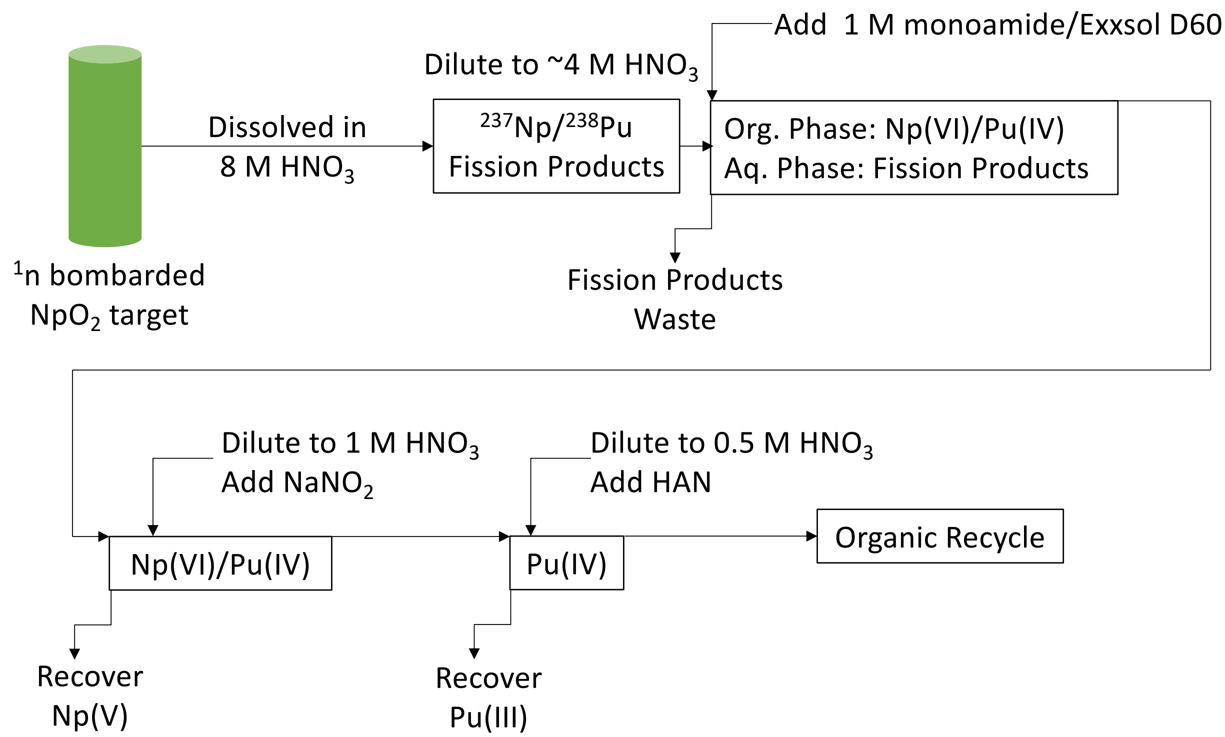


Figure 1.14: Separation scheme with a monoamide: MonoAmide Plutonium Neptunium EXtraction (MAPNEX)

CHAPTER 2

INTRODUCTORY STUDIES INTO ACTINIDE EXTRACTION AND SEPARATION BY *N,N*-DIALKYLAMIDES

The previous chapter discussed many previous studies that examined actinide extraction by *N,N*-dialkylamides. Recall that the literature studies focused on Th(IV), Pu(IV), and U(VI) [41, 52-54] for decades and have recently expanded into Np(IV), Np(VI), Am(VI), and Pu(VI) [37, 55, 70, 78] being partitioned using *N,N*-dialkylamides. This chapter focuses on gaining insight into Np and Pu extraction behavior by comparing my experimental results with the literature values. The bulk of the work reported in this chapter was published in conference proceedings [79, 80]. These findings indicated that *N,N*-dihexyloctanamide (DHOA) or *N,N*-dihexylhexanamide (DHHA) would be ideal for Np(VI)/Pu(IV) separation although it was difficult to stabilize Pu as Pu(III) for efficient stripping.

2.1 Experimental Details

2.1.1 Monoamide Synthesis, Purification, and Characterization

The *N,N*-dialkylamides DHHA, DHOA, N,*N*-diethylhexylbutanamide (DEHBA), and *N,N*-diethylhexylisobutanamide (DEHiBA) were synthesized under a N_2 atmosphere by adding the corresponding acyl chloride dropwise into a mixture of triethylamine with dihexylamine or di(2-ethylhexyl)amine in dichloromethane in a 0.15: 0.122: 0.131: 0.7 molar ratio cooled in an ice-water bath. The ratio of reagents used is similar to other reports [55]. After all the acyl chloride was added, the ice-water bath was removed to allow the reaction to proceed at room temperature for one hour.

The resulting mixture was diluted with 2 - 3 times the starting volume of diethyl ether and then vacuum filtered through a Celite plug on a layer of silica gel (technical grade 230-400 mesh particle size) to remove the precipitated salts [81, 82]. The separated salt initially had a salmon color but rinsing with diethyl ether removed the color from the salt. The combined filtrate and diethyl ether rinse was then rotary evaporated to remove the dichloromethane and diethyl ether to yield the monoamide product. The resulting monoamides were then purified using vacuum distillation. During distillation, the system pressure varied from 0.75 to 0.64 torr at temperatures between 50 and 70 °C. Initial drops formed around 50 °C for all monoamide solutions. Collection of the distilled monoamide began when the condensate was colorless. The temperature and pressure were adjusted to give a steady flow rate of a drop every five seconds. Final product is colorless and odorless. The monoamides were verified to be better than 98% purity by ^{1}H NMR (JEOL 500 MHz liquid state NMR) in deuterated chloroform. The range of the peaks are expressed as δ (parts per million). The ^{1}H NMR results for the monoamides (recall that structures are shown in Figure 1.8 and Figure 1.9) are as follows:

DHHA: δ = 0.82 – 0.90 (9H from CH_3), 1.20 – 1.35 (16H from CH_2), 1.44 – 1.65 (6H from CH_2), 2.24-2.28 (2H from CH_2), 3.16 – 3.29 (4H from N-CH_2)

DHOA: 0.80 – 0.89 (9H from CH_3), 1.19-1.33 (20H from CH_2), 1.43-1.64 (6H from CH_2), 2.24-2.30 (2H from CH_2), 3.14 – 3.29 (4H from N-CH_2)

DEHBA: 0.83 – 0.91 (9H from CH_3), 0.92 – 0.96 (8H from CH_2 and CH_3), 1.15 – 1.35 (6H from CH_2), 1.54 – 1.61 (4H from CH_2), 1.62-1.70 (2H from CH), 2.25-2.29 (2H from CH_2), 3.11 – 3.32 (4H from N-CH_2)

DEHiBA: δ = 0.80 – 0.88 (6H from CH_3), 1.05 – 1.09 (6H from CH_3), 1.20 – 1.35 (6H from CH_2), 1.32 – 1.13 (12H from CH_2), 1.48-1.55 (4H from CH_2), 1.62-1.68 (2H from CH) , 2.73-2.82 (1H from CH), 3.12 – 3.27 (4H from N-CH_2)

2.1.2 Actinide Solutions

Uranium-233 (^{233}U) in 1 M HNO_3 was purified by extraction chromatography with a UTEVA column [83]. Neptunium-237 (^{237}Np) and plutonium-239 (^{239}Pu) were taken from laboratory stocks and used without further purification. The Pu(III) solution was made by reducing the plutonium with 0.43 M hydroxylamine hydrochloride in 1 M HNO_3 [34]. Solutions of Np(IV) were produced by reducing Np(V) with 0.1 M ferrous sulfamate [27]. Pu(IV) was made by oxidizing the Pu(III) solution with 0.03 M sodium nitrite [84]. Hexavalent Np and Pu were prepared by oxidation with potassium bromate ($KBrO_3$) at 80 °C. The oxidation states of the resulting plutonium and neptunium solutions were separately verified by solvent extraction [85].

2.1.3 Solvent Extraction

Weighed amounts of the monoamides were diluted in Exxsol D60 to yield solutions of the desired extractant concentration. The monoamide solutions were pre-equilibrated twice with the appropriate nitric acid concentrations (0.1 - 6 M), with a 1:2 volume ratio of organic:aqueous phases before use. The concentrations of the nitric acid solutions, created by diluting Ultrex-grade nitric acid in 18.3 MW water, were determined by titration with standardized sodium hydroxide to the phenolphthalein endpoint. A fresh aqueous phase with an aliquot of the actinide (An) tracer ($<1 \times 10^{-5}$ M An) prepared in the desired oxidation state was vigorously contacted with an equal volume of the pre-equilibrated organic phase. The resulting mixture was centrifuged and the phases were separated for actinide determination by liquid scintillation counting. The following redox agents were added with the Np and Pu to stabilize the intended oxidation states: 0.43 M hydroxylamine hydrochloride for Pu(III), 0.002 M sodium nitrite and 0.005 M ammonium metavanadate for Pu(IV), 0.1 M of ferrous sulfamate, and 0.01 mM potassium bromate for Np(VI) and Pu(VI). The oxidation states were checked again using solvent extraction [85]. The two phases were then centrifuged and separated. Aliquots of each phase were taken for radioactive counting to determine the relative actinide concentration in each phase using a HIDEX 300 SL counter with Ultima Gold AB liquid scintillation cocktail. The U, Np, and Pu (An) distribution ratios were determined as $D_{An} = [An]_{org} / [An]_{aq} = (cpm\ An)_{org} / (cpm\ An)_{aq}$.

2.2 Comparison of DEHiBA and DHOA for Neptunium Separation

The separation and purification of Np is fundamental to ^{238}Pu production, but the extraction chemistry of Np in monoamide systems is poorly studied. This study compares the neptunium extraction behavior of two monoamides: non-branched DHOA and branched DEHiBA as an initial step in evaluating the potential of monoamides for ^{238}Pu production. This study was necessary because there were only two comprehensive studies of Np extraction using DHOA [37, 38], and the reports conflicted. While their research showed similar distribution ratios for Np(VI) extraction by DHOA, the Np(IV) distribution ratios are an order of magnitude lower in Kumari et al.'s work [37] than in Gasparini and Grossi's work[38]. It was important to confirm the extraction behavior of Np(IV) since the former work concluded that DHOA extracted the Np(IV, VI) as well as TBP overall. Previous studies [86] of TBP-Np extraction support the observation that TBP will extract Np(VI) better than Np(IV) in HNO_3.

Separately, it has been reported that a branched monoamide will extract U(VI) better than Pu(IV) [42]. This is significant because DEHiBA displays an extraction behavior whereby the tetravalent actinide, Pu(IV), can be preferentially stripped from the organic phase over hexavalent U(VI) [46]. It was unknown if this potentially beneficial behavior persists for Np extraction. Even though this research has been expanded recently, this chapter succinctly compares DHOA's with DEHiBA's extraction ability of U(VI) vs. Np(VI) and Pu(IV) vs. Np(IV).

2.2.1 Results and Discussion

The extraction of Np(IV) and Np(VI) by representative branched (DEHiBA) and unbranched (DHOA) monoamide extractants in Exxsol D60 are summarized in Figure 2.1 and Figure 2.2. Figure 2.1 directly compares our experimentally determined tracer-scale distribution ratios for Np(IV) with literature values for Np(IV) and Pu(IV) using DHOA [37] and DEHiBA [46].

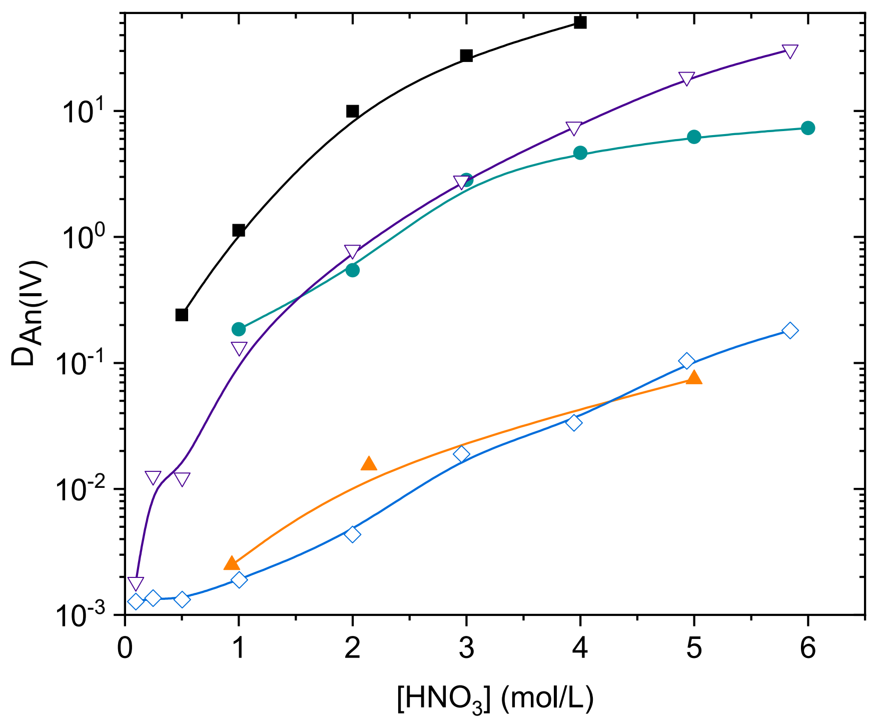


Figure 2.1: Nitric acid dependence of the distribution ratios of Pu(IV) and Np(IV) extracted in an aliphatic solvent. Literature studies of extraction by 1.1 M monoamide: DHOA-Pu ( ) and DHOA-Np ( ) [37], DEHiBA-Pu ( ) [46]. Current studies of extraction by 1 M monoamide: DHOA-Np ( ) DEHiBA-Np ( ). Lines are plotted as a visual guide.

DEHiBA extraction of Pu(IV) and Np(IV) follows the same trend with insignificant extraction across the range of nitric acid concentrations for both ions. The branched alkyl groups of DEHiBA have been hypothesized [87] to sterically hinder binding of tetravalent actinides to DEHiBA and therefore the poor and indistinguishable extraction of Pu(IV) and Np(IV) is expected.

In contrast, the nonbranched monoamide, DHOA, is a substantially better extractant for both Pu(IV) and Np(IV). The DHOA-Np(IV) extraction curve indicates that Np partitioning rapidly rises with increasing nitric acid concentration and that useful extraction, defined as a distribution ratio greater that 1, begins at approximately 2.5 M HNO_3. The previous study of Np(IV) extraction by DHOA suggested that Np extraction levels off with distribution ratios of approximately 4 to 7 above 3 M HNO_3 [37]. On the other hand, our results clearly show the Np(IV) extraction by DHOA steadily increases as the concentration of HNO_3 increases, reaching a distribution ratio of approximately 30 for 6 M HNO_3, similar to the trend established for Pu(IV) extraction by DHOA [37].

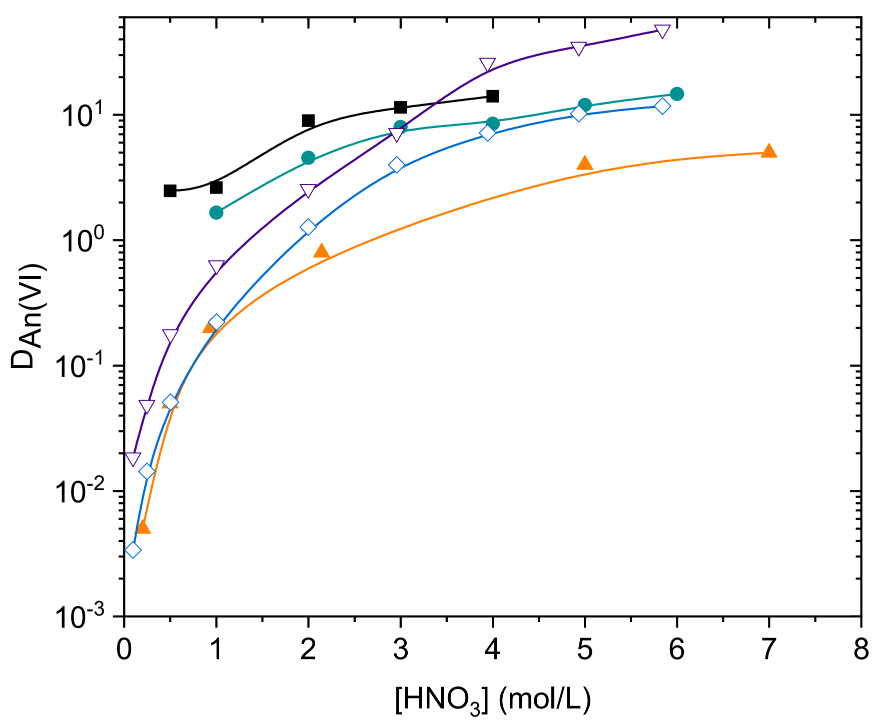


Figure 2.2: Nitric acid dependence of the distribution ratios of U(VI) and Np(VI) extracted in an aliphatic solvent. Literature studies of extraction by 1.1 M monoamide: DHOA-U ( ) and DHOA-Np ( ) [37], DEHiBA-U ( ) [46]. Current studies of extraction by 1 M monoamide: DHOA-Np ( ) DEHiBA-Np ( ). Lines are plotted as a visual guide.

The similar distribution ratios of Np(IV) and Pu(IV) shown in Figure 2.1 imply that separation of Np from Pu will require selective manipulation of the oxidation states of Np and Pu.

Figure 2.2 compares distribution ratios for the extraction of U(VI) and Np(VI) by DEHiBA and DHOA from the literature with our measured distribution ratios for Np(VI). Both DEHiBA and DHOA are capable of extracting hexavalent U or Np from nitric acid solutions above 2 - 3 M HNO_3. Np(VI) extraction increases continually with increasing HNO_3 concentration until at least 6 M, where DHOA and DEHiBA display distribution ratios of approximately 40 and 10, respectively. Again, these distribution ratios are larger than those reported for Np extraction in the literature. Our results summarized in Figure 2.2 also show that Np(VI) stripping is feasible for both DEHiBA and DHOA and that hexavalent actinides can be stripped at low acidities. The improved stripping we observe at low acidities also suggest that our highly purified monoamide extractants and our procedures for producing and maintaining the desired Np oxidation states give more consistent and accurate descriptions of the Np extraction behavior in both oxidation states.

While DEHiBA is a less efficient extractant for Np(VI) and U(VI) than DHOA, DEHiBA does extract hexavalent U and Np when the HNO_3 concentration exceeds 3 M, in contrast to its behavior with tetravalent actinides. Consequently, DEHiBA might be considered for the separation of Np(VI) from Pu(IV) if other contaminating species such as fission products or radioactive progeny do not also need to be removed from the mixture.

2.2.2 Conclusions Regarding Trace Np Extraction by DHOA and DEHiBA

Non-branched monoamide extractants such as DHOA appear to be more effective extractants for Np(IV) and Np(VI) than substantially branched monoamides such as DEHiBA. Both oxidation states of Np are well extracted by DHOA at aqueous HNO_3 concentrations ca. 2.5 M, while DEHiBA only extracts hexavalent actinides, such as Np(VI) well. Based on these results, DHOA shows promise for separating Pu(IV) and Np(IV) if a reductive strip of Pu, similar to that practiced in variation on the PUREX process, could be implemented. Our data also indicates that DEHiBA could be used alone for a Np(VI)/Pu(IV) separation if other contaminants are not absent.

2.3 Using DHHA for Plutonium-238 Purification

While there have been few studies of Pu extraction by DHHA, it shows promise for extracting Pu(IV) well [62, 88]. Unfortunately, recovering Pu from DHHA after reduction to Pu(III) by hydroxylamine nitrate (HAN) is reported to be hampered at higher acidities [34]. (At higher acidities, ferrous sulfamate is a more effective reducing agent than HAN, but the ferrous sulfamate would contribute to the waste burden, whereas HAN is incinerable [12]. Additionally, it was reported that at acidities higher than 1 M nitric acid, spontaneous re-oxidation of Pu(III) back to the extractable Pu(IV) becomes appreciable [89].

To understand the potential of DHHA for Np/Pu separations, the extraction of ^{239}Pu from nitric acid solutions by 1 M DHHA was studied. Even though previous reports indicate that Pu(VI) is not as well extracted as Pu(IV) [69, 73], the partitioning of Pu(III), Pu(IV), and Pu(VI) by DHHA in Exxsol D60 was considered to understand the utility of Pu(VI) in the purification of ^{238}Pu. Also, the extraction of Pu(III), Pu(IV), and Pu(VI) by DHHA were compared and contrasted with that of the baseline TBP system. Comparison with the literature values for TBP extraction indicate that extraction of Pu(IV) and Pu(VI) is comparable for the two different extractants, as are the patterns of Pu(III) extractability at low acidities. Lastly, the average Pu:DHHA stoichiometries of the extraction complexes of Pu(IV) and Pu(VI) were compared directly with those of the other three monoamides studied (DHOA, DEHBA, and DEHiBA) to demonstrate the similar extractant dependence with Pu between the monoamides.

2.3.1 Pu(III, IV, VI) Extraction and Pu(IV, VI) Stoichiometry

The results for the extraction of Pu(III), Pu(IV), and Pu(VI) by 1 M DHHA in Exxsol D60 across a range of equilibrium aqueous nitric acid concentrations are compared with available literature values in Figure 2.3. The extraction of Pu(IV) and Pu(VI) is similar at aqueous nitric acid concentrations of 1 M or lower. However, the extraction preference at concentrations above 2 M nitric acid changes to Pu(IV) > Pu(VI) >> Pu(III).

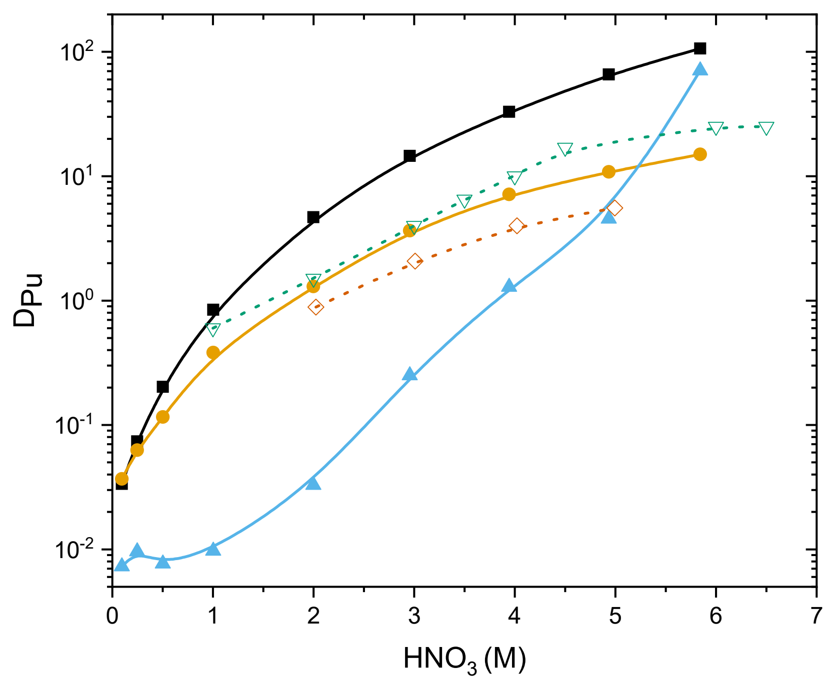


Figure 2.3: Extraction of Pu in various oxidation states by DHHA. Experimental data: 1 M DHHA extracting Pu(III) (solid triangle), Pu(IV) (solid square), and Pu(VI) (solid circle). Literature data for 0.5 M DHHA extracting Pu(IV) [62] **(**open inverse triangle**)** and 1 M DHHA extracting Pu(VI) [73] (open diamond). The trendlines serve as visual aids.

The distribution ratios for Pu(VI) show the same trends as what is seen in the literature , In addition, this experimental data extends the range of acidities where Pu(VI) distribution ratios have been studied to acidities below 2 M nitric acid, [73] a region of interest for Pu(VI) stripping. The present results show that while the Pu(VI) is poorly extracted in that acid range, Pu(VI) extraction is significantly higher than Pu(III) extraction. The extraction preference for Pu(IV) over Pu(VI) is also seen with TBP [37, 90]. Overall, DHHA seems to extract Pu(VI) as well as TBP and extracts Pu(IV) better than TBP at higher acidities (> 4 M HNO_3) but not at the lower acidities. This indicates that the Pu(IV) could be more readily stripped from DHHA than TBP.

Our experimental data for Pu(IV) extraction was indirectly compared to the literature as the data were collected with different DHHA concentrations. We measured the DHHA:Pu(IV) stoichiometry at 1 and 4 M HNO_3 shown in Figure 2.4 (left and right- respectively) with slopes reported in Table 2.1, with the other monoamides as a comparison. Other *N,N*-dialkylamide studies indicate that Pu(IV) is extracted as a mixture of plutonium-nitrate complexes containing 2 to 3 dialkylamide ligands. When 3 monoamides are present, the third *N,N*-dialkylamide is purported to bind in the outer coordination sphere of the extracted complex, especially at higher acidities.[46, 91] Taking the difference in DHHA concentration into account, that suggests the D_{Pu} values measured for Pu(IV) extraction by 1 M DHHA should be five times higher than the corresponding literature values measured for 0.5 M DHHA. Comparison of the data in Figure 2.3 show a four to five-fold difference in the two sets of Pu(IV) distribution ratios between 2 M and 6 M HNO_3. With this correction, the trends in our experimental values and the literature data for Pu(IV) are similar between 2 and 4.5 M nitric acid. However, at lower and higher acidities the experimental results deviate from the literature data in a manner that again suggests the possible presence of impurities in the DHHA used for the literature experiments.

The slopes reported in Table 2.1 are consistent between the nonbranched monoamides and similar to what has been reported for Np(IV) [78], with one notable exception, DEHiBA. However, there is a larger error associated with low distribution ratios at 1 M HNO_3. Whereas at the higher acidity (4 M HNO_3), the extractant dependence of Pu(IV):DEHiBA is closer to the expected value. It is curious that the slope for DEHBA drops significantly from 1 to 4 M HNO_3 because this trend is the reverse of what is expected; the Pu(IV):monoamide complexes show a 1:2 complex stoichiometry at lower acidities (< 4 M HNO_3) and a 1:3 complex at the higher acidities (> 4 M HNO_3). It is interesting that this behavior is not observed for Pu(VI):monoamide complexes, as the stoichiometry is around 2 or lower, Figure 2.5. Accordingly, the neutral $PuO_2(NO_3)_2$(monoamide)$_2$ complex probably has a similar structure to the uranyl-monoamide [72].

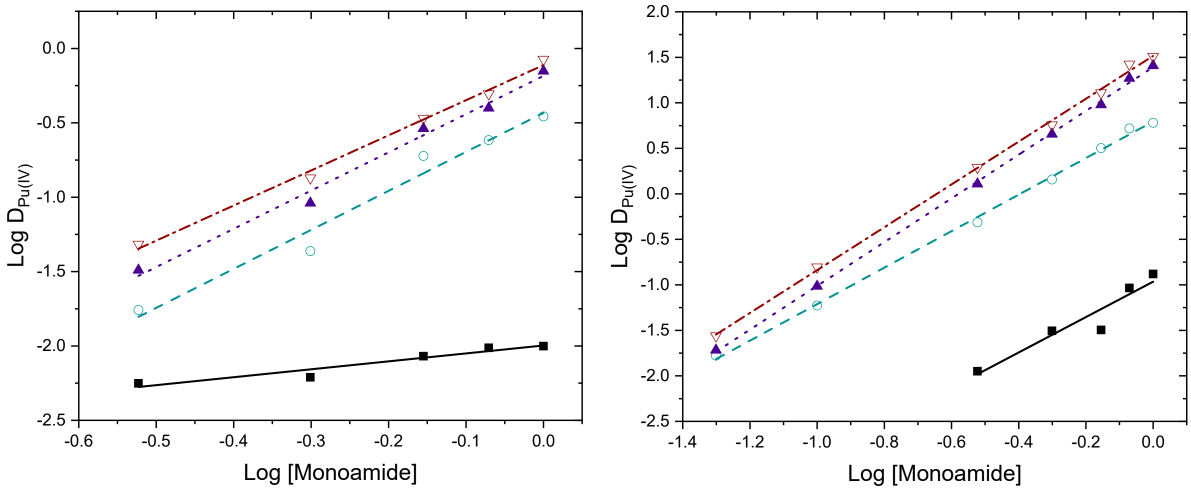


Figure 2.4: Distribution ratios with varying extractant concentration. Extracting Pu(IV) from 1 M HNO_3 (left) and 4 M HNO_3 (right). DEHiBA (square), DEHBA (circle), DHOA, (triangle), and DHHA (inverse triangle). Lines are best linear fit.

Table 2.1: Slope analysis of average N,N-dialkylamide:Pu(IV) stoichiometry extracted from 1 and 4 M HNO_3.

Dialkylamide	Slope: m,	Dialkylamide:Pu(IV)ratio
	1 M HNO_3	4 M HNO_3
DEHiBA	0.53 ± 0.09	1.94 ± 0.36
DEHBA	2.62 ± 0.26	2.01 ± 0.04
DHOA	2.57 ± 0.16	2.40 ± 0.03
DHHA	2.36 ± 0.10	2.35 ± 0.04

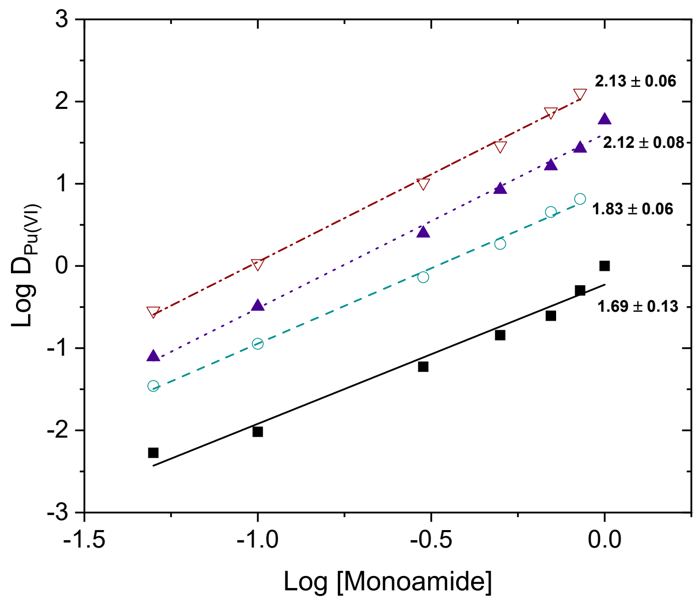


Figure 2.5: Distribution ratios with varying extractant concentration. Extracting Pu(VI) from 4 M nitric acid with 0.01 M $KBrO_3$. Lines are best linear fit: DEHiBA (square), DEHBA (circle), DHOA, (triangle), and DHHA (inverse triangle).

The extraction of Pu(III), in Figure 2.3, shows a different trend from Pu(IV) and Pu(VI). The steady climb in the extraction of Pu(III) with nitric acid concentration is most likely due to Pu(III) oxidizing to Pu(IV) because it has been shown elsewhere that TBP extracts Pu(III) poorly and that the Pu(III)-Pu(IV) couple is readily adjusted in either the aqueous or organic phase [89, 92]. Under the experimental conditions of this study, it is likely that oxidation of Pu(III) to Pu(IV) is nearly complete in 6 M HNO_3, as the distribution ratios of the systems that initially contained Pu(III) or Pu(IV) are approximately the same at this acidity. However, this may not be achieved under process conditions with higher concentrations of metal ions and substantially higher radiation fields. This study, using trace scale Pu(III), confirms that the holding reducing agent, 3% hydroxylamine, will be insufficient for maintaining Pu(III) at this acidity.

Generally, the additional non-incinerable redox agent ferrous sulfamate is used to stabilize Pu(III) in TBP-based separations. Unfortunately, there is no data to compare for using DHHA to extract Pu(III) under similar conditions. Regardless of what is occurring with the Pu(III), 1 M DHHA in Exxsol D60 extracts Pu(IV) well and Pu(VI) moderately well.

2.3.2 Comparison of Np(IV,VI) and Pu(IV, VI) Extraction

The primary goal of this work is to purify Pu from Np in a phosphorus-free extraction system. Figure 2.6 compares the distribution ratios of Np and Pu in the tetravalent and hexavalent oxidation states as a function of acidity. The extraction preferences of DHHA below 3 M acid is Pu(IV) ≈ Np(VI) > Pu(VI) > Np(IV), but the extractabilities of Pu(VI) and Np(IV) reverse at 3 M nitric acid. Overall, at acidities above 4 M nitric acid DHHA extracts both oxidation states of Np and Pu well. Decreasing the acidity to 1 M shows that Np(IV) will be poorly extracted (D_{Np} ~ 0.1) and Pu(VI) also will be stripped (D_{Pu} ~ 0.4), while Np(VI) and Pu(IV) are still extracted with distribution ratios of ~ 5.

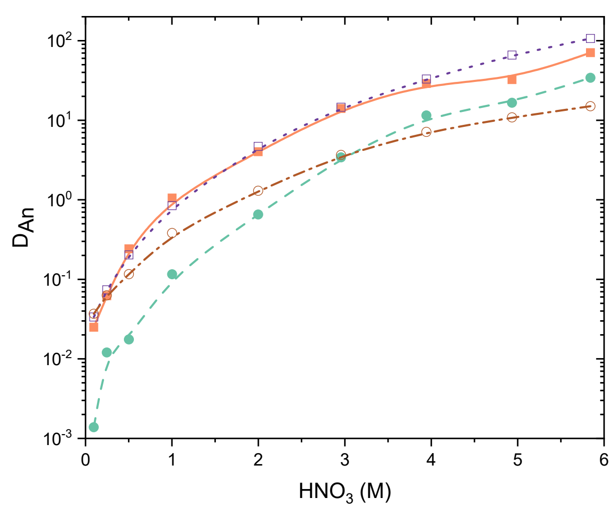


Figure 2.6: Comparison of 1 M DHHA extracting Pu(IV) (open square), Pu(VI) (open circle), Np(IV) (solid circle), and Np(VI) (solid square). The trendlines serve as visual aids.

The metal ions best extracted by DHHA, Pu(IV) and Np(VI), show remarkably similar distribution ratios across the range of acidities studied, and are both efficiently stripped only in dilute nitric acid. Direct separation of these two species by varying the acidity would be difficult. However, either ion, Pu(IV) or Np(VI), could be selectively reduced to poorly extracted Pu(III) or

Np(V) in order to be recovered at intermediate acidities. Above ca. 2.5 M HNO_3 the solutions are sufficiently oxidizing that would be difficult to reduce the metals, as is seen for Pu in Figure 2.3. In this light, the preferred strategy for separating Np(VI) and Pu(IV) extracted by DHHA might be selective reduction of Np(VI) to Np(V) with nitrous acid. This one-electron, reversible reduction is fast, Np(V) is comparatively stable, [93] Pu(IV) is stabilized by nitrous acid, and substantial concentrations of nitrous acid are expected to be rapidly extracted by DHHA into the organic phase.

An additional stripping step would be required if the feed solution were to contain a mixture of the common oxidation states: Np (IV, V, VI) and Pu (III, IV, V, VI). In this case, the tetravalent and hexavalent species of both actinides would be extracted significantly. With nitrous acid reduction, Np(VI) would be efficiently stripped as Np(V) but Np(IV) would remain in the organic phase. Reduction of both Pu(VI) and Pu(IV) to Pu(III) by ferrous sulfamate would still enable Pu stripping. However, this would leave residual Np(IV) in the organic phase. A low acid strip of Np(IV) would then be required to recover that Np and recycle the solvent.

2.3.3 Conclusions

The extractants TBP and DHHA show similar abilities to extract Pu(III), Pu(IV), and Pu(VI) from nitric acid. Pu(III) is poorly extracted by DHHA, however it is difficult to completely stabilize trivalent plutonium using only the incinerable redox agent hydroxylamine unless the aqueous acidity is maintained at 1 M HNO_3 or lower. Although at these acidities, neither Np(IV) nor Np(VI) are strongly extracted. Consequently, other Pu reducing agents that are effective at higher acidity, less efficient Pu stripping at a higher acidity with more stripping stages, or selective reduction of Np(VI) to Np(V) in the presence of extractable Pu(IV) should be considered for the separation of Np and Pu using DHHA.

CHAPTER 3

NEPTUNIUM EXTRACTION BY *N,N*-DIALKYLAMIDES

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Jarrod M. Gogolski, Peter R. Zalupski, Travis S. Grimes, Mark P. Jensen

3.1 Introduction

Irradiated nuclear fuel contains neptunium-237 (^{237}Np, $t_{1/2} = 2.14 \times 10^6$ years), a byproduct of neutron capture reactions, that can either be permanently disposed or used in limited applications, such as the production of plutonium-238 (^{238}Pu, $t_{1/2} = 87.7$ years). Solvent extraction is the principal way to separate ^{237}Np from irradiated nuclear fuel. The extractant tributylphosphate (TBP), adapted from the well-known PUREX process [94], has been used for large scale separation and purification of ^{237}Np from nitric acid solutions since the 1960s [95, 96]. The major extraction equilibria of Np(IV) and Np(VI) nitrates with TBP have been identified [16, 96] and are shown in the following equations with the overhead bar denoting organic phase species.

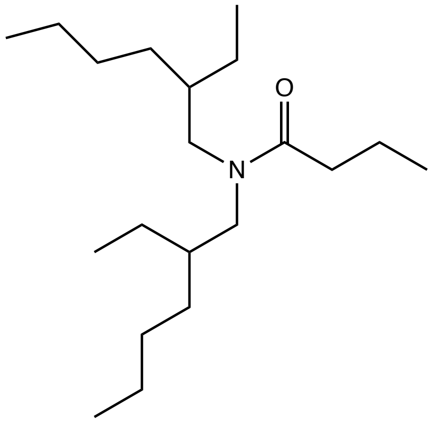
$$\mathrm{NpO_2^{2+} + 2NO_3^- + 2\overline{TBP} \Leftrightarrow \overline{NpO_2(NO_3)_2(TBP)_2}} \tag{3.1}$$

$$\mathrm{Np^{4+} + 4NO_3^- + 2\overline{TBP} \Leftrightarrow \overline{Np(NO_3)_4(TBP)_2}} \tag{3.2}$$

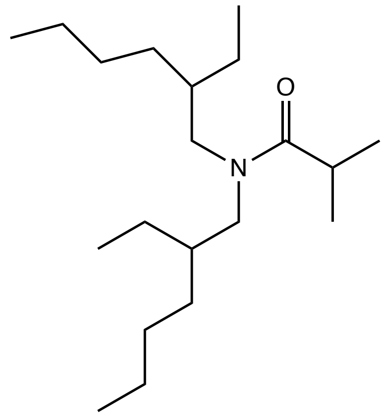
While the chemistry of ^{237}Np in TBP extraction is well-understood [97], TBP can become a burden to the use of the Np or its eventual waste disposal. The radiolytic phosphorus-containing degradation products of TBP interfere with actinide stripping [98], promote the formation of insoluble phosphate compounds [39, 40], and limit the amount of waste that can be loaded into each waste package.

These difficulties with TBP could be circumvented with carefully selected extractants adhering to the CHON principle: extractants that only contain carbon, hydrogen, oxygen and nitrogen are readily incinerated, which reduces the waste burden [42]. *N,N*-Dialkylamides are a promising class of actinide extractants that conform to the CHON principle and have the additional advantages over TBP that their degradation products neither form insoluble compounds nor significantly interfere in extraction equilibria [52, 63, 77]. Many of these monoamides are also highly soluble in aliphatic organic solvents with no observed third phase formation between 0.1 – 6 M HNO_3, even at high metal loadings.

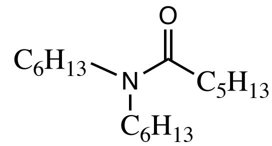
Due to all of these advantages, *N,N*-dialkylamides might be particularly well suited to ^{237}Np separations. Selected monoamides have been pursued as TBP replacements in PUREX-style extractions of U and Pu from nitric acid [38, 41, 47, 48]. However, while the partitioning behavior and organic phase separation of U and Pu have been well studied in monoamide systems [46, 67], the behavior of Np in monoamide extraction systems has received only preliminary attention [37, 38, 70, 99]. Unfortunately, some of the reported studies present contradictory results and are of limited use for understanding the fundamentals of ^{237}Np behavior with monoamide extractants. Furthermore, there is an overall incomplete understanding of the behavior of Np(V) in solvent extraction processes [68, 100]. To bridge this gap and understand if substituting a monoamide for TBP is feasible for practical ^{237}Np separations, the partitioning behavior was studied for nitric acid solutions of the three common solution oxidation states of Np: Np(IV), Np(V), and Np(VI), in contact with solutions of four *N*,*N*-dialkylamides, *N*,*N*-dihexyloctanamide (DHOA), *N*,*N*-dihexylhexanamide (DHHA), *N*,*N*-di(2-ethylhexyl)butanamide (DEHBA), and *N*,*N*-di(2-ethylhexyl)isobutanamide (DEHiBA). The chemical structures of the extractants are shown in Figure 3.1.



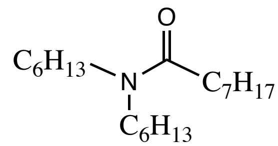
DEHBA



DEHiBA



DHHA



DHOA

Figure 3.1: Monoamide Structures.

These four monoamides: DHOA [37], DHHA [62], DEHBA, and DEHiBA [46], have shown promise for actinide extraction but prior work has mainly focused on the extraction of U(VI) and Pu(IV). With the exception of recent studies of DHOA, these previous works on monoamide extraction behavior did not systematically study Np extraction by itself; however these studies do indicate that tetravalent actinides (An(IV)) ions may not extract as well as hexavalent actinides (An(VI)) ions using these monoamides. The three common valence states of Np in nitric acid solutions are of interest because each valence state displays unique separation chemistry. The lowest valence state, Np(IV), can be oxidized to Np(V) if there is insufficient reducing agent present in an oxygenated solution, depending on the Np concentration and acidity [28]. Pentavalent Np(V) is nearly unextractable by TBP and DEHBA [21, 68]. Neptunium(V) is stable in various aqueous solutions but it can disproportionate or oxidize in nitric acid [16-20], establishing an equilibrium between Np(IV), Np(V), and Np(VI) made possible in nitric acid because of the presence of the oxidizing and reducing agents, nitrate and nitrous acid, respectively [19-21]. Consequently, poor control of the Np oxidation state in solution can interfere with the Np separation. Of particular concern are the occurrence of Np(V) oxidizing to Np(VI) in solutions containing more than 3 M nitric acid and the possibility of Np(IV) forming if an excess of reducing agents is added.

In this work the extraction behavior of ^{237}Np in its common solution oxidation states (+4, +5, +6) was investigated using the abovementioned monoamides to evaluate the potential of dialkylamide extractants for Np separations. Extractant and nitric acid dependencies were measured for each monoamide. The overall behavior of the Np in the HNO_3/dialkylamide extraction system followed the expected trends in order of increasing extraction using the four monoamides: Np(V) << Np(IV) < Np(VI).

3.2 Experimental

3.2.1 Neptunium Solutions

Radiochemically pure $^{237}Np(V)$ in equilibrium with ^{233}Pa was obtained from laboratory stock solutions at the Colorado School of Mines or the Idaho National Laboratory. Solutions of Np(VI) were prepared by oxidizing Np(V) with 0.1 M $KBrO_3$ heated in a 80^{o}C water bath for 30 minutes [38]. Solutions of Np(IV) were produced by reducing Np(V) with 0.1 M ferrous sulfamate [27]. The neptunium oxidation states of the resulting solutions were verified using optical spectroscopy in 1.00 cm cuvettes on a Cary spectrophotometer 6000i [101] or by solvent extraction [85].

3.2.2 Monoamide Synthesis

DHHA, DHOA, DEHBA, and DEHiBA were synthesized under a N_2 atmosphere by adding the corresponding acyl chloride dropwise into a mixture of triethylamine with dihexylamine or di(2-ethylhexyl)amine in dichloromethane in a 0.15: 0.122: 0.131: 0.7 molar ratio cooled in an ice-water bath. After all the acyl chloride was added, the ice-water bath was removed to allow the reaction to proceed at room temperature for one hour. The resulting mixture was diluted with 2-3 times the starting volume of diethyl ether and then vacuum filtered through a Celite plug on a silica gel (technical grade 230-400 mesh particle size) layer to remove the insoluble salts that were formed [43, 82]. The separated salt initially had a salmon color but rinsing with diethyl ether removed the color from the salt. The combined filtrate and diethyl ether rinse was then rotary evaporated to remove the dichloromethane and diethyl ether to yield the product. The resulting monoamides were then purified using vacuum distillation to better than 98% purity, as verified by ^{1}H NMR (JEOL 500 MHz liquid state NMR).

3.2.3 Solvent Extraction

Weighed amounts of monoamide were diluted in Exxsol D-60 to yield monoamide solutions of the desired extractant concentration. Before use, the monoamide solutions were pre-equilibrated twice with the appropriate nitric acid concentrations (0.1 - 6 M), with a 1:2 volume ratio of organic:aqueous phases. The concentrations of the nitric acid solutions were determined by titration with standardized sodium hydroxide to the phenolphthalein endpoint.

Equal volumes (400 μL) of fresh aqueous and pre-equilibrated organic phases were spiked with ^{237}Np solutions. Extractant dependencies were done at the tracer level (<1 x 10^{-5} M ^{237}Np). Nitric acid dependencies were done at a semi-macro concentration (0.001 – 0.006 M ^{237}Np). As a precaution to keep Np(VI) or Np(IV) from being reduced or oxidized in solution, 10 μL of 1 M $KBrO_3$ or 15 μL of 2.2 M of ferrous sulfamate was added to the aqueous phases as appropriate. The two phases were vortexed for one minute and then centrifuged for two minutes at room temperature. After centrifugation, the phases were separated, and aliquots were taken for radiometric determination of the ^{237}Np content. The Np distribution ratio, D, was determined as $D_{Np} = [Np]_{org} / [Np]_{aq} = (\text{cpm Np})_{org} / (\text{cpm Np})_{aq}$.

Two radiometric methods were used to determine the relative ^{237}Np concentrations after separation of the phases. A calibrated HPGe detector was used to measure the γ-spectrum of 300 μL of aqueous or organic phases in Np(V) and Np(VI) systems for one hour. Neptunium-237 has a strong γ emission at 86 keV (11.4 % abundance) [102], however the daughter product of ^{237}Np, ^{233}Pa, also emits a γ-ray at 86 keV with 2.61 % abundance. The count rate of the 86 keV peak was corrected for the contribution from the radioactive decay of ^{233}Pa using the intensity of the 311 keV γ line of ^{233}Pa to determine the amount of ^{233}Pa in solution and then subtract a proportionate activity from the 86 keV peak of ^{237}Np [102, 103]. Np activities were also determined by liquid scintillation counting using a HIDEX 300 SL counter with Ultima Gold AB liquid scintillation cocktail. The distribution ratios determined by γ-spectroscopy and liquid scintillation counting were compared in select cases for accuracy and agreed within the counting error (Figure A.1).

3.3 Results and Discussion

3.3.1 Extraction of Np(VI)

The distribution ratios for Np(VI) as a function of nitric acid concentration are shown in Figure 3.2. The extraction results fall into two distinct sets with the nonbranched monoamides, DHHA and DHOA, demonstrating higher Np(VI) extraction across the range of the nitric acid concentrations studied as compared to the 2-ethylhexyl substituted monoamides, DEHBA and DEHiBA. However, regardless of the branching degree of the monoamide substituents, the Np(VI) distribution ratio of all four extractants show similar acid dependences with an average 1.8 power dependence on the equilibrium aqueous [HNO_3] between 0.25 and 6 M HNO_3.

This data can be compared to the Np(VI) extraction results reported by Kumari et al. for 1.1 M DHOA/*n*-dodecane [37]. The distribution ratios between 4 and 6 M HNO_3 are similar for both studies; however, at lower acidities our observed distribution ratios are significantly lower than reported by Kumari et al. The measured Np(VI) distribution ratios track those reported for the more widely studied hexavalent actinide, UO_2^{2+} [62, 66] as well as those reported for NpO_2^{2+} [37] and PuO_2^{2+} [69]. Separately, DEHiBA was seen to extract U(VI) and Np(VI) similarly, and to extract both more efficiently than Pu(VI) [46]. On the other hand, the distribution ratio curve for extraction of U(VI) by DEHBA, which lacks branching on the acyl carbon, is slightly higher than the Np(VI) distribution ratio curve, indicating that U(VI) is better extracted than Np(VI) with this monoamide [46].

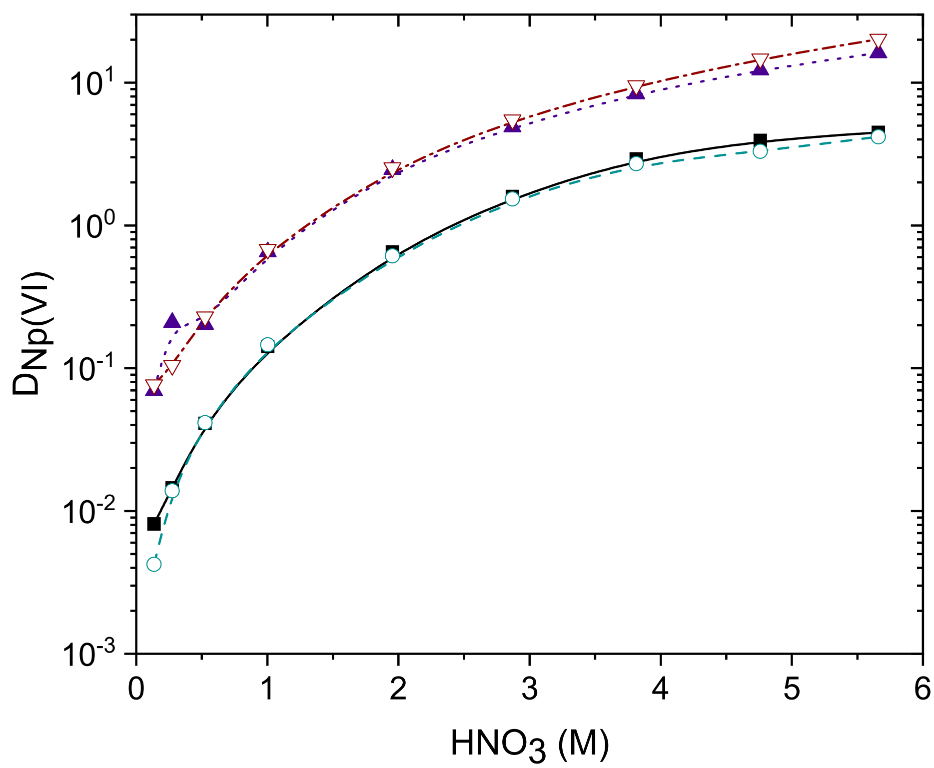


Figure 3.2: Acid dependence of the distribution of 3.67 mM Np(VI) into 1 M monoamide/Exxsol D60. Lines are plotted as a visual guide: DEHiBA (—■—), DEHBA (- - ○- - -), DHOA, (····▲···), and DHHA (- · ▽- ·).

The extractant dependencies of Np(VI) with each of the four monoamides are summarized for aqueous phases containing 4 M and 1 M HNO_3 in Figures 3.3 and 3.4 respectively, which give insight into the stoichiometry of the NpO_2^{2+}-monoamide complexes formed in the extraction.

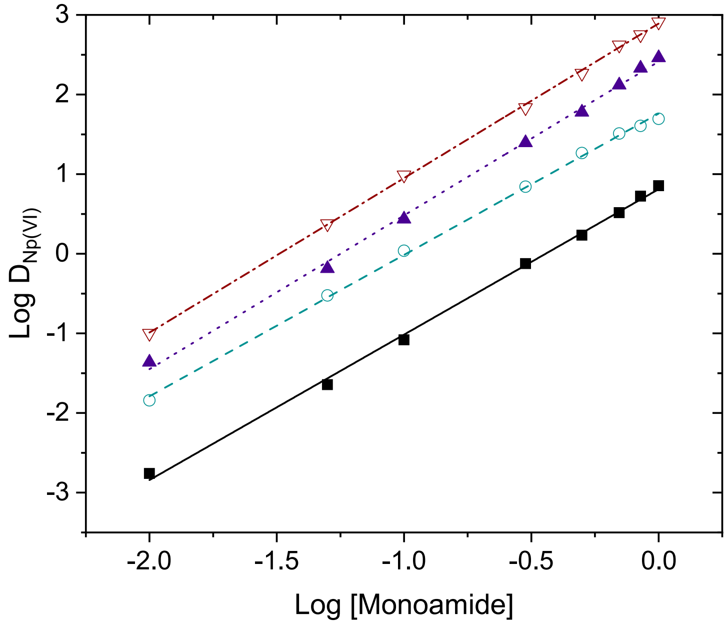


Figure 3.3: Variation of distribution ratios with extractant concentration. Extracting < 0.01 mM Np(VI) from 4 M nitric acid with 0.01 M $KBrO_3$. Data vertically offset for clarity, for DEHBA by log 0.5, for DHOA by log 1.0, and for DHHA by log 1.5 (DEHiBA is not offset). Lines are best linear fit: DEHiBA (—■—), DEHBA (– – ○– –), DHOA, (· · · ▲ · · ·), and DHHA (–·▽–·).

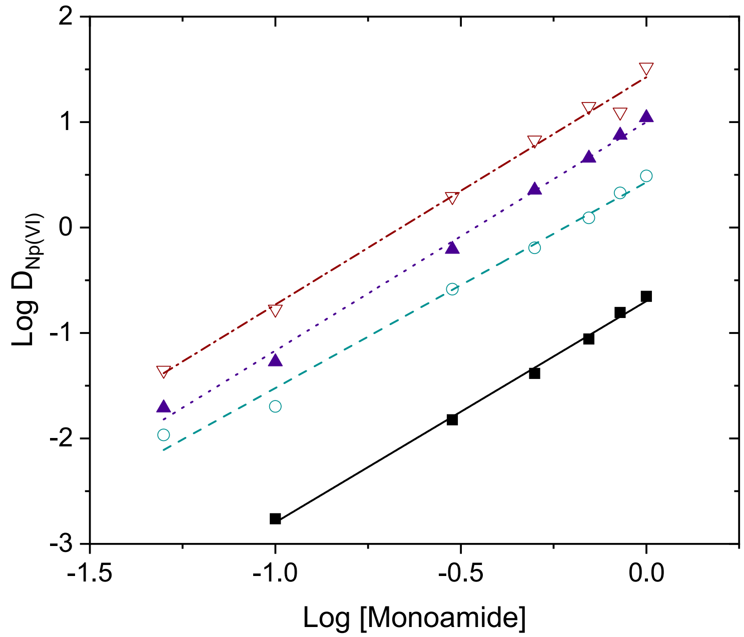


Figure 3.4: Variation of distribution ratios with extractant concentration. Extracting < 0.01 mM Np(VI) from 1 M nitric acid with 0.01 M $KBrO_3$. Lines are best linear fit: DEHiBA (—■—), DEHBA (– – ○– –), DHOA, (· · · ▲ · · ·), and DHHA (–·▽–·).

When the nitric acid concentration exceeds approximately 4 M, anionic complexes of tetra and hexavalent actinides can be extracted by dialkylamides [46, 91]. At lower acidities, however, the partitioning of the common Np(VI) nitrate complexes from aqueous nitric acid into monoamide-containing organic phases can be summarized by two general equilibria [46],

$$\mathrm{NpO_2^{2+}} + n\,\mathrm{NO_3^-} \Leftrightarrow \mathrm{NpO_2(NO_3)_n^{2-n}} \tag{3.3}$$

and

$$\mathrm{NpO_2^{2+}} + 2\mathrm{NO_3^-} + \overline{\mathrm{Monoamide}} \Leftrightarrow \overline{\mathrm{NpO_2(NO_3)_2(Monoamide)}_m} \tag{3.4}$$

characterized by the equilibrium constants

$$\beta_\mathrm{n} = \frac{[\mathrm{NpO_2(NO_3)}_n^{2-n}]}{[\mathrm{NpO_2^{2+}}][\mathrm{NO_3^-}]^n} \tag{3.5}$$

and

$$\mathrm{K_{ex}} = \frac{\left[\overline{\mathrm{NpO_2(NO_3)_2(Monoamide)}_m}\right]}{\left[\mathrm{NpO_2^{2+}}\right][\mathrm{NO_3^-}]^2\left[\overline{\mathrm{Monoamide}}\right]^m}\,. \tag{3.6}$$

If the monoamide concentration is much larger than the neptunium concentration, Equation 3.5 and Equation 3.6 can be combined with the definition of the distribution ratio,

$$\mathrm{D} = \frac{[\mathrm{Np}]_\mathrm{org}}{[\mathrm{Np}]_\mathrm{aq}} = \frac{\left[\overline{\mathrm{NpO_2(NO_3)_2(Monoamide)_m}}\right]}{[\mathrm{Np}]_\mathrm{aq}} = \frac{\left[\overline{\mathrm{NpO_2(NO_3)_2(Monoamide)_m}}\right]}{\left[\mathrm{NpO_2^{2+}}\right]\left(\sum_{\mathrm{i=0}}^{\mathrm{n_{max}}} \beta_\mathrm{i}[\mathrm{NO_3^-}]^\mathrm{i}\right)} \tag{3.7}$$

to yield a linear relationship between the logarithms of the distribution ratio and the monoamide concentration at constant acid concentrations [46, 104],

$$\log \mathrm{D} = m \log\left[\overline{\mathrm{Monoamide}}\right]_{total} + (\log \mathrm{K_{ex}} + 2 \log[\mathrm{NO_3^-}] - \log \textstyle\sum_{i=0}^{\mathrm{n_{max}}} \beta_i [\mathrm{NO_3^-}]^i), \tag{3.8}$$

where n_{max} is the maximum number of NO_3^- coordinated to Np in the aqueous phase and $\beta_0 = 1$. When $[Np]_{total} << [Monoamide]_{total}$ and changes in the organic phase (e.g. variations in the average stoichiometry of HNO_3-monoamide adducts or the activity coefficients of the organic phase species) can be neglected, the slope of the logarithmic dependence between the distribution ratio and the monoamide concentration, *m*, corresponds to the average monoamide:Np stoichiometry of the extracted complexes in the organic phase.

Slope analysis of the experimental data in Figures 3.3 and 3.4 are summarized in Table 3.1. The average monoamide:Np ratios for both acidities indicate that extraction of $NpO_2(NO_3)_2$ requires two monoamide ligands. Furthermore, the average stoichiometry of the extracted NpO_2^{2+}-monoamide complexes is similar for all of the monoamides studied regardless of the intrinsic affinity of the monoamides for Np(VI) extraction or the degree of branching on the alkyl substituents. In this light, the principal NpO_2^{2+}-monoamide complexes formed in the organic phase should have structures similar to the crystalline bis(*N,N*-dibutylbutanamide)uranyl(VI)nitrate complex reported by Acher et al. [72] with two bidentate nitrate anions and two extractant molecules coordinated through the amide oxygen atoms present in the equatorial plane of the NpO_2^{2+} cation.

3.3.2 Extraction of Np(IV)

Figure 3.5 shows the distribution ratios for Np(IV) as a function of nitric acid concentration. In this case, the distribution ratios for all of the monoamides decrease compared to Np(VI) extraction (Figure 3.2). This effect is observed for plutonium as well, and efficient binding of the metal ion, Np^{4+}, to the monoamides can be hindered by the energetic and steric requirements of the four nitrate anions required to balance the charge and extract the Np^{4+} cation [49]. As expected from Pu(IV) extraction, DEHiBA is a much weaker extractant for Np(IV) than DHHA, DHOA, and DEHBA, which all show similar Np distribution ratios. The similarity in the distribution ratios for DHHA, DHOA, and DEHBA indicate that branching of the 2-ethylhexyl groups on the nitrogen, does not severely affect a monoamide's extraction potential for Np(IV). Rather, poor extraction of Np(IV) is caused by branching on the acyl side of the extractant, such as the isobutyl group in DEHiBA.

The trend for the non-branched extractants DHOA and DHHA extraction of Np(IV) follows the same trend as seen by Kumari et al. with 1.1 M DHOA, even at the lower the acidities. Comparison to other studies with these nonbranched monoamides also suggest the common tetravalent actinide, Pu(IV), is extracted better than Np(IV) [37, 62]. Alternately, extraction of Np(IV) and Pu(IV) by the partly branched monoamide DEHBA show similar trends with a slightly higher preference for Pu(IV) [46]. The fully branched monoamide, DEHiBA, extracts the tetravalent actinides Np and Pu poorly and most likely will not efficiently extract other tetravalent actinides.

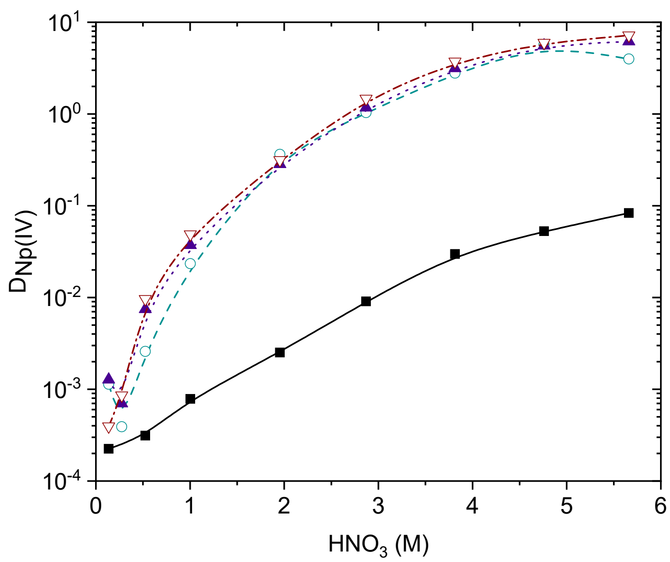


Figure 3.5: Acid dependence of the distribution of 1 mM Np(IV) into 1 M monoamide/Exxsol D60. DEHiBA (—■—), DEHBA (– – ○ – –), DHOA, (· · · ▲ · · ·), and DHHA (–·▽–·). Lines are plotted as a visual guide.

The number of monoamide molecules needed to extract Np(IV) (Figure 3.6 and Table 3.1) is higher than for Np(VI). This indicates that more monoamides are required to extract the Np^{4+} cations than NpO_2^{2+} neptunyl cation (m = 2 – 3 for Np(IV) instead of m = 2 for Np(VI)). The general equilibrium relationships for Np(IV)-monoamide complexes are shown in Equations 3.9 and 3.10. The non-integral values of m reported in Table 3.1 for Np(IV) extraction may arise from the simultaneous presence of multiple equilibria with different m values, for example a 50:50 mixture of reactions with m = 2 and m = 3 would give an observed extractant dependence of 2.5.

$$\mathrm{Np^{4+}} + 4\mathrm{NO_3^-} + m\,\overline{\mathrm{Monoamide}} \Leftrightarrow \overline{\mathrm{Np(NO_3)_4(Monoamide)}_m} \tag{3.9}$$

$$\mathrm{K_{ex}} = \frac{\left[\overline{\mathrm{Np(NO_3)_4(Monoamide)}_m}\right]}{[\mathrm{Np^{4+}}][\mathrm{NO_3^-}]^4\left[\overline{\mathrm{Monoamide}}\right]^m} \tag{3.10}$$

The increase in the average number of monoamides required to extract Np(IV) compared to Np(VI) has been hypothesized to indicate that the additional monoamide is binding in the outer coordination sphere of the Np-nitrate complex [37, 46]. Recent EXAFS studies of the Pu(IV) complexes extracted by DEHBA and DEHiBA revealed differences in the complexes formed with these two extractants [72]. The extractant DEHBA was observed to form the $Pu(NO_3)_4(DEHBA)_2$ complex, as expected from Equation 3.9 with m = 2, which is fully consistent with our slope analysis of the Np(IV) distribution ratio data (Table 3.1). Since it is likely that the Pu(IV)-monoamide and Np(IV)-monoamide structures are similar, Np(IV) would bind with four bidentate nitrate groups and two DEHBA in this complex. This is different than An(VI) extraction which requires coextraction of only two bidentate nitrates and coordination of two DEHBA to give a hexagonal bipyramidal structure [72]. It also contrasts the behavior of DEHiBA.

Table 3.1: Slope analysis of average *N,N*-dialkylamide:Np stoichiometry for Np(VI) and Np(IV) extraction from nitric acid.

	Slope: m, Dialkylamide:Np ratio			Intercept: $\log K_{ex} + n \log[NO_3^-] - \log \sum_{i=0}^{n_{max}} \beta_i [NO_3^-]^i$		
Dialkylamide	Np(VI)/4 M HNO_3	Np(VI)/1 M HNO_3	Np(IV)/4 M HNO_3	Np(VI)/4 M HNO_3	Np(VI)/1 M HNO_3	Np(IV)/4 M HNO_3
DEHiBA	1.82 ± 0.03	2.10 ± 0.06	2.7 ± 0.4	0.81 ± 0.03	-0.70 ± 0.03	-1.4 ± 0.1
DEHBA	1.78 ± 0.03	1.95 ± 0.09	2.1 ± 0.1	1.26 ± 0.02	-0.07 ± 0.06	0.38 ± 0.05
DHOA	1.93 ± 0.04	2.17 ± 0.07	2.42 ± 0.04	1.41 ± 0.03	0.00 ± 0.04	0.87 ± 0.02
DHHA	1.94 ± 0.02	2.16 ± 0.08	2.45 ± 0.03	1.39 ± 0.02	-0.07 ± 0.05	1.03 ± 0.02

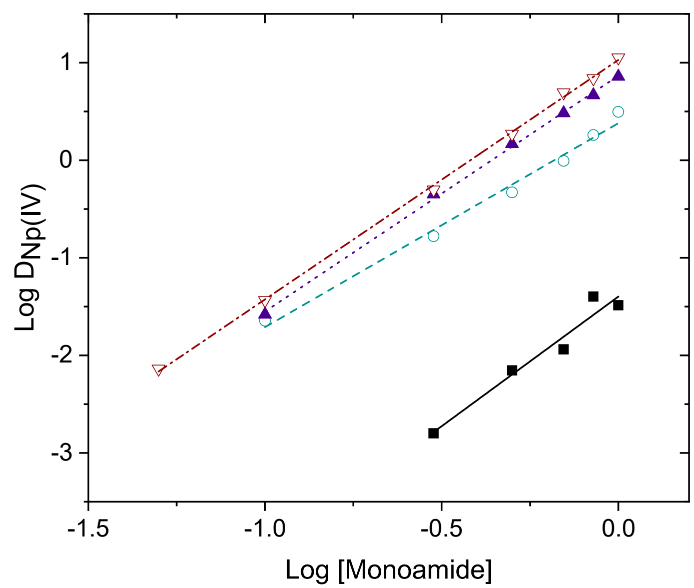


Figure 3.6: Variation of distribution ratios with extractant concentration. Extracting < 0.01 mM Np(IV) from 4 M nitric acid with 0.1 M Fe(II). Lines are best linear fit: DEHiBA (—■—), DEHBA (– – ○ – –), DHOA, (· · · ▲ · · ·), and DHHA (– · ▽ – ·).

The extractant DEHiBA appears to extract Pu(IV) by at least one other equilibrium [72] generically represented as,

$$\mathrm{Pu}^{4+} + 4\mathrm{NO}_3^- + n\mathrm{HNO}_3 + \overline{m\mathrm{Monoamide}} \Leftrightarrow \overline{\mathrm{Pu(NO_3)_4(Monoamide)}_m \cdot n\mathrm{HNO}_3}, \qquad (3.11)$$

forming one or more anionic plutonium nitrato complexes containing five or six inner sphere coordinated nitrates that are charge balanced by the Pu(IV) cation and coextracted H^+ ions. The coextracted H^+ in Eq. 11 from hydrogen bonds between coordinated nitrates and molecules of DEHiBA in the outer coordination sphere. The low distribution ratios for Np(IV) with DEHiBA and the high value of *m* derived from the DEHiBA extractant dependence experiments (2.7 ± 0.4) are consistent with a similar change in the Np coordination environment and some degree of outer sphere interaction with DEHiBA that allows participation of more than two DEHiBA molecules in the extracted complex.

While the inherent properties of the Np(IV) complex coupled with the additional energy input required to transfer two additional nitrate anions into the organic phase are likely the main reasons for the less efficient Np(IV) extraction, it is worthwhile to briefly consider the stability of Np(IV) in solution and other factors that could depress Np(IV) extraction for all monoamides, such as aqueous complexation of Np. Oxidation of tetravalent Np(IV) can occur at higher acidities [105]. To investigate this possibility, the stability of Np(IV) in 4 M HNO_3 was checked spectroscopically after 12 hours, confirming that less than 0.5 % Np(IV) oxidized to Np(V) (Figure A.2). Therefore, over the course of a set of our experiments, a negligible amount of Np would have been oxidized to its unextractable state Np(V).

Another explanation for the lower Np(IV) distribution for all the monoamide studied is the presence of a Np(IV) complexant that could interfere with the Np(IV) extraction into the organic phase. The principal possibilities for forming aqueous complexes that interfere with Np(IV) extraction are hydrolysis of Np or binding to the reducing agent or a monoamide degradation product. At millimolar concentrations, Np(IV) hydrolysis at pH ≈ 1.5 – 3 can generate Np colloids [106] that are not extracted by the monoamides. While this would explain reduced Np(IV) extraction at the lowest acidities, appreciable amounts of hydrolysis will not occur at molar concentrations of nitric acid. Alternatively, the reducing agent used, ferrous sulfamate, can decompose at high acidities to form bisulfate or sulfate ions that would form complexes with Np(IV) [27]. However, there is no indication of significant sulfamate or sulfate complexation at millimolar concentrations of reductant in the optical spectra of our Np(IV) solutions (Figure A.3) and increasing the concentration of reductant to 0.08 M did not cause a decrease in the Np distribution ratio. An aqueous soluble monoamide radiolysis product [77] could also complex Np(IV) and interfere with Np(IV) extraction. While the 0.001 – 0.006 M concentrations of Np used for this study are higher than previous tracer scale studies, these Np concentrations are still low compared to industrial-scale process conditions and the maximum dose done to the monoamides from radiolysis would be 0.025 Gy. Therefore, generations of radiolytic degradation products would be unobservable in our studies [63, 75].

3.3.3 Extraction of Np(V)

Previous studies of Np extraction by monoamides generally do not include systematic studies of Np(V) extraction because isolated experiments suggest NpO_2^+ is not readily extracted from nitric acid solutions by monoamides [37, 68]. The extraction of 6 mM Np(V) from HNO_3 solutions using all four monoamides is quantified in Figure 3.7. The Np distribution ratio never exceeds one, regardless of the acidity or the monoamide used for extraction, however the amount of Np extracted from nitric acid does steadily increase until ca. 2 M HNO_3, leveling off at higher acidities. Similar behavior also has been observed for TBP extraction of Np(V) with the onset of noticeable extraction occurring at the same nitric acid concentration [86].

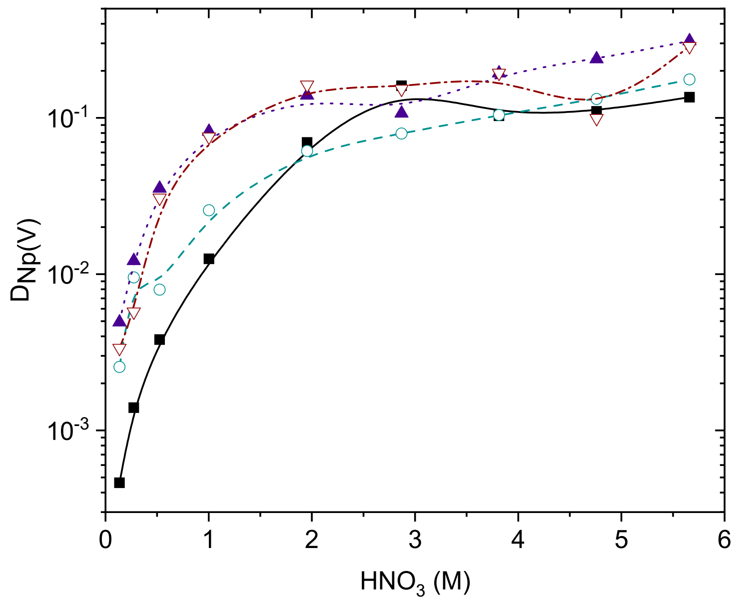


Figure 3.7: Acid dependence of the distribution of 6 mM Np(V) into 1 M monoamide/Exxsol D60. Lines are plotted as a visual guide: DEHiBA (—■—), DEHBA (– – ○– –), DHOA, (· · · ▲· · ·), and DHHA (– · ▽– ·).

In that case, the Np extraction was attributed to oxidation of a fraction of the poorly extractable Np(V) to readily extracted Np(VI) by nitrate ions or low concentrations of nitrous acid [20] at higher nitric acid concentrations. This is demonstrated experimentally by observing the oxidation of Np(V) in aqueous 4 M HNO_3 that had not been contacted with an organic phase. Over 10 hours at room temperature 43% of Np(V) originally present in the solution was oxidized to Np(VI) (Figure 3.8). In contrast, Np(V) was neither oxidized nor reduced over an 18 hour period in 0.1 M HNO_3 (Figure A.4). Even though it is unlikely that the Np(V) is being extracted in significant quantities and that the extracted Np has mainly been oxidized to Np(VI), this behavior can have a significant impact on the amount of Np extracted from HNO_3 solutions containing more than 2 M acid and gram quantities of Np.

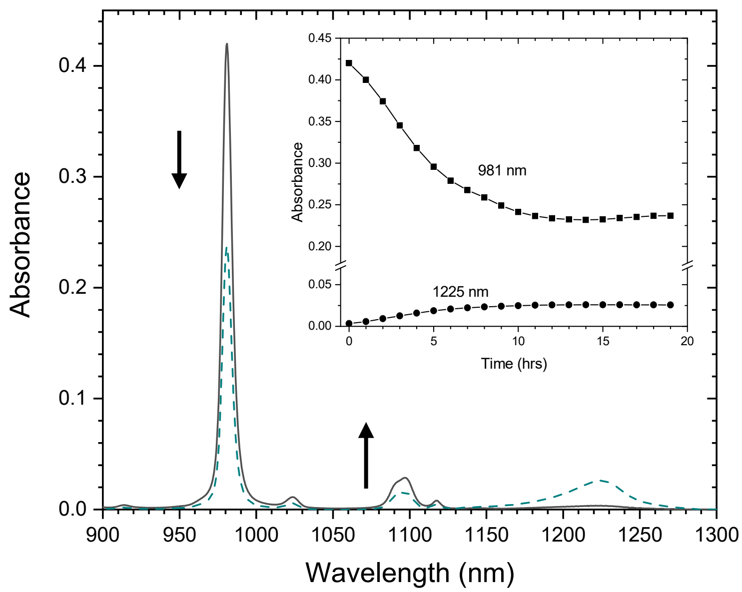


Figure 3.8: Oxidation state changes of Np in 4 M nitric acid over 19 hours at 22 °C. The solution initially contained 1.5 mM Np(V) and no Np(IV). The Np(VI) peak at 1225 nm increases from 0% Np(VI) initially to 43 ± 2 % at 12 hours. Black solid line is the initial Np(V) solution. Dashed dark cyan line is the solution after 19 hours. Inset: change in absorbance at peak maxima.

3.3.4 Neptunium Extraction Potential of Monoamides

The nonbranched monoamides (DHOA and DHHA) offer more flexibility for partitioning of millimolar concentrations of Np(IV) and Np(VI) compared to the branched monoamides (DEHBA and DEHiBA). The results of our extraction studies suggest that the nonbranched monoamides DHHA and DHOA could be used to extract Np(VI) and Np(IV) from solutions containing at least 3 M HNO_3. Since the Np(VI) and Np(IV) distribution ratios drop below 1 for 1 M solutions of monoamides at acidities less than 1 M HNO_3, the nonbranched monoamides are also readily stripped.

Even though DEHBA does not extract Np(VI) as well as the nonbranched monoamides, DEHBA is a better extractant than DEHiBA for Np(IV). The presence of alkyl group branching on the carbonyl group of the branched monoamides sterically hinders the formation of the AnO_2^{2+}-monoamide complexes for U [46, 47] and Np [49], however the effect is much greater for tetravalent actinides. The access of the metal to the carbonyl binding site can be further obstructed if there is a branched carbon chain present near the carbonyl and the amide [72]. Alkyl group branching on both the nitrogen and the carbonyl, as is present in DEHiBA, strongly reduces overall extractability. Figure 3.2 shows that the distribution ratio for Np(VI) using DEHiBA is less than 10 at best, which indicates that DEHiBA would not work well for Np extraction, as was seen for U(VI) extraction by Musikas et al. [47]. The extremely poor extraction of Np(IV) by DEHiBA, is underscored by comparison of the data in Figures 3.5 and 3.7, which indicate that the ability of DEHiBA to extract Np(IV) is actually similar to its ability to extract Np from solutions of Np(V). However, it has been suggested to use a mixture of DEHBA and DEHiBA to partition the actinides, Pu(IV) and U(VI) [46]. This is possible because as the nitric acid concentration decreases, the Pu(IV) will readily strip from DEHiBA whereas U(VI) would stay in the organic phase because of the presence of DEHBA.

Overall, our results suggest it can be advantageous to choose a monoamide without steric hindrance near the carbonyl group for Np binding, such as a nonbranched straight chain monoamide. However, the options for a different dialkylamides are limited because increasing the number of carbon atoms increases a monoamide's propensity to form a third phase in aliphatic diluents [50]. One possibility is *N,N*-dihexyldecanamide (DHDA) [66, 99], which has slightly longer carbon chains. DHDA may show better selectivity for Np(VI) over Np(IV) than DHOA or DHHA [70]. However, DHDA will likely be useful only in limited applications because DHDA has a significantly higher chance of forming a third phase than either DHOA or DHHA with high metal loading and acidities less than 5 M HNO_3 [107].

3.4 Conclusions

The nonbranched monoamides DHHA and DHOA are promising reagents for extraction and subsequent stripping of Np(IV) and Np(VI), as their extraction potential is similar to TBP, shown in Table 3.2. However, the nonbranched monoamides are more likely both to generate problematic radiolysis products and to form third phases than the butanamides DEHiBA and DEHBA. The branched monoamides studied, DEHiBA and DEHBA, do not extract Np as well as the nonbranched monoamides as reemphasized in Table 3.2. DEHiBA does not extract Np(IV) appreciably, most likely due to the additional steric hinderance of its isobutyl group, and both DEHiBA and DEHBA show reduced Np(VI) extraction compared to the nonbranched dialkylamides studied. Np(V) is not extracted well by any of the amides studied regardless of nitric acid concentration. However, at higher nitric acid concentrations some of the Np(V) is oxidized to Np(VI) which can then be extracted by the monoamides, resulting in distribution ratios that are higher than those observed for Np(IV) with DEHiBA. To separate Np from other actinides coextracted with dialkylamides, the Np could be extracted as Np(IV) or Np(VI) by DHHA or DHOA and stripped as Np(V) by selective manipulation of the oxidation states, held in the unextractable pentavalent oxidation state while other actinides are extracted by DHHA or DHOA, or reduced to Np(IV) while hexavalent actinides are extracted by DEHiBA.

Table 3.2: Comparison of distribution ratios of Np(IV), Np(V), and Np(VI) at 0.1 and 4 M HNO_3 by 1 M *N,N*-dialkylamide in Exxsol D-60 or for 30 % TBP/n-alkane.

Extractant	Np(IV)	Np(V)	Np(VI)	Np(IV)	Np(V)	Np(VI)
	0.1 M HNO_3			4 M HNO_3		
DEHiBA	2.2×10^{-4}	4.6×10^{-4}	8.1×10^{-3}	0.03	0.10	2.9
DEHBA	1.1×10^{-3}	2.6×10^{-3}	4.8×10^{-3}	2.8	0.10	2.9
DHOA	1.3×10^{-3}	4.7×10^{-3}	0.22	3.2	0.19	8.2
DHHA	3.9×10^{-4}	3.3×10^{-3}	0.077	3.7	0.19	9.5
TBP [97]				4.9	0.02	17

CHAPTER 4

USING *N*,N-DIALKYLAMIDES FOR NEPTUNIUM PURIFICATION FROM OTHER ACTNIDES FOR SPACE APPLICATIONS

The following chapter was modified from its submission to Separation Science and Technology

Jarrod M. Gogolski, Peter Zalupski, Travis Grimes, and Mark P. Jensen

4.1 Introduction

As traditional nuclear power reactors fission uranium-235 (^{235}U) with thermal neutrons to produce energy, other nuclear reactions occur that form a mixture of actinides (An), including neptunium. While the applications for neptunium are limited, long-lived neptunium-237 (^{237}Np, $t_{1/2}$ = 2.14 x 10^6 years) is of particular interest as a source material for plutonium-238 (^{238}Pu) to use in radioisotope thermoelectric generators (RTGs). The ^{237}Np is initially purified from existing neptunium stockpiles that contain trace contaminants of thorium and plutonium using di-(2-ethylhexyl)phosphoric acid (HDEHP). Neutron irradiation of the $^{237}NpO_2$ targets transmutes the ^{237}Np to plutonium-238 (^{238}Pu). Unfortunately, the transmutation process results in conversion of less than 20 % of the ^{237}Np to ^{238}Pu and also creates fission products [12].

Solvent extraction using the extractant tributylphosphate (TBP) is the current method to separate the plutonium and neptunium and to also purify them from fission products. However, chemical or radiolytic degradation of both TBP and HDEHP creates reactive organic and inorganic phosphates, which are not easily removed and contaminate both the ^{238}Pu product and the recycled ^{237}Np [12]. A possible solution for this issue is to switch from an organophosphorus extractant to an incinerable extractant. Extractants that are solely composed of the elements carbon, hydrogen, oxygen, and nitrogen (CHON) can be fully incinerated. Various nitrogen containing compounds are being considered as potential alternatives to TBP in nuclear fuel reprocessing for their resistance to radiolysis and hydrolysis [75, 94]. However, implementation of a new extractant for

^{238}Pu production requires an understanding of its extraction potential for targeted elements and impurities.

This study considers *N,N*-dialkylamides for neptunium purification and recycle from actinides relevant in production of ^{238}Pu. Siddall pioneered the use of *N,N*-dialkylamides, also known as monoamides, as substitutes for TBP in the extraction of tetravalent and hexavalent actinides in traditional reprocessing of U(VI) and Pu(IV) [41]. Since that time research on *N,N*-dialkylamide extraction has expanded to include other elements, mainly actinides [38, 57, 73, 88]. While neptunium extraction by monoamides has received recent attention [70, 71, 78], important aspects of the extraction behavior of Np in its most important oxidation states (IV, V, VI) relative to other actinides (Th, Pa, U, Pu, Am) remain unexplored.

The complexity of actinide chemistry presents some challenges for the efficient purification of neptunium from these actinides. While many actinides are quite stable in a particular oxidation state in solution, such as Th(IV), Pa(V), U(VI), or Am(III), the primary oxidation state of others can vary widely depending on the solution conditions, particularly Np(IV, V, VI), and Pu(III, IV, V, VI). This complex redox chemistry of neptunium [25] is oftentimes singled out as being burdensome for an efficient separation from plutonium [97, 108]. Efficient separation of Np and Pu from the other actinides therefore requires selective manipulation of neptunium's or plutonium's oxidation state and an understanding their relative extraction ability using a specific extractant (e.g. monoamides). Accordingly, the ability to extract an actinide based on its oxidation state has been explored with several structural variations of *N,N*-dialkylamides [42, 54, 70, 72, 78].

The carbon length and branching of the dialkyl or acyl sides of *N,N*-dialkylamides (indicated in Figure A.5) have been shown to impact the extraction ability of monoamides. Having a nonbranched or branched configuration or otherwise adjusting the structure of a monoamide can increase its extraction potential for an individual metal ion in a specific oxidation state. For instance, monoamides can be used to separate different actinides in the same oxidation state (e.g. Pu(IV) > Np(IV) > Th(IV)) or to preferentially extract an individual actinide based off its oxidation state (e.g. Np(VI) > Np(IV) >> Np(V)) [41, 42, 46, 52, 54, 56, 70, 72, 73, 78, 109]. This study investigates the capability of four *N,N*-dialkylamides with varying structures (Figure A.5) *N,N*-dihexyloctanamide (DHOA) [37, 70], *N,N*-dihexylhexanamide (DHHA) [78], *N,N*-di(2-ethylhexyl)butanamide (DEHBA), and *N,N*-di(2-ethylhexyl)isobutanamide (DEHiBA) [68, 69, 71], for their ability to efficiently separate neptunium from other actinides, with particular emphasis on the Np/Pu and Np/Th separations that are essential for RTG production.

While recent research has focused on the possible complexes of Th(IV), U(VI), and Pu(IV) with nitrate being extracted by *N,N*-dialkylamides [72, 110], research into monoamide-Np complexes have mostly focused on monoamide:Np stoichiometric ratios without an analysis of possible monoamide:nitrate:Np complexes [69-71, 78]. This presents an opportunity to determine if Np(IV) and Np(VI) form anionic complexes with a monoamide at higher acidities (in addition to the neutral complexes), which have been observed for Pu(IV), Pu(VI), and U(VI) [72].

The other facet of this study presents possible coextraction and separation procedures for Np separation from Th and from Pu. A branched monoamide, DEHBA or DEHiBA, is ideal for Np(VI) purification from Th(IV) using multiple scrub steps. While a nonbranched monoamide, DHHA or DHOA, extracts Pu(IV) and Np(VI) quite well, the problematic redox chemistry of Np and Pu complicates effective separation. The proposed separation scheme using selective reducing agents has significant drawbacks when applied at trace metal concentrations.

4.2 Materials and Methods

4.2.1 Actinide Solutions

Neptunium-237 was taken from laboratory stocks and used without further purification. Plutonium-239 in ca. 2 M HNO_3 was prepared by dissolving $^{239}PuO_2$ powder in a solution of 0.2 M silver nitrate and 0.5 M potassium persulfate in 3 M HNO_3 [111]. The resulting ionic Pu(VI) was then recovered by extraction into 0.15 M trioctylphosphine oxide (TOPO) in dodecane. Any residual polymeric Pu, unextractable by TOPO, was left in the aqueous phase [112]. The plutonium was stripped from the TOPO, acidified to 7.5 M HNO_3 and subsequently purified by anion exchange chromatography with AG 1-X4 Resin [83]. After metathesizing the eluted matrix from hydrochloric acid to ca. 2 M nitric acid, the plutonium was adjusted to its desired oxidation state.

The Pu(III) solution was made by reducing the plutonium with 0.43 M hydroxylamine hydrochloride in 1 M HNO_3 [34]. Pu(IV) was made by oxidizing the Pu(III) solution with 0.03 M sodium nitrite ($NaNO_2$) [84]. Pu(VI) was prepared by oxidation with potassium bromate ($KBrO_3$) at 80 °C. The oxidation states of the Np solutions were adjusted as previously described [78]. The oxidation states of the resulting plutonium and neptunium solutions were separately verified by solvent extraction [85]. Optical spectroscopy was used for analysis of semi-macro Np(IV) and Np(VI) in the aqueous and organic phases. Samples were placed in 1.00 cm cuvettes and scanned using a Cary 6000i or 5E spectrophotometers.

Uranium-233 (^{233}U) in 1 M HNO_3 was purified by extraction chromatography with a UTEVA column [83]. Radiochemically pure americium-241 (^{241}Am) in 2 M HNO_3 was used from laboratory stocks. Thorium-232 (^{232}Th) was prepared by dissolving $^{232}Th(NO_3)_4$ hydrate (Strem Chemicals, 99.8% ^{232}Th) in 1 M HNO_3. Trace level quantities were used in the extraction experiments for all the actinides except thorium. The ^{232}Th concentration ranged from 1 x 10^{-3} (for nonbranched monoamide extraction) to 1 x 10^{-2} M (for branched monoamide extraction).

4.2.2 Actinide Solvent Extraction

The monoamides DHOA, DHHA, DEHBA, and DEHiBA were prepared and purified as previously described [78]. Organic phases were prepared by dissolving weighed amounts of monoamide in Exxsol D60. Equal volumes of pre-equilibrated organic and fresh aqueous phases were mixed with a spike from the actinide stock solutions. The following redox agents were used to stabilize the ^{239}Pu and ^{237}Np oxidation states during solvent extraction: 0.43 M hydroxylamine hydrochloride for Pu(III), 0.005 M ammonium metavanadate (NH_4VO_3) and 0.02 M $NaNO_2$ for Pu(IV), 0.1 M ferrous sulfamate for Np(IV), and 0.01 M $KBrO_3$ for Pu(VI) and Np(VI). The organic and aqueous phases were vortexed for two minutes and centrifuged. Afterwards, the phases were separated and sampled for radiometric analysis. Aliquots of each phase were mixed with Ultima Gold AB liquid scintillation cocktail and assayed for radioactivity by liquid scintillation counting (LSC) using a HIDEX 300 SL with alpha-beta discrimination. The distribution ratio of each actinide, D_{An}, was determined as ratio of the actinide concentration in the organic phase to that in the aqueous phase, $D_{An} = [An]_{org} / [An]_{aq}$ = (counts per minute $An)_{org}$ / (counts per minute $An)_{aq}$.

4.2.3 Thorium Analysis

Due to the exceptionally low specific activity of ^{232}Th, the Th concentration was measured spectrophotometrically. After the phases were separated and sampled for counting as described above, the thorium-containing organic phases were stripped with two volumes of fresh 0.01 M HNO_3. Aliquots of these solutions or the aqueous phases from the initial extractions were diluted and mixed with Arsenazo III for spectroscopic determination of the Th concentration at 659 nm

[113]. The spectroscopic extinction coefficients of Th(IV) followed Beer's Law between 6 x 10^{-4} and 6 x 10^{-3} M Th and displayed absorbances insensitive to the final nitric acid concentration used in the cuvettes, 2 – 3 M HNO_3.

4.2.4 ^{232}Th/^{237}Np Separation

Coextraction and separation of ^{232}Th and ^{237}Np was studied over the course of three stages. The first stage began with equal volumes of pre-equilibrated organic phase and an aqueous phase containing the desired concentration of nitric acid, $Th(NO_3)_4$, and $NpO_2(NO_3)_2$. A portion of the loaded organic phase from the initial solvent extraction stage was mixed with an equal volume of fresh aqueous phase at the previous acidity for Stage 2 or scrub stage. Stage 3, the strip stage, consisted of an equal mixture of the organic phase from Stage 2 and fresh 2 M HNO_3. The thorium content of the phases was analyzed by spectrophotometry as described above using oxalic acid to mask Np(VI) [113]. The low specific activity of ^{232}Th allowed for analysis of ^{237}Np by LSC. To avoid color quenching effects from Arsenazo III in the radiometric analysis, separate aliquots were used for LSC and spectroscopic analysis.

4.2.5 ^{239}Pu/^{237}Np Separation

Coextraction and separation of ^{237}Np and ^{239}Pu was studied over the course of five stages. The first stage had equal volumes of pre-equilibrated organic phase and a fresh aqueous phase containing nitric acid and 0.005 NH_4VO_3, spiked with Np(VI) and Pu(III). Complete oxidation of Pu(III) to Pu(IV) under these conditions was confirmed by solvent extraction [85]. Stage 2, the scrub stage, included a portion of organic phase from Stage 1 mixed with an equal volume of fresh nitric acid with no redox agent present. A portion of Stage 2's organic phase was mixed with an equal volume of 100 mM $NaNO_2$ in 1 M HNO_3 for Stage 3. The $NaNO_2$ forms nitrous acid (HNO_2), a reducing agent for Np(VI), in acidic solutions. Stage 4 rinsed a portion of the organic phase from

Stage 3 with an equal volume of 1 M HNO_3. The final stage, Stage 5, used an aqueous phase of 0.275 M hydroxylamine hydrochloride in 0.25 M HNO_3. The ^{237}Np concentration of each phase was determined by gamma counting using a Canberra QCW2523 to measure an aliquot of aqueous or organic phases for 45 minutes. (Samples with little to any ^{237}Np were counted overnight or for several days.) The counts of ^{237}Np at 86 keV were corrected from the ^{233}Pa counts using the method previously described [78]. The alpha activity from ^{237}Np, calculated from the ^{237}Np concentration determined by gamma counting, was then subtracted from the total alpha activity obtained by LSC to determine the ^{239}Pu activity.

4.3 Results and Discussion

4.3.1 Extraction Behavior and Speciation of Hexavalent Actinides

The distribution ratios for extraction of hexavalent U, Np, and Pu ($D_{An(VI)}$) by the four monoamides are shown as functions of the equilibrium aqueous nitric acid concentration in

Figure 4.1. As expected, the 1 M solutions of monoamides in Exxsol D60 extract the hexavalent actinides well, except for DEHiBA with Pu(VI). While there seems to be an extraction preference where Np(VI) is favored over Pu(VI) for all the monoamides, U(VI) and Np(VI) are extracted approximately equally for DHHA and DEHBA. (Experimentation was not done for U(VI) with the extensively studied DEHiBA and DHOA.) The extraction of Pu(VI) using DEHBA is marginally smaller than the nonbranched monoamides, indicating that the branching off the second acyl carbon does not severely impact Pu(VI) binding. It is possible that the steric hinderance from the iso-butyl in DEHiBA prevents efficient extraction of the slightly smaller ionic radius of Pu(VI) - 0.71 Å, compared to Np(VI) - 0.72 Å [114].This would also cause the extraction difference between Np(VI) and Pu(VI) for DEHiBA to be greater than for the other monoamides studied.

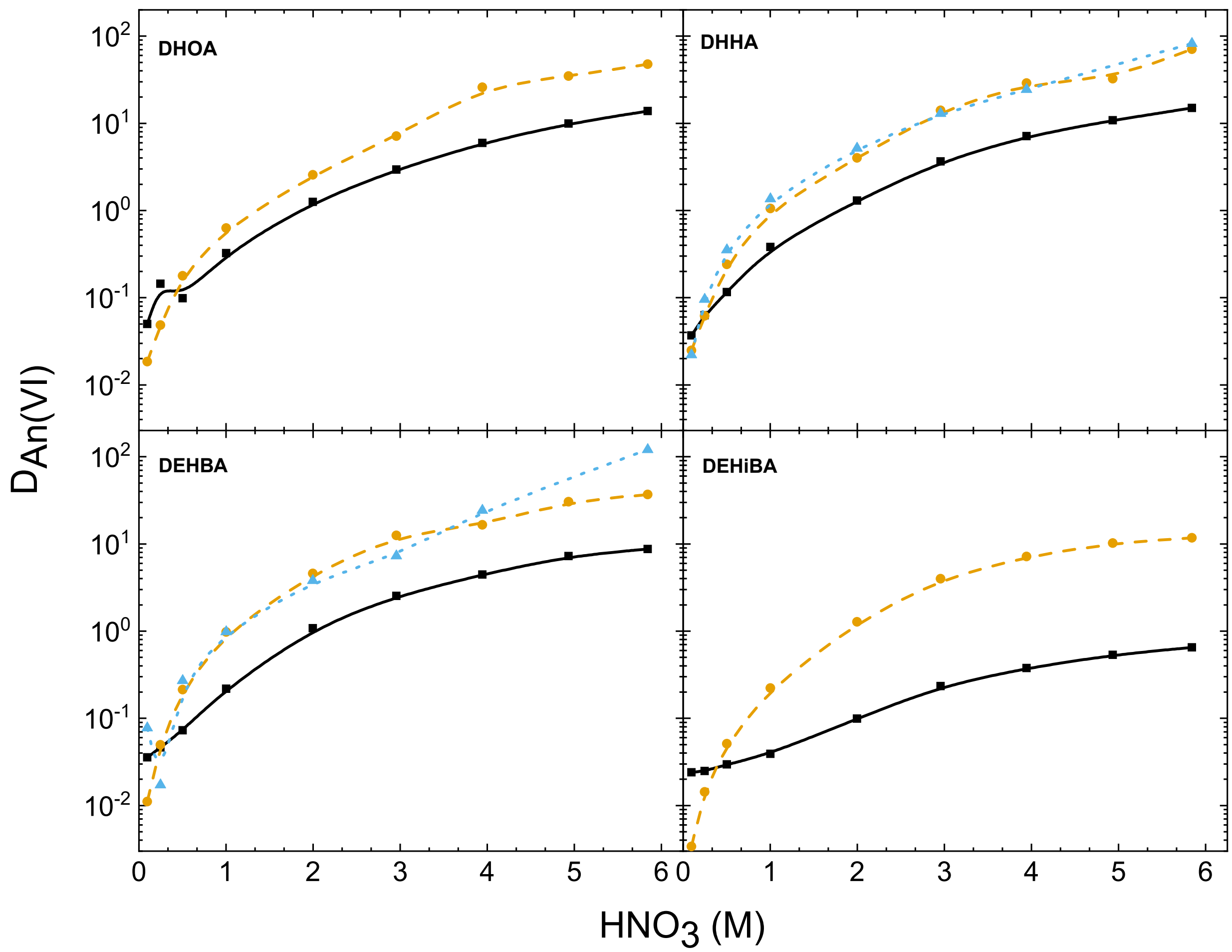


Figure 4.1: Distribution ratios as functions of acidity for hexavalent actinides Pu(VI) (square), Np(VI) (circle), and U(VI) (triangle) using 1 M monoamide/Exxsol D60. Lines are plotted as a visual guide.

Overall, the nonbranched (DHOA and DHHA) and partially branched (DEHBA) monoamides extract the hexavalent actinides well, outperforming TBP [115]. The hexavalent extraction preference would then be represented as U(VI) ≈ Np(VI) > Pu(VI). These results are similar to other studies by McCann et al. and Kumari et al. that have the distribution ratios of U(VI) and Np(VI) within 10 % of each other for the DEHiBA system and 20 % for the DHOA system [37, 69]. These differences are reasonably close to validate the reported observation that the distribution ratios of U(VI) are approximately equal to those of Np(VI).

It was previously suggested that the overall extraction preference of U(VI) and Np(VI) is noticeably greater than Pu(VI) because Pu(VI) does not readily form additional complexes with the monoamides, specifically anionic complexes [69]. However later research [73] and this study indicate that there is commonality of the An(VI):monoamide (U, Np, and Pu) complexes because they can all form both neutral 1:2 metal:nitrate and anionic 1:3 metal:nitrate configurations. A comparison of the spectra of Pu(VI)-monoamide complexes with tetraethylammonium (TEA) trinitratodioxoplutonate(VI) in nitromethane showed that anionic Pu(VI) trinitrate complexes were binding to protonated monoamides [73, 116]. Other spectroscopic studies with U(VI):monoamides theorized that shifts in the UV-Vis spectrum at high acidity were due to U(VI) being able to form a similar anionic species [46]. Those spectra compare well with TEA trinitratodioxouranate(VI), thereby confirming that U(VI) also forms anionic complexes like Pu(VI) [116].

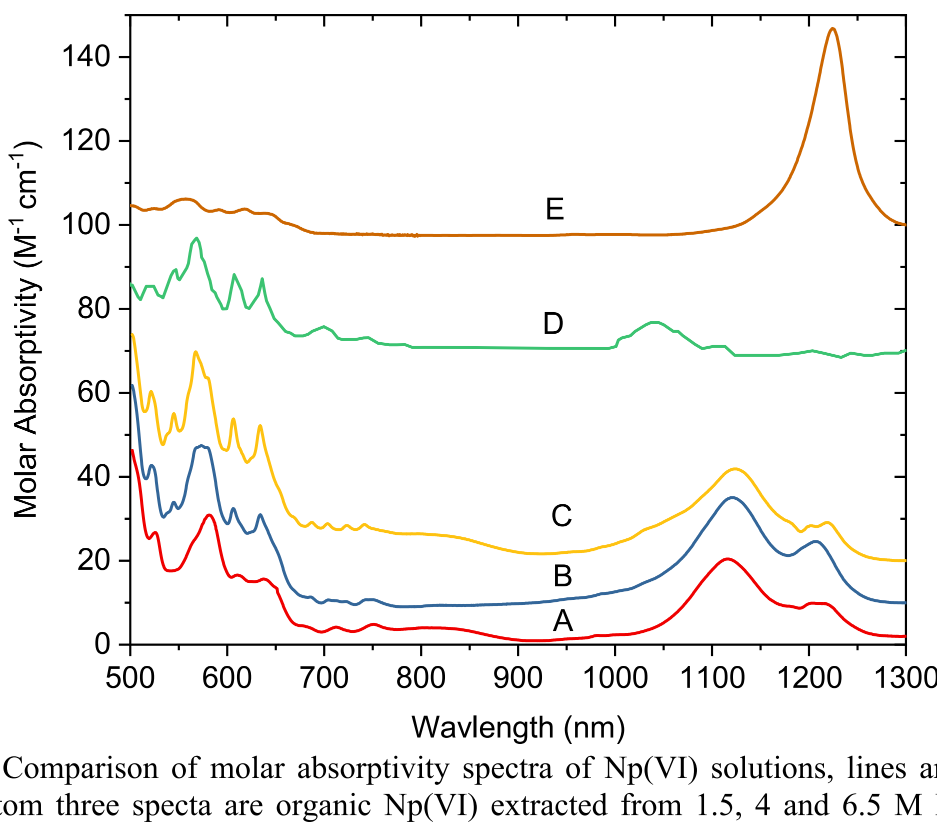


Figure 4.2: Comparison of molar absorptivity spectra of Np(VI) solutions, lines are offset for clarity. Bottom three specta are organic Np(VI) extracted from 1.5, 4 and 6.5 M HNO_3 (A-C respectively) using pre-equilibrated 1 M DHOA. The top two spectra are TEA trinitratodioxoneptunate(VI) (D) [116], and aqueous Np(VI) in 4 M HNO_3 (E).

To determine if Np(VI) would also form anionic species with monoamides, like Pu(VI) and U(VI), the spectra of the organic phases consisting of Np(VI) in 1 M DHOA/Exxsol D60 after extraction from 1.5, 4, and 6 M HNO_3 are compared to the spectrum of TEA trinitratodioxoneptunate(VI) [116] in Figure 4.2. The similarity of the two spectra between 500 and 675 nm, indicates that a stable anionic trinitrate Np(VI), $NpO_2(NO_3)_3^-$, has indeed formed in the organic phase (Equation 4.1) [116]. Additionally, the relatively broad peak ca. 1120 nm with the adjacent peak ca. 1210 nm is due to a monoamide:$NpO_2(NO_3)_2$ complex in the organic phase (Equation 4.2) [25, 117, 118], similar to the well-known $NpO_2(NO_3)_2(TBP)_2$ complex [119].

$$\mathrm{NpO_2^{2+}} + \mathrm{H^+} + 3\mathrm{NO_3^-} + \overline{\mathrm{Monoamide}} \Leftrightarrow \overline{\mathrm{NpO_2(NO_3)_3(H \cdot Monoamide)}} \tag{4.1}$$

$$\mathrm{NpO_2^{2+}} + 2\mathrm{NO_3^-} + \overline{2\mathrm{Monoamide}} \Leftrightarrow \overline{\mathrm{NpO_2(NO_3)_2(Monoamide)_2}} \tag{4.2}$$

Therefore U(VI), Np(VI), and Pu(VI) can all form an anionic 1:3:1 (An(VI): NO_3:monoamide) and neutral 1:2:2 complexes in the organic phase. Furthermore, the 500 – 675 nm bands increase relative to the 1000 – 1300 nm bands as the acidity increases. This is also similar to the observations of Berger et al. for U(VI) extraction by a monoamide that there should be a mix of the two stoichiometries (anionic and neutral complexes) starting at a low acidity and the percentage of the extracted trinitrate complex increasing with acidity [120].

4.3.2 Extraction Behavior of Stable Pentavalent Actinides

Out of all the actinides that can occupy the pentavalent oxidation state (Pa, U, Np, Pu, Am, Cm), only Pa and Np are reasonably stable at the concentrations encountered in ^{238}Pu purification and under the acidic conditions used in this study. Comparing their extraction behavior may offer insight into how to efficiently separate them from each other and other actinides. The separation of Np from Pa is of particular interest because the energetic beta emitting radionuclide ^{233}Pa ($t_{1/2}$ = 27.4 days) is the product of ^{237}Np alpha decay and rapidly accumulates in ^{237}Np materials. Even though the mass of ^{233}Pa is minuscule compared to the amount of ^{237}Np or ^{238}Pu, ^{233}Pa has to be removed from ^{237}Np because of protactinium's high specific activity and gamma dose emission. Although the ^{233}Pa initially is removed using column chromatography prior to any work with neptunium purification for NpO_2 targets [12], during and after the irradiation of the targets, the ^{233}Pa will continue to accumulate.

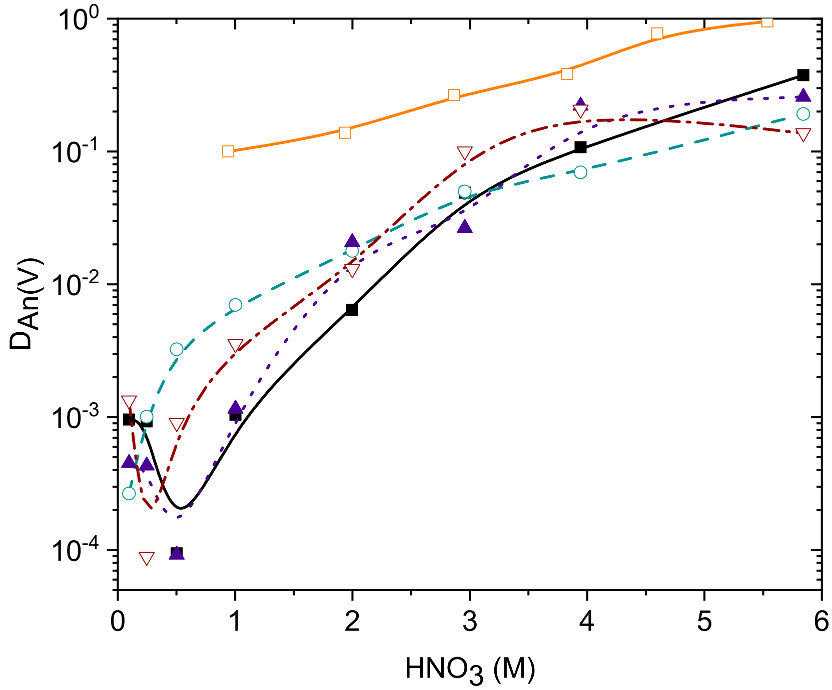


Figure 4.3: Distribution ratios as functions of acidity for Pa(V) 1 M DEHiBA/dodecane (open square) [121] vs. Np(V) DEHiBA (solid square), DEHBA (circle), DHOA, (triangle), and DHHA (inverse triangle) using 1 M monoamide/Exxsol D60. Lines are plotted as a visual guide.

Protactinium has been observed elsewhere to be somewhat extractable using DEHiBA, Figure 4.3 [121], although the distribution ratios are less than 1 up to 5.5 M nitric acid. Additionally, Pa(V) is proposed to be better extracted by monoamides with long alkyl chains, meaning that DHOA will better extract Pa(V) than DHHA [122]. The extracted complex for Pa(V) has been suggested to be the neutral species, $Pa(OH)_2(NO_3)_3(H_2O)$, which is stoichiometrically equivalent to $PaO(NO_3)_3(H_2O)_2$, in a 1:1 Pa(V):monoamide complex [122, 123]. However, the nitric acid dependence of Pa extraction suggests the participation of less than 2 nitrates in the extracted complex (Figure 4.3). In contrast, the other common pentavalent actinide, Np(V), is not well extracted by TBP [86] or by monoamides, but the degree of extraction varies strongly with the nitric acid concentration (Figure 4.3). It is therefore likely that Np(V) is being oxidized to well-extracted Np(VI), which causes the observed increase in distribution ratios at the higher acidities [78]. In any case, the low distribution ratios of Pa(V) and Np(V) in nitric acid systems imply that multiple scrub steps within a solvent extraction process will remove both Np(V) and Pa(V) efficiently at moderate acidities.

4.3.3 Extraction Behavior and Speciation of Tetravalent Actinides

Unlike the extraction of the hexavalent actinides shown earlier, extraction of the tetravalent actinides by the four monoamides has a distinct trend (Pu(IV) > Np(IV) > Th(IV)), as indicated in Figure 4.4, that agrees with many other studies [37, 46, 48, 62, 70, 71, 78, 91, 110, 124]. The distribution ratios for the branched monoamide DEHBA reaches ~ 10 for Pu(IV) and 3 for Np(IV) at 4 M HNO_3. (The aqueous conditions for extracting actinides are usually ~4 M HNO_3.) Although, DEHBA does not extract quite as well as DHHA or DHOA, where the distribution ratios for Pu(IV) and Np(IV) are ~100 by 4 M HNO_3, indicating that DEHBA could still be reliably used for extracting Pu(IV) and Np(IV). As expected, the isobutyl group on DEHiBA effectively prevents extraction of the tetravalent actinides. The distribution ratios observed for the DEHiBA system are rather low, 0.1 for Pu(IV) and 0.03 for Np(IV) in 4 M HNO_3. Interestingly, to compare Figure 4.3 and Figure 4.4 for DEHiBA, shows that the distribution ratios for solutions initially containing only Np(V) surpasses those of Np(IV) at 2 M HNO_3 [78] and they are then approximately equal to those of Pu(IV) at 4 M HNO_3. However, as mentioned previously, Np(V) is likely oxidized at high nitric acid concentrations to extractable Np(VI).

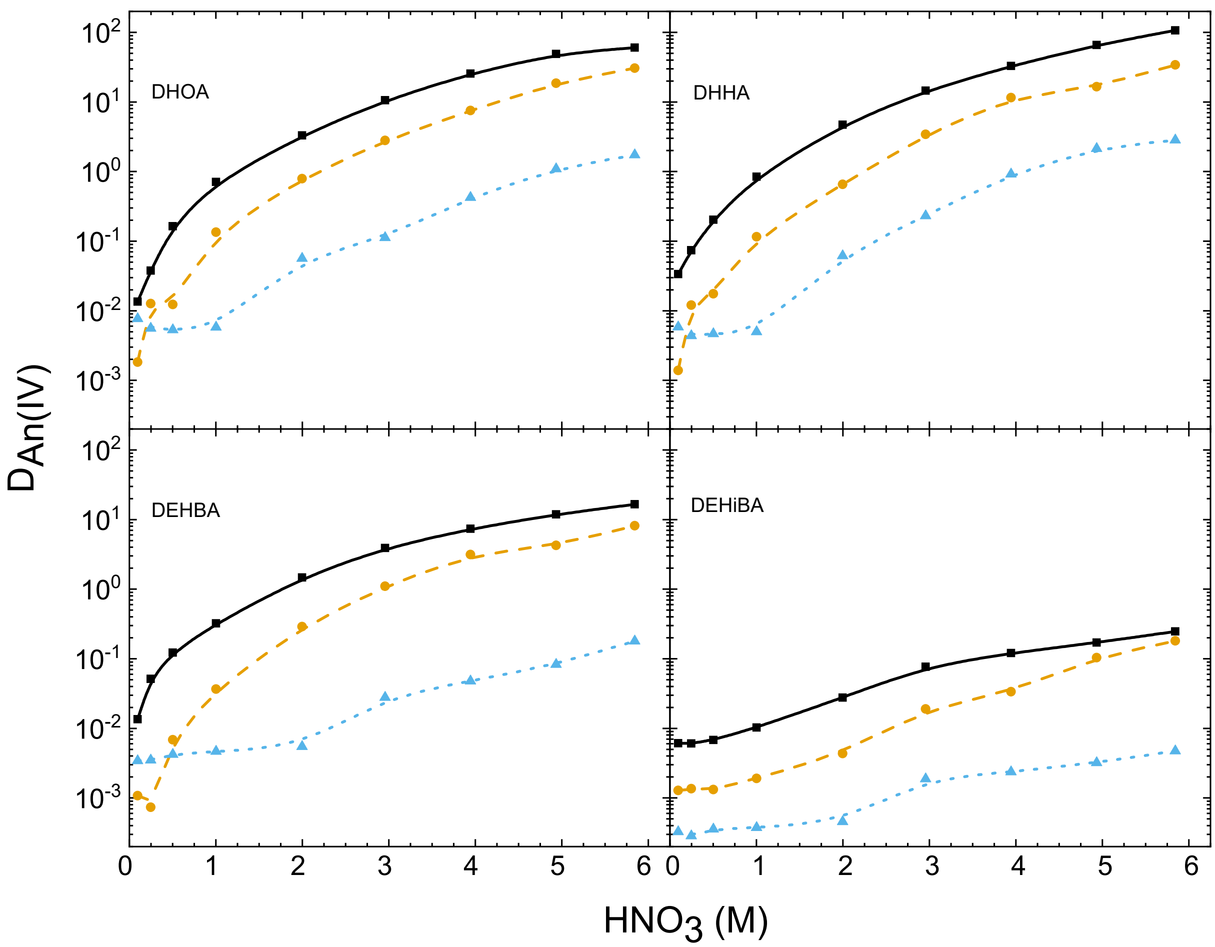


Figure 4.4: Distribution ratios as functions of acidity for tetravalent actinides Pu(IV) (square), Np(IV) (circle), and Th(IV) (triangle) using 1 M monoamide/Exxsol D60. Lines are plotted as a visual guide.

None of the monoamides displayed a distribution ratio higher than 0.01 at acidities below 2 M HNO_3 for Th(IV). The nonbranched monoamides barely extract Th(IV) (D > 1) by 5 M HNO_3. Th(IV) does not partition into the organic phase noticeably (D ~0.1) until after 5 M HNO_3 using branched DEHBA. DEHiBA does not noticeably extract Th(IV) across the entire range of nitric acid concentrations -- the distribution ratio never exceeds 0.01. The thorium distribution ratios of all four monoamides agree well with the values reported in the literature at 4 M HNO_3 [56, 121].

The poor extraction of Th(IV) has been attributed to an overall weaker binding affinity to the monoamides. Specifically, the lower charge density of Th(IV), compared to Np(IV) and Pu(IV), is not conducive to strong binding [125]. Interestingly, it seems that Th(IV) does not form anionic nitrate complexes at high nitric acid concentrations like Pu(IV) [46, 110]. This would be peculiar because it seems that the other relatively stable tetravalent actinide, Np(IV), does form an anionic complex like Pu(IV).

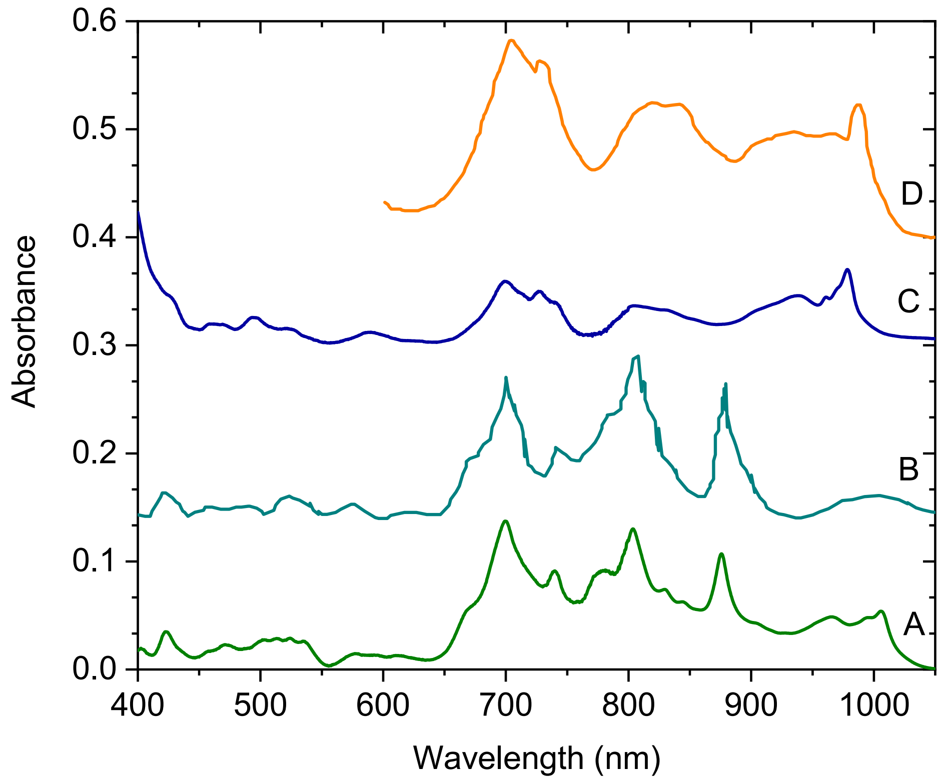


Figure 4.5: Comparison of absorbance spectra for Np(IV). 3.7 mM Np^{4+} extracted from 4 M HNO_3 using pre-equilibrated 1 M DHOA (A), TEA hexanitratodioxoneptunate(IV) (B) [116], and Np(IV) in 4 M HNO_3 aqueous solution (C). 1 M TBP extracting Np(IV) [126] (D).

Support for this hypothesis comes from the organic spectra of the Np(IV):DHOA complex extracted from 4 M HNO_3 which agrees well, within 400-900 nm, with the spectra of Np(IV):TEA hexanitratoneptunate(IV) complexes in Figure 4.5 [116]. The similarity in the spectra (DHOA complex vs. TEA-neptunium salt) indicate that Np(IV) is forming a six-coordinated hexanitrate anion in the organic phase [127], as shown in Equation 4.3. A similar anionic Pu(IV):monoamide complex has also been observed elsewhere [73]. The 900 - 1050 nm region of the spectra indicates that DHOA forms another complex that is not present in $TEA_2Np(NO_3)_6$ salt solution. Instead the DHOA-Np(IV) spectra in that region resembles the TBP-Np(IV) spectra, which would support the formation of the neutral $DHOA_2Np(NO_3)_4$ complex [126, 127].

$$Np^{4+} + 2H^{+} + 6NO_3^{-} + \overline{2\text{Monoamide}} \leftrightarrow \overline{Np(NO_3)_6(H \cdot \text{Monoamide})_2} \qquad (4.3)$$

Even though the spectra for DHOA indicates the presence of the anionic hexanitrate species, it is theorized that an anionic pentanitrate complex $Np(NO_3)_5$(H•monoamide) can also form [70]. The capability of Np(IV) and Pu(IV) forming additional complexes, whereas Th(IV) might not, could be a contributing factor that explains their overall increase in extraction.

4.3.4 Extraction Behavior of Trivalent Actinides

Neptunium(III) rapidly oxidizes under atmospheric conditions, but the trivalent oxidation state of the trans-neptunium actinides is considerably more stable than that of Np(III) [25]. Since the trivalent actinides are not well extracted by monoamides [38, 52, 70], it is relatively easy to separate An(III) from either Np(IV) or Np(VI). Figure 4.6 shows distribution ratios as functions of acidity for Am(III) (left), and Pu(III) (right). Less than 1% of Am(III) is extracted across the entire range of acidities studied. However, the extraction of Pu(III) shows different behavior. The extraction of Pu(III) by the nonbranched monoamides and DEHBA follows Am(III) extraction until 1 M HNO_3 and then the Pu distribution ratios steadily rise despite the presence of the hydroxylamine. The branched monoamide, DEHiBA, differs from other monoamides studied in that the $D_{Pu(III)}$ does not noticeably increase until after 5 M HNO_3. This general upward trend reinforces that hydroxylamine is insufficient to keep Pu^{3+} from oxidizing at > 1 M HNO_3, even at comparatively high concentrations. Comparing Figure 4.4 and Figure 4.6, the distribution ratios for solutions initially containing Pu(III) and Pu(IV) are approximately the same by 6 M HNO_3. Since DEHiBA extracts Pu(VI) > Pu(IV), this observation concludes that the Pu(III) is oxidizing to Pu(IV) under these conditions and not oxidizing further to Pu(VI).

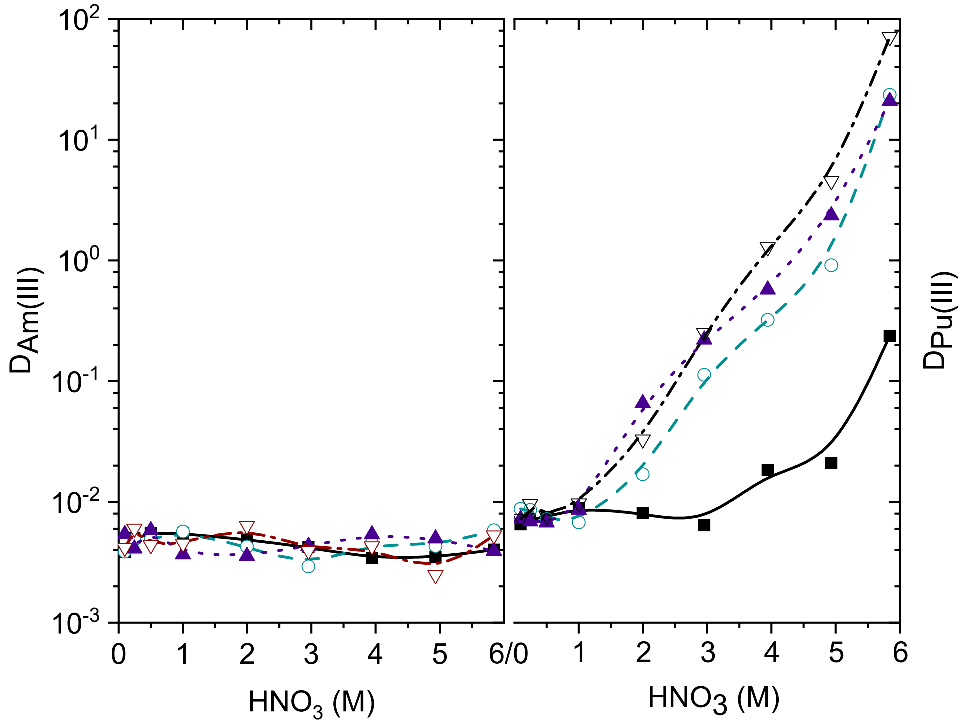


Figure 4.6: Distribution ratios as functions of acidity for extracting Am(III) (left) and Pu(III) with 0.43 M hydroxylamine (right). DEHiBA (square), DEHBA (circle), DHOA, (triangle), and DHHA (inverse triangle) using 1 M monoamide/Exxsol D60. Lines are plotted as a visual guide.

Pu(III) will oxidize back to Pu(IV) unless a strong reducing agent such as Fe(II) is used at higher acidities [33, 92]. Unfortunately, using a non-incinerable reducing agent would incur more waste to later dispose. Alternatively, U(IV) is a popular reducing agent for U(VI)/Pu(IV) separations [128]. However, for a Np/Pu separation, the uranium would need to be eventually cleaned from the Np product. Therefore, an incinerable reducing agent such as hydroxylamine is being used to reduce Pu(IV) to Pu(III) but at the lower acidities [12].

4.3.5 Actinide Extraction Trends

Compiling the information from the proceeding sections gives extraction trends for the actinides in their various oxidation states for a specific monoamide. These details can be used to choose a monoamide for a specific separation scheme. Overall, the general trend of extractability for the nonbranched monoamides DHHA and DHOA under extracting conditions is straightforward:

$$U(VI) \approx Np(VI) \approx Pu(IV) > Np(IV) > Pu(VI) > Th(IV) \approx Pu(III) > Np(V) > Am(III)$$

As noted earlier, the increasing extraction of Pu(III) and Np(V) observed at higher acidities, is most likely caused by their oxidation to the more strongly extracted oxidation states, Pu(IV) and Np(VI). Both DHHA and DHOA display a slightly higher distribution coefficient for Pu(VI) than Np(IV) until 3 M HNO_3 where the distribution ratios are approximately equal. After 3 M HNO_3 the preference switches to Np(IV) being slightly better extracted than Pu(VI). This indicates that Np(IV) will be slightly better extracted and stripped compared to Pu(VI) under the conditions expected for ^{238}Pu purification.

The extraction trend of the branched monoamide, DEHBA is similar to the nonbranched monoamides:

$$U(VI) \approx Np(VI) > Pu(IV) \approx Pu(VI) > Np(IV) > Pu(III) > Np(V) > Th(IV) > Am(III)$$

The most important difference between extraction by DHOA or DHHA and DEHBA is that the extraction of Th(IV) by DEHBA is substantially weaker, only better than extracting Am(III). While DEHBA does not extract the actinides studied as well as DHHA or DHOA, DEHBA still represents a potential alternative to TBP for ^{238}Pu purification because it extracts tetravalent and hexavalent Np and Pu well.

In contrast to the other monoamides studied, the actinide extraction behavior of DEHiBA is split into two relationships depending on the nitric acid concentration. At 1 M HNO_3 the extractability varies according to the series,

Np(VI) > Pu(VI) > Pu(III) ≈ Pu(IV) ≈ Am(III) > Np(IV) > Np(V) > Th(IV)

While at 4 M HNO_3 a different pattern is observed

Np(VI) > Pu(VI) > Pu(IV) ≈ Np(V) > Np(IV) ≈ Pu(III) > Am(III) ≈ Th(IV)

It is interesting that the extraction of trivalent actinides and Np(V) by DEHiBA is comparable to that of the tetravalent actinides. It is important to recall that depending on the acidity, the distribution ratios for Np(V) likely represent a mixture of Np(V) and Np(VI). Also, if another strong reducing agent, such as ferrous sulfamate, was used to stabilize Pu(III) then those distribution ratios should be approximately the same as Am(III) [71]. The poor extraction of DEHiBA for actinides not in the hexavalent state could suggest that DEHiBA has an overall binding affinity threshold for efficiently extracting the metals. If the charge density of a metal-nitrate complex is slightly less than the hexavalent actinides then the metal will not be appreciably extracted. However, other factors like DEHiBA-actinide complex solubility and kinetics are also affecting the extraction ability of DEHiBA.

A major contributor to the differences in the extraction preference for certain actinides, in various oxidation states, is the overall stability the An:monoamide complex. Since the monoamides can form anionic complexes with the hexavalent (U, Np, Pu) actinides, it seems that they can extract multiple complexes (neutral and anionic). However, for the tetravalent (Th, Np, and Pu) actinides anionic Th(IV) appears to form with much greater difficult, if at all, and may not be important in monoamide extractions like anionic Np(IV) and the well-known anionic Pu(IV) complexes. Introducing branching on the monoamide's acyl side will sterically hinder or otherwise significantly obstruct the monoamide from dexterously binding to an actinide that is not in the hexavalent state.

4.3.6 Neptunium and Thorium Extraction and Separation

The Np/Th mixture encountered in Np purification contains mostly Np [12]; therefore an ideal separation scheme would selectively extract Th(IV) and leave Np in the aqueous phase. Unfortunately, this is impractical using the studied monoamides because of their poor extraction of Th(IV) and the redox behavior of Np(V-VI) at the high nitric acid concentrations needed for Th extraction, where unextractable Np(V) can switch to its extractable state Np(VI) at higher acidities [78]. The alternative approach to Np/Th separations would be to use a branched monoamide that extracts Np(VI) well and Th(IV) poorly. Since it may be disadvantageous from a mass flow perspective to remove the Np before the Th, this study considers a procedure for coextracting Th and Np and removing the Th from the organic phase with subsequent scrub stages, with the possibility of a Th(IV) strip stage at moderate acidity (2 M HNO_3).

Figure 4.7 and Table 4.1 report the Np(VI) distribution ratios for DEHBA and DEHiBA over a range of acidities for Stages 1 (extraction of Np(VI) and Th(IV) from 0.01 M $KBrO_3$ with nitric acid), 2 (scrub with fresh nitric acid) and 3 (strip at low concentrations of nitric acid). Interestingly, the distribution ratios are higher for Stage 2 than for Stage 1 for nitric acid concentrations above 4 M HNO_3 using DEHBA. Also, both Stage 1 and Stage 2 display moderately lower distribution ratios that we observe for thorium-free systems.

Table 4.1: Distribution ratios as a function of the initial acidity of an aqueous 7.5 mM Np(VI)/4 mM Th(IV) using 1 M DEHiBA. (Data for Th free column are the Np(VI) distribution ratios for DEHiBA taken from
Figure 4.1)

HNO_3 (M)	Stage 1	Stage 2	Stage 3	Th free
5	7.7	8.9	2.0	10.2
6	7.5	8.2	1.6	11.7

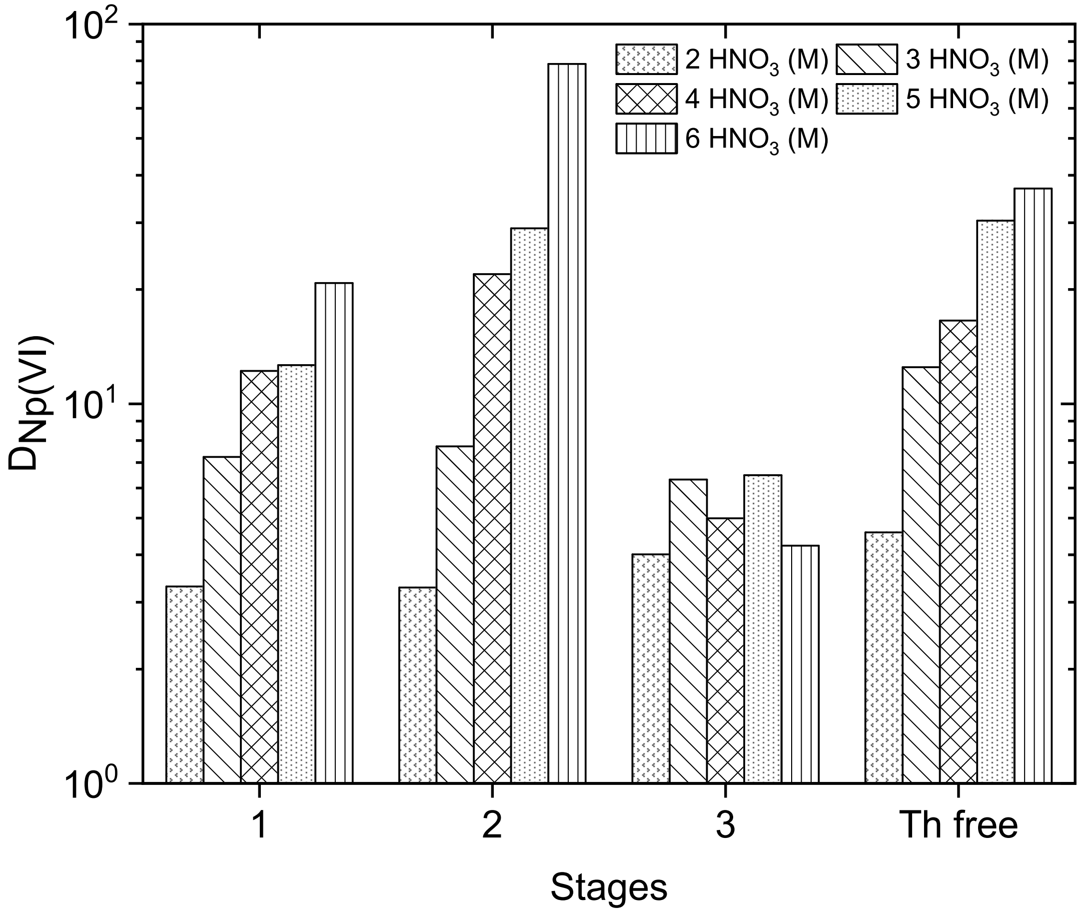


Figure 4.7: Distribution ratios as functions of acidity for 7.5 mM Np(VI) that was mixed with 4 mM Th(IV) using 1 M DEHBA/Exxsol D60. Data for Np(VI) line is taken from
Figure 4.1 (Th free). The legend denotes the initial acidic concentrations. Distribution ratios for Th(IV) are omitted for clarity.

The branched monoamides are effective in separating Th(IV) and Np(VI). More than 90% of the Th(IV) extracted in Stage 1 is removed from the organic phase in Stage 2 for all acidities (Figure A.6 and Table A.1). In Stage 3, the organic phase is contacted with 2 M HNO_3 to strip

Np(VI). Under these conditions most of the remaining Th is also stripped (< 0.5% of the initial thorium concentration). The Np(VI) is principally retained in the organic phase ($D_{Np(VI)} \geq 2$, see Table 4.1 and Figure 4.7). However, higher Np distribution ratios would be desirable in Stage 3. Therefore, a more efficient method would be multiple scrub stages at higher acidity to remove the Th and retain the Np(VI), replacing Stage 3 with multiple instance of Stage 2. After the desired amount of thorium is scrubbed from the organic phase, the Np(VI) could then be stripped by lowering the acidity to ca. 0.1 M HNO_3.

4.3.7 Neptunium and Plutonium Extraction and Separation

Since Np(VI) and Pu(IV) are stable at higher acidities, the use of DHHA or DHOA would be ideal materials to coextract these species. A reduction step is needed to partition the actinides, either reducing Np(VI) to Np(V) or Pu(IV) to Pu(III) for simple stripping. However, the comparable redox potentials of Np(V-VI) and Pu(III-IV), allow either metal to switch from a poorly-extracted to a well-extracted state in an acidic solution [25, 129]. This complicates an efficient separation of the two actinides because some reducing agents, such as hydroxylamine, will reduce both actinides. While the Np/Pu mixture envisioned for ^{238}Pu production contains mostly Np, it is difficult to strip the Pu first without aqueous complexing agents because Np(VI) is more readily reduced than Pu(IV). An alternative would be to use a particularly strong reducing agent to take Np further down to Np(IV), which is still retained in the organic phase, and to first strip Pu as Pu(III). This approach, such as that taken by Mahanty et al. [70] using reductants to stabilize aqueous Pu(III) and selectively extract Np(IV) with a monoamide is less desirable for our application as it would require a subsequent set of extractions to purify the ^{238}Pu. In the absence of a strong reducing agent, nitrous acid is the preferred reductant for a Np/Pu mixture because it can stabilize Pu as Pu(IV) while reducing Np(VI) to Np(V) [12, 32].

Table 4.2 shows the Pu distribution ratios for extraction from 3, 4, 5, or 6 M HNO_3 by 1 M DHHA with Np(VI) present (Stage 1), scrubbing of the organic phase at the same acidity (Stage 2), a Np strip with 33 mM HNO_2 (Stages 3) at 1 M HNO_3 and Pu strip with hydroxylamine at 0.5 M HNO_3 (Stage 4). The distribution ratios of Pu(IV) in Stages 1 and 2 are lower than what was reported for Pu(IV) by themselves (Figure 4.4). Also, the distribution ratios did not appreciably change from Stages 1-2, which indicates that little Pu was present in the unextractable oxidation state, Pu(III). While the low distribution ratios of Pu in Stage 4 would suggest that Pu was successfully reduced to Pu(III) with the hydroxylamine, it was found that the Np(VI) was not completely reduced in Stage 3. This experiment was repeated with an additional Np(VI) reduction step using 1 M DHHA with 3 M and 6 M HNO_3 as the starting acidity, shown in Figure 4.8.

Table 4.2: Distribution ratios for Pu from a 4-stage process with the column headers denoting the initial aqueous phase acidity

Stages	3 M HNO_3	4 M HNO_3	5 M HNO_3	6 M HNO_3
1	7.9	21	35	65
2	8.6	18	29	39
3	1.1	1.3	1.4	1.5
4	2.0×10^{-2}	1.3×10^{-2}	3.1×10^{-2}	1.7×10^{-2}

The difference between the tests summarized in Table 4.2 and Figure 4.8 is that the Np strip was split into two stages for the Figure 4.8 trial: Stage 3 used 100 mM HNO_2 in 1 M HNO_3 and Stage 4 was the rinse (scrubbing of the organic phase with fresh 1 M HNO_3). The distribution ratios for Stages 1 and 2 are similar to those in Table 4.2. Pu(IV) is extracted marginally better than Np(VI) at both acidities for Stages 1 - 4. It is apparent in in Figure 4.8 that nitrite reduction of Np(VI) was incomplete because of the closeness between the Np distribution ratios in Stage 3 and those reported in

Figure 4.1 at 1 M HNO_3. The rapid kinetics of Np(VI) reduction using nitrous acid is well known [93] so it is perplexing why the Np(VI) is not being fully reduced by 33 or 100 mM HNO_2. It is possible that HNO_2 might be having deleterious side reactions with monoamide itself. It has been observed elsewhere that one of degradation products of HNO_2 , NO^-, reacts with amides [130]. The slightly lower ratio of the distribution coefficients of Pu to Np in Stage 5 would suggest that Pu was reduced to Pu(III) with the hydroxylamine while the Np mostly remained in the organic phase. However, it is important to note the higher error associated with Stage 5 due to the low distribution ratio and the extremely low Np activity in these final samples.

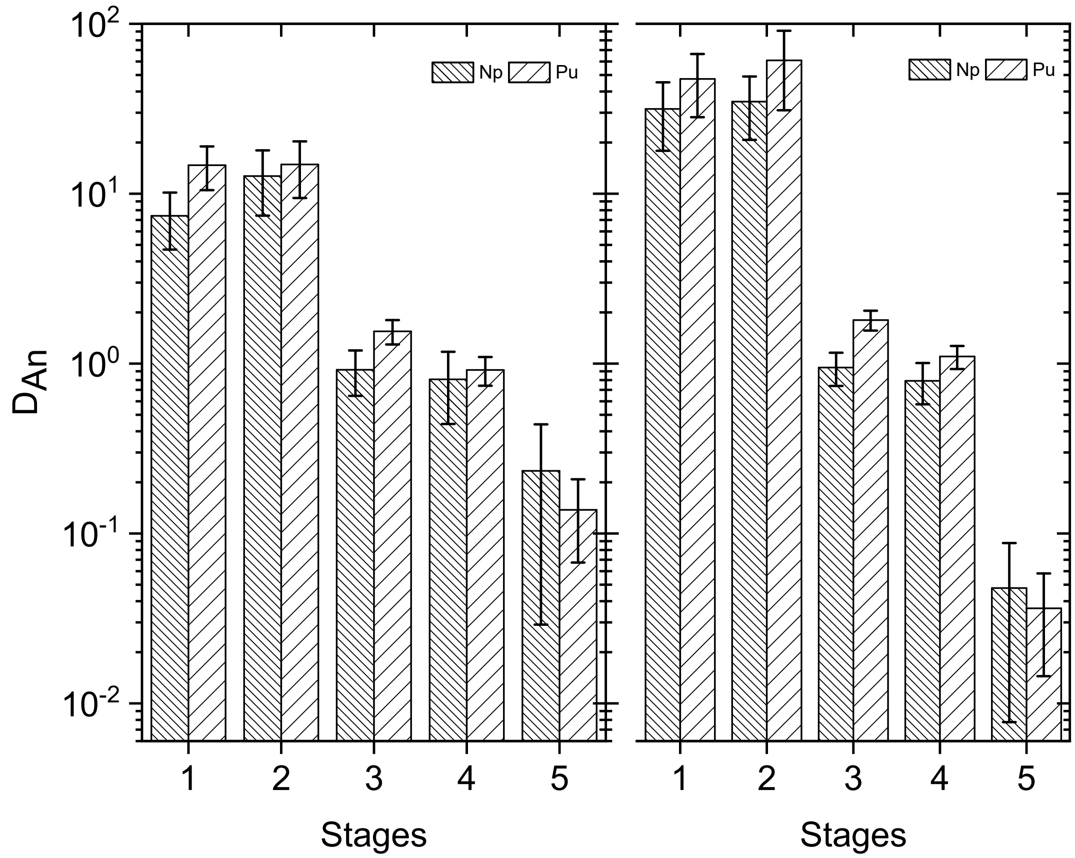


Figure 4.8: Distribution ratios for Np(VI) that was mixed with Pu(IV) over several stages using 1 M DHHA/Exxsol D60. The graphs are separated based off their initial acidities 3 M HNO_3 (left) and 6 M HNO_3 (right). Overal uncertainty is represented by the error bars.

4.4 Summary

Overall, DEHBA and DEHiBA have been shown to extract the hexavalent actinides better than the tetravalent actinides. Therefore, a branched monoamide could be ideal for Np(VI)/Th(IV) separation because of the poor extractability of Th(IV) even in 6 M HNO_3. Even at the highest acidity studied, five scrub stages will reduce a 1 mM Th(IV) starting concentration to 0.01 μM Th(IV). The Np can then be recovered by lowering the acidity to stripping conditions.

The remarkably similar extraction of Np(VI) and Pu(IV) using DHHA or DHOA across the acidic range studied (compare

Figure 4.1 and Figure 4.4), complicates Np(VI)/Pu(IV) separation. A redox stage is necessary to selectively strip either actinide in those respective oxidation states. It has been observed that controlling the redox chemistry of trace quantities of multiple metals is challenging under process conditions. Dramatically increasing the metal concentration would substantially decrease the counting error for the later stages and be able to isolate the possible effects HNO_2 has on monoamides.

CHAPTER 5

BEHAVIOR AND EFFECTS OF NITROUS ACID WHEN EXTRACTED BY *N,N*-DIALKYALMIDES

Manuscript prepared for submission to Solvent Extraction and Ion Exchange

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5.1 Introduction

Redox agents are often used to manipulate the oxidation state of metals, such as the actinides, to encourage an efficient separation of targeted metals in solvent extraction processes [29, 32, 128, 131]. For instance, Np(VI) is reduced to Np(V) so that it can be stripped from tributylphosphate (TBP) in the plutonium uranium reduction extraction (PUREX) process [16, 132]. While employing redox behavior for efficient separations it is important to be aware of the extractability of the redox agents used to manipulate oxidations states. In the PUREX process, in addition to extracting desired cation metals, TBP can also extract other compounds besides actinides, such as redox agents, acids, and other undesired metals [133-135]. Extracting other compounds can lead to unintended occurrences that decrease the separation efficiency of the desired metals and incur additional costs to achieve the desired purification [133]. Several extractants have been studied as replacements for TBP in the PUREX process [56], and one important class of extractants being explored are the *N,N*-dialkylamides, often referred to as monoamides [41, 42, 46, 52].

Two important characteristics of the monoamides that make them enticing direct replacements for TBP in the PUREX process are their incinerability and nondetrimental degradation products [39, 46, 77]. To date, the literature on monoamide extractants has focused on actinide extraction with limited exploration of the extraction potential of other components seen in the PUREX system such as fission products and some acids [136, 137]. One potentially problematic compound that has not been examined is nitrous acid, a weak acid (3.16 pKa [138, 139]) that is exploited in actinide separations to reduce Np(VI) to Np(V). Nitrous acid can be introduced into an acidic aqueous solution as sodium nitrite, by sparging with nitric oxide (NO) [14], or by radiolytic decomposition of nitric acid [19]. Interestingly, at low concentrations, HNO_2 becomes a catalyst in nitric acid solutions and will help oxidize instead of reducing metals including Np(V) [20, 32]. It has been hypothesized that this behavior is due to formation of N(IV) through a reaction between nitrite and nitrate [140].

Nitrous acid is unstable and appreciably decomposes over time if not regenerated by one of the above mentioned processes. The gradual decomposition of HNO_2 into gases will occur in different acidic aqueous solutions (e.g. perchloric, sulfuric, nitric) [141]. While the decomposition can be significantly slowed by using an inert gas or a liquid seal in the head space, neither method fully prevents HNO_2 decomposition [142, 143]. An example of the generation and decomposition of nitrous acid reaching equilibrium transpires during the processing of high activity radionuclides. The equilibrium is governed by the radiation dose [144-146].

Nitrous acid also partitions into many organic phases in solvent extraction and, due to its inherent instability, both the aqueous and organic phase concentrations of nitrous acid can change significantly over the course of solvent extraction processes. Although previous studies have shown that TBP appreciably extracts nitrous acid [134, 144, 147], it is uncertain if extraction of HNO_2 by monoamides will be similar to that of TBP. While monoamides extract nitric acid similarly to TBP [135, 137], no published studies have quantified the nitrous acid extraction by *N,N*-dialkylamides.

The extraction of nitric acid by *N,N*-dialkylamides has been studied quantitatively. The organic phase monoamide-HNO_3 complex is mostly a 1:1 [137] complex formed by hydrogen bonding between the hydrogen of nitric acid and the carbonyl oxygen of the monoamide. This is shown in Equation 5.1, where the overhead bar denotes species in the organic phase. It is likely that HNO_2 will similarly bind to the monoamide, Equation 5.2.

$$\mathrm{HNO_3} + \overline{\mathrm{monoamide}} \rightarrow \overline{\mathrm{monoamide} \cdot \mathrm{HNO_3}} \tag{5.1}$$

$$\mathrm{HNO_2} + \overline{\mathrm{monoamide}} \rightarrow \overline{\mathrm{monoamide} \cdot \mathrm{HNO_2}} \tag{5.2}$$

Tributylphosphate forms similar 1:1 complexes with both HNO_3 and HNO_2, as shown in Figure 5.1 [134, 140]. Even though the stoichiometry of both acids with TBP are the same, the hydrogen bonding for HNO_3 is stronger than the bond strength for HNO_2 [134]. If this holds for monoamide extractants as well it could mean that the monoamide-HNO_2 complex (Figure 5.1) will not form as easily as monoamide-HNO_3 complexes. Even though HNO_2 in the TBP-HNO_2 complexes are more stable than free nitrous acid in aqueous solutions [134], it is unknown how stable HNO_2 is when extracted as the monoamide-HNO_2 complex.

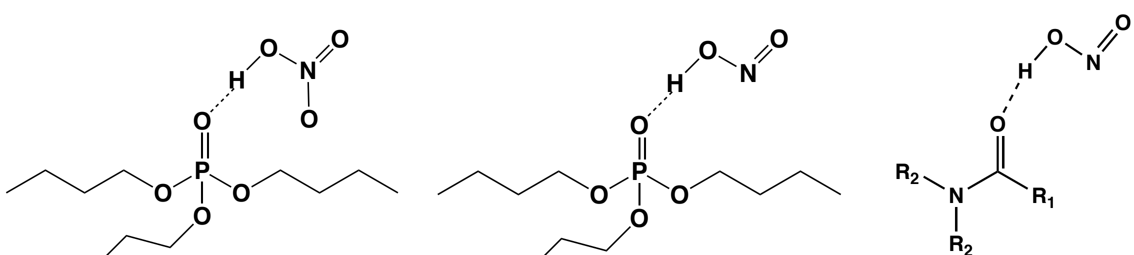


Figure 5.1: Structures of TBP-HNO_3 (left), TBP-HNO_2 complex (center), and a proposed *N,N*-dialkylamide-HNO_2 complex (right)

This study quantifies the HNO_2 concentrations extracted into aliphatic organic phases by a series of *N,N*-dialkylamides, the extractant dependency of HNO_2, and the associated stability of HNO_2 in the organic and aqueous phases using UV-Vis spectroscopy. The extraction of HNO_3 using *N,N*-dialkylamides was also studied to corroborate findings with the literature. Various *N,N*-

dialkylamides were explored to determine if extractant structure impacted HNO_2 extraction and stability, specifically: *N,N*-dihexylbutanamide (DHBA), *N,N*-dihexylhexanamide (DHHA), *N,N*-dihexyloctanamide (DHOA), *N,N*-dihexyl-(2-ethyl)hexanamide (DH2EHA), *N,N*-di-(2-ethylhexyl)butanamide (DEHBA), and *N,N*-di-(2-ethylhexyl)isobutanamide (DEHiBA). The *N,N*-dialkylamide structures are shown in Figure A.7. It was also found that at high nitric acid concentrations, nitrous acid will interact with monoamides to form new complexes. A behavior not observed with TBP. The structure of these complexes is uncertain and it is unclear what the impact will be on implementation of monoamides at process scale conditions.

5.2 Experimental

5.2.1 Liquid-Liquid Extraction of HNO_3

All monoamides studied were synthesized and purified as previously described [78]. The organic phases were prepared by diluting known amounts of monoamide with Exxsol D60 to the desired concentration. Aqueous HNO_3 solutions were prepared from Ultrex II grade nitric acid diluted with 18.3 MΩ water and standardized by titration with NaOH using phenolphthalein as an indicator. Equal volumes of fresh organic and aqueous phases were vortexed for two minutes at 20 °C ± 2 °C and then centrifuged. The nitric acid extracted into the organic phase was subsequently stripped by contacting with water at a 3:1 (aqueous to organic) volume ratio and analyzed for nitrate spectrophotometrically using a slightly modified version of a method developed by Cataldo et al. [148]. The aqueous strip solutions were diluted with a known amount of water to have a final NO_3^- concentration ca. 4 mM. A 100 µL aliquot of the NO_3^- solution was then mixed with 400 µL of 5 % salicylic acid in sulfuric acid. After 20 minutes, this mixture was diluted to 10 mL with sufficient sodium hydroxide (NaOH) to a final concentration of 2 M NaOH. The resulting solution has a strong absorbance at 410 nm that is proportional to the original nitrate concentration [148]. All UV-visible spectra were measured using a Cary 300 UV-Vis spectrophotometer.

5.2.2 Nitrous Acid Solutions

The concentration of aqueous nitrous acid in nitric acid solutions, $[HNO_2]_{aq}$, was determined using UV spectroscopy. The experimental molar extinction coefficient (ε) found at 369 nm was 48.6 M^{-1} cm^{-1}. This value was used for determining the concentration of HNO_2 since it is within 1.14 % error of measured mass of sodium nitrite ($NaNO_2$) dissolved in a HNO_3 solution and within 2 % of the value determined in the literature [138]. The organic phase nitrous acid concentrations, $[HNO_2]_{org}$, were found by the difference between the initial aqueous nitrous acid concentration $[HNO_2]_{initial}$ and the nitrous acid concentration of the aqueous phase at equilibrium $[HNO_2]_{final}$. Because of the acidity of the aqueous phases, at least 99 % of the total aqueous nitrite was present as HNO_2.

5.2.3 Liquid-Liquid Extraction of HNO_2

The *N,N*-dialkylamide containing organic phases were pre-equilibrated twice with the appropriate nitric acid at a 1:2 volume ratio of organic and aqueous, respectively. The aqueous phase was prepared by adding an aliquot of a recently prepared aqueous $NaNO_2$ solution to fresh HNO_3 solutions (0.1 - 6 M HNO_3). Equal volumes (1 mL) of both phases were vortexed for 2 min in glass vials with minimal head space, which is necessary to arrest loss of HNO_2 from the solution phase when vortexing. After vortexing the phases, centrifuged for two minutes, and separated, the aqueous phase was pipetted into a plastic cuvette (designed for an assay range down to 340 nm) and the organic phase in a quartz cuvette; both cuvettes had a 1.00 cm pathlength. Spectrophotometric analysis confirmed the presence of HNO_2 in both phases. The concentrations in both phases and the corresponding distribution ratio of nitrous acid (D_{HNO_2}, Equation 5.3) were calculated from the absorbance of the aqueous sample at 369 nm.

$$D_{HNO_2} = \frac{[HNO_2]_{org}}{[HNO_2]_{aq}} = \frac{[HNO_2]_{initial}-[HNO_2]_{final}}{[HNO_2]_{final}} \quad (5.3)$$

5.2.4 LC-ESI Measurements

Aliquots of organic phases containing DEHBA before and after contact with aqueous phases containing HNO_3 or mixtures of HNO_2 and HNO_3 were diluted by a factor of 500 in HPLC grade acetonitrile. The diluted samples (volume = 5 µL) were injected through a LC column (100 x 3 mm) into a SCIEX X500r QTOF with TURBO V™ source for mass spectrometric analysis in the positive ionization mode for 5 minutes for LC and MS analysis. Gas 1 and 2 pressures were both at 50 psi with the declustering voltage set to 20 V. Note that only the single MS method applying the quadrupole (kept at 250 ºC) was used and not MS/MS so that the distribution of unknown compounds could be found within the mass/charge (*m/z*) range of 100 – 1000. The liquid chromatography eluent consisted of 100 % acetonitrile with 0.1 M formic acid with a flow rate of 0.4 mL/min. Nitrogen gas was used as for the curtain gas (to prevent contamination of the instrument) and nebulizing the samples with a spray voltage of 5500 V.

5.2.5 Additional Materials and Methods

Monoamide purity and various monoamide complexes were analyzed using ^{13}C and ^{1}H NMR (JEOL 500 MHz liquid state NMR). The 1 M TBP (98 % purity) was diluted in dodecane (anhydrous >99 %). Uranium-233 (^{233}U) was obtained from existing stock solutions. Radiometric distribution ratios were determined by the ^{233}U counts per minute (cpm) in the organic phase divided by the cpm ^{233}U in the aqueous phase. The organic and aqueous solutions were mixed with alpha-beta discrimination liquid scintillation cocktail so the cpm could be measured using a HIDEX 300 SL liquid scintillation counter.

5.3 Results/Discussion

5.3.1 Nitric acid Extraction by *N,N*-Dialkylamides and TBP

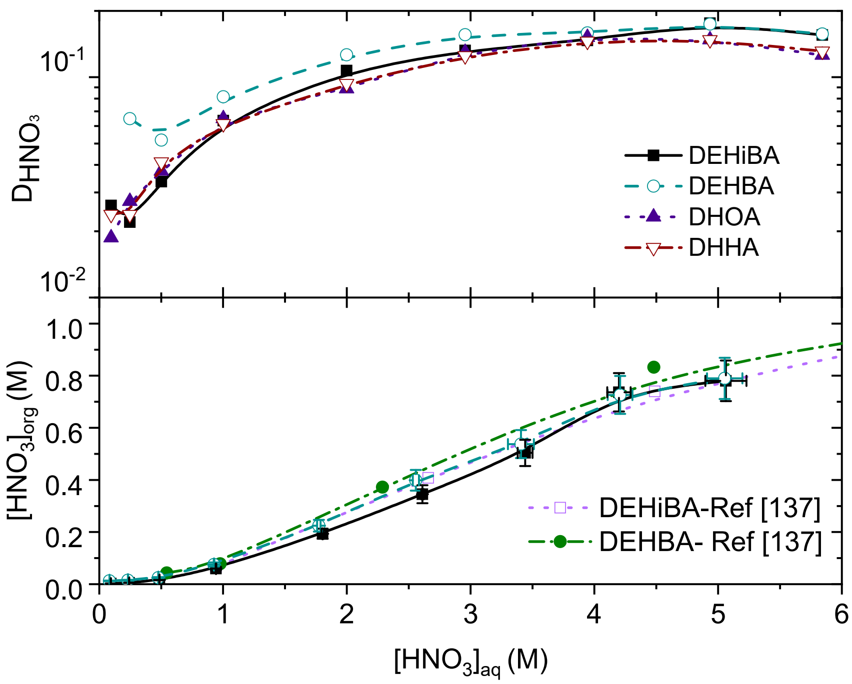


Figure 5.2: (Top) Distribution ratios of nitric acid being extracted by 1 M monoamide/Exxsol D6O as a function of initial nitric acid concentration. (Bottom) HNO_3 in the organic phase vs. HNO_3 in the aqueous phase for DEHBA and DEHiBA: comparing values obtained by spectroscopy and the literature. Lines are plotted as a visual guide.

The extraction of nitric acid by 1 M solutions of monoamides in Exxsol D60 is summarized in Figure 5.2. Figure 5.2 (top) shows the distribution ratio increases as the aqueous nitric acid concentration increases, reaching a distribution ratio of 0.1 at 2 to 3 M HNO_3. At higher acidities, the distribution ratio remains approximately constant. Nitric acid distribution ratios around 0.1 for 1 M monoamide were expected, as this was previously reported for the branched monoamides (DEHBA and DEHiBA) [137] and TBP [149]. The experimentally determined $[HNO_3]_{org}$ was compared against $[HNO_3]_{aq}$ for DEHBA and DEHiBA with values from the literature [137], which agree well, shown in Figure 5.2 (Bottom). The similarity in nitric acid extraction (Figure 5.2) by the different monoamides studied shows that unlike metal ion extraction, the branching of the carbon chains does not impact extraction of nitric acid.

While Equation 5.1 represents the 1:1 stoichiometry of the primary monoamide-HNO_3 complex formed in the organic phase, prior work suggests additional organic phase complexes, with 1:2 and 2:1 monoamide:nitrate stoichiometries are formed in the acid range used in this study (0.1 to 6 M HNO_3) [137]. The nitric acid extraction equilibria can be expanded from Equation 5.1 to be expressed in the following general expression (Equation 5.4) [137, 150], with the nitric acid equilibrium thermodynamic constant, $K_{ij}(HNO_3)$. This equilibrium would be affected if other components are added to the system, such as different acids.

$$iH^{+} + iNO_3^{-} + \overline{j\text{Monoamide}} \leftrightarrow \overline{iHNO_3 \cdot j\text{Monoamide}} \quad (5.4)$$

5.3.2 Extraction of Nitrous Acid by *N,N*-Dialkylamides and TBP

Aqueous HNO_2 displays multiple sharp peaks (346 and 357 nm) near the broad peak of HNO_3 at ca. 300 nm, a spectrum of multiple conditions of $NaNO_2$, HNO_3, and a mix of the two is shown in Figure A.8. The spectra in Figure A.8 illustrate that at different nitric acid concentrations, the concentration of nitrous acid remains unchanged. Figure A.9 contains spectra of the aqueous solutions after contact with 1 M DHOA over 0.1 to 6 M HNO_3. Even though HNO_2 is decomposing into nitrogen oxide gases, such as dinitrogen trioxide which is observed as a peak at 625 nm [151] in solutions that have greater than 4 M HNO_3 [138], it is a reasonable assumption that the molar attenuation coefficients for the HNO_2 peaks are not impacted by absorbances of nitrogen oxide derivatives, at least at the HNO_2 concentrations used in this study.

The extraction of nitrous acid by 1 M solutions of various monoamides is summarized in Figure 5.3. The decreasing extraction of HNO_2 with increasing HNO_3 concentrations observed for each monoamide is similar to what has been reported for TBP [152], and is most likely due to the monoamides preferentially binding nitric acid over nitrous acid, similar to TBP [144]. This results in a significantly higher organic phase concentration of HNO_3, compared to the HNO_2. As with the extraction of nitric acid, all the monoamides studied show similar HNO_2 extraction behaviors. Therefore, the overall *N,N*-dialkylamide structure does not noticeably interfere with extraction of HNO_2 across the range of acidities studied.

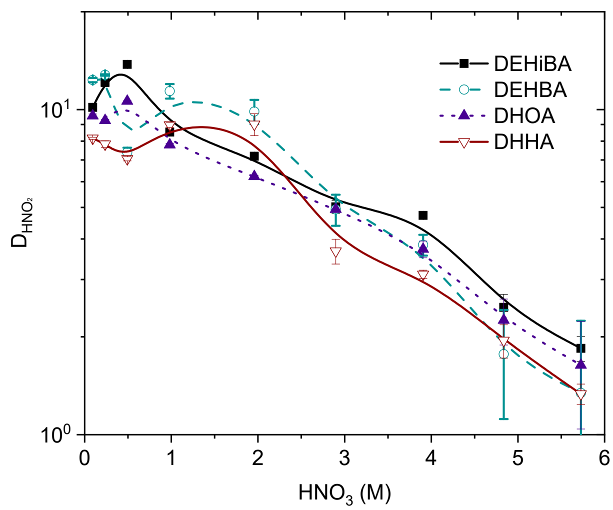


Figure 5.3: Distribution ratios of nitrous acid as a function of the HNO_3 concentration extracted by 1 M monoamide: DEHiBA (square), DEHBA (circle), DHOA, (triangle), and DHHA (inverse triangle). Lines are plotted as a visual guide.

Given the similarity of HNO_2 extraction by different monoamides, the average stoichiometries of the extracted monoamide-nitrous acid complexes were studied for aqueous solutions containing 0.1, 1, or 4 M HNO_3. The logarithmic distribution ratios of HNO_2 as a function of the logarithmic monoamide concentrations are shown in Figure 5.4. The corresponding slopes calculated by linear regression are reported in Table 5.1, they represent the average of monoamide-nitrous acid stoichiometry. The results confirm that the dominant stoichiometry of the extracted monoamide-HNO_2 complex is 1:1 for 0.1 M and 1 M nitric acid.

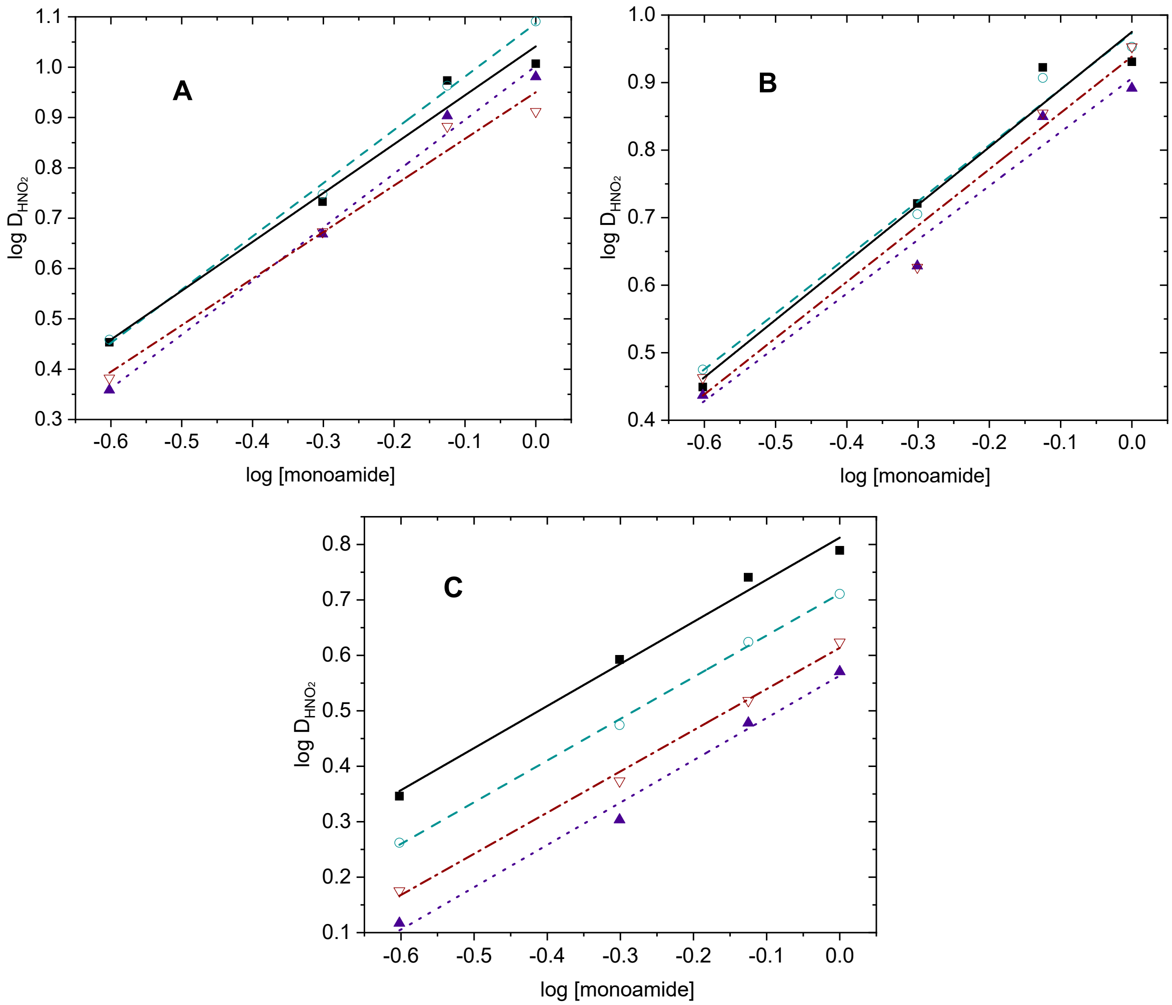


Figure 5.4: Extractant dependence of the distribution ratios of HNO_2 for various monoamides extracting 0.02 M nitrous acid from (A) 0.1 M, (B) 1 M and (C) 4 M HNO_3. DEHiBA (square), DEHBA (circle), DHOA, (triangle), and DHHA (inverse triangle). Lines are best fit.

Table 5.1: Monoamide stoichiometry slope analysis of HNO_2 at 0.1, 1, and 4 M HNO_3. Error reflects absolute uncertainty.

***N,N*-Dialkylamide**	**0.1 M HNO_3**		**1 M HNO_3**		**4 M HNO_3**	
	m	**y-int**	**m**	**y-int**	**m**	**y-int**
DEHiBA	1.0 ± 0.1	1.04 ± 0.04	0.9 ± 0.1	0.98 ± 0.04	0.76 ± 0.06	0.81 ± 0.02
DEHBA	1.06 ± 0.04	1.09 ± 0.01	0.94 ± 0.08	0.99 ± 0.03	0.75 ± 0.02	0.711 ± 0.007
DHHA	1.0 ± 0.1	0.95 ± 0.03	1.03 ± 0.06	0.96 ± 0.02	0.829 ± 0.002	0.623 ± 0.001
DHOA	1.07 ± 0.07	1.00 ± 0.02	0.98 ± 0.09	0.98 ± 0.03	0.76 ± 0.06	0.56 ± 0.02

Since HNO_3 can also form 1:2 or 2:1 complexes with monoamides at varying acidities [137], either monoamide-$(HNO_2)_2$ or (monoamide)$_2$-HNO_2 complexes could also be forming at these two acidities if HNO_2 behaves similarly to HNO_3. Interestingly, the stoichiometric slope decreases for the monoamides at 4 M nitric acid, which suggests a roughly equal mixture of monoamide-(HNO_2) and monoamide-$(HNO_2)_2$ complexes that form during contact with HNO_2 in 4 M HNO_3. With higher concentrations of nitric acid in the aqueous phase, more nitric acid is extracted, leaving less free monoamide to bind nitrous acid, favoring the 1:2 monoamide:nitrous acid stoichiometry. Moreover, these measurements give no indication of a 2:1 monoamide:nitrous acid complex in the organic phase. This is unlike nitric acid, where the (monoamide)$_2$-HNO_3 complex is reported to be the second most important complex between 1 and 6 M HNO_3 [137]. This implies that the monoamide-HNO_2 hydrogen bond is substantially weaker than the corresponding monoamide-HNO_3 hydrogen bond.

The general equation for HNO_2 extraction by monoamides can be written as Equation 5.5,

$$x\mathrm{H}^+ + x\mathrm{NO_2^-} + \overline{y\mathrm{Monoamide}} \leftrightarrow \overline{x\mathrm{HNO_2} \cdot y\mathrm{Monoamide}} \tag{5.5}$$

$$\mathrm{K_{xy}(HNO_2)} = \frac{\overline{\mathrm{xHNO_2 \cdot yMonoamide}}}{(\mathrm{H^+})^{x} \cdot (\mathrm{NO_2^-})^{x} \cdot (\overline{\mathrm{Monoamide}})^{y}} \tag{5.6}$$

The equilibrium constant expression, $K_{xy}(HNO_2)$, given in Equation 5.6 represents the extraction constant of nitrous acid, with an. As previously noted, nitric acid competes with the nitrous acid at higher nitric acid concentrations. This competition is represented by the exchange equilibrium constant (K_{ex}), Equation 5.7.

$$\overline{\mathrm{HNO_3 \cdot Monoamide}} + \mathrm{HNO_2} \overset{\mathrm{K_{ex}}}{\leftrightarrow} \overline{\mathrm{HNO_2 \cdot Monoamide}} + \mathrm{HNO_3} \tag{5.7}$$

5.3.3 Nitrous Acid Binding to *N,N*-Dialkylamides

The spectra of DHOA-HNO_2 complexes, shown in Figure 5.5, were consistent with TBP-HNO_2 complexes at low acidities [147, 153]. Markl et al. [147] observed possible quenching effects from the increased amount of HNO_3 present in the organic phase, concluding that pre-equilibrated organic phases with 0.2 – 0.5 M HNO_3 were optimal for spectral studies. Regardless, as seen in Figure 5.5, the characteristic peaks of nitrous acid are present up to a 6 M HNO_3 pre-equilibrated organic phase.

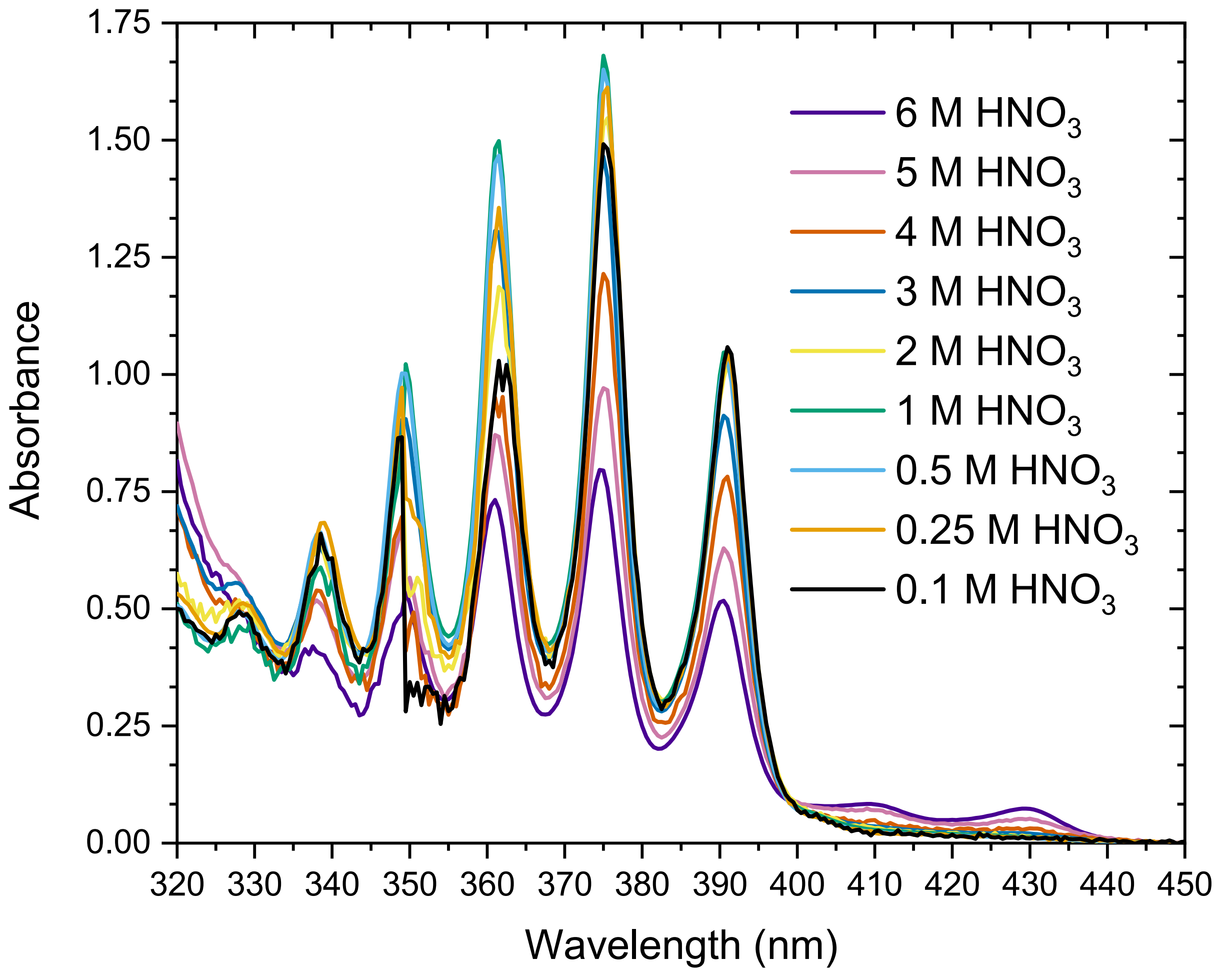


Figure 5.5: Absorption spectra of 0.02 M nitrous acid extracted into 1 M DHOA/Exxsol D60 from various nitric acid concentrations.

The molar extinction coefficients (ε) of the monoamide-HNO_2 complex in the organic phase can be approximated using Beer's Law. This was done by dividing the absorbance by one of the organic peaks (375 nm) with the $[HNO_2]_{org}$ that was calculated earlier using Equation 5.3. The ε values for the $[HNO_2]_{org}$ are reported in Table 5.2. These values compare reasonably well to the findings by Markl et al. [147] for TBP-HNO_2 complexes (ε = ~95). The ε values were not investigated at higher acidities due to the quenching effect from HNO_3 just mentioned.

Table 5.2: The ε (M^{-1} cm^{-1}) of monoamides-HNO_2 at low acidities measured at 375 nm.

HNO_3 (M)	DEHiBA	DEHBA	DHHA	DHOA
0.1	93.00	102.99	92.64	90.16
0.25	83.50	93.17	86.06	99.16
0.5	87.83	108.96	90.19	96.96
1	98.82	121.36	87.96	100.1

Since HNO_2 will decompose faster in aqueous solutions at high acidity vs. solutions with low acidity, this behavior was investigated for organic solutions using UV-Vis spectroscopy. Figure 5.6 shows the stability of nitrous acid in organic solutions that were pre-equilibrated with HNO_3. Recall that the pre-equilibrated 1 M monoamide solutions will have ca. 2 to 15 % of the nitric acid in the organic phase depending on the nitric acid concentration. (i.e. a 1 M monoamide solution that was pre-equilibrated with 6 M HNO_3 will have ca. 0.6 M HNO_3.) Two additional monoamides, DHBA and DH2EHA were considered for this analysis to further illustrate that differences in the monoamide structure does not impact the HNO_2 stability in the organic phase. The monoamide-HNO_2 complexes in pre-equilibrated organic solution with 0.1 M HNO_3 show minimal degradation over time for DHBA (Figure 5.6A) and DH2EHA (Figure 5.6B). Figure 5.6 also shows the rapid nitrous acid degradation in 6 M HNO_3 pre-equilibrated organic solutions (DHBA in Figure 5.6C and DH2EHA in Figure 5.6D). Therefore, the rates of nitrous acid decomposition in the aqueous or organic phase depend on the nitric acid concentration. Although, as the nitrous acid absorbance fades, two prominent signals appear at 409 nm and 428 nm, which suggests that a new compound is being formed (herein referred to as compound-X). Considering that the ε of $[HNO_2]_{org}$ is almost 100, the ε of compound-X is suspected to be comparatively high as well.

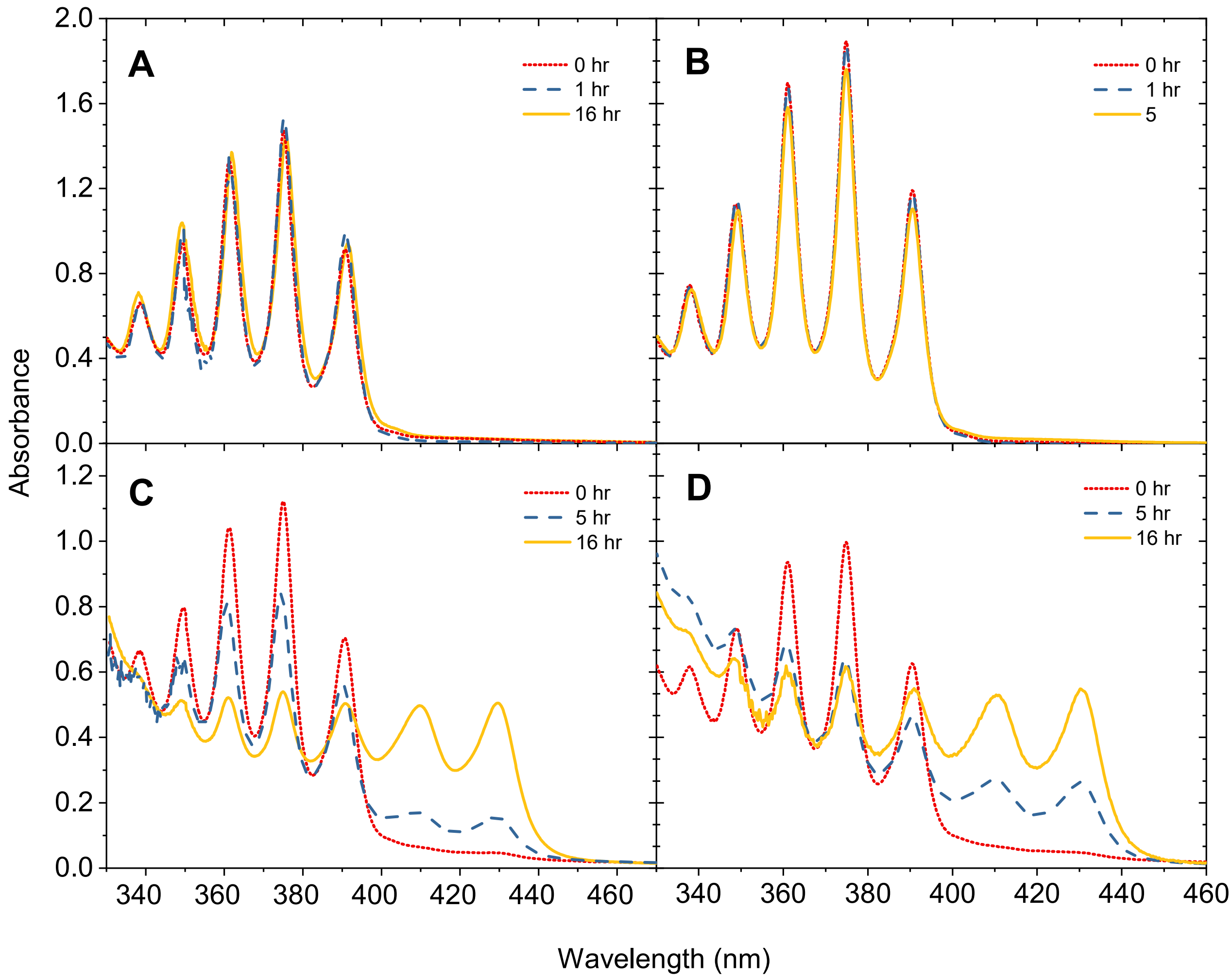


Figure 5.6: 20 mM nitrous acid decomposition in HNO_3 pre-equilibrated monoamide over time: 0.85 M DHBA with 0.1 M HNO_3 (A) and 6 M HNO_3 (C) and 1 M DH2EHA with 0.1 M HNO_3 (B) and 6 M HNO_3 (D)

Spectra of compound-X were evaluated with time (17 days total) to determine its growth and subsequent decay rate, Figure 5.7. The Figure 5.7 inset shows the changes in the absorbance over time at three different wavelengths that represent the monoamide-HNO_2 (375 nm), compound-X (428 nm), and a possible mix of those two complexes (390 nm). The inset indicates that the rapid growth at 428 nm is equivalent to the rapid decay at 375 nm. This would imply that as the monoamide-HNO_2 complex decays, the compound-X complex takes its place, assuming the molar absorptivity is equal. However, after two days the compound-X complex starts to decay away close to the same rate as the monoamide-HNO_2 complex.

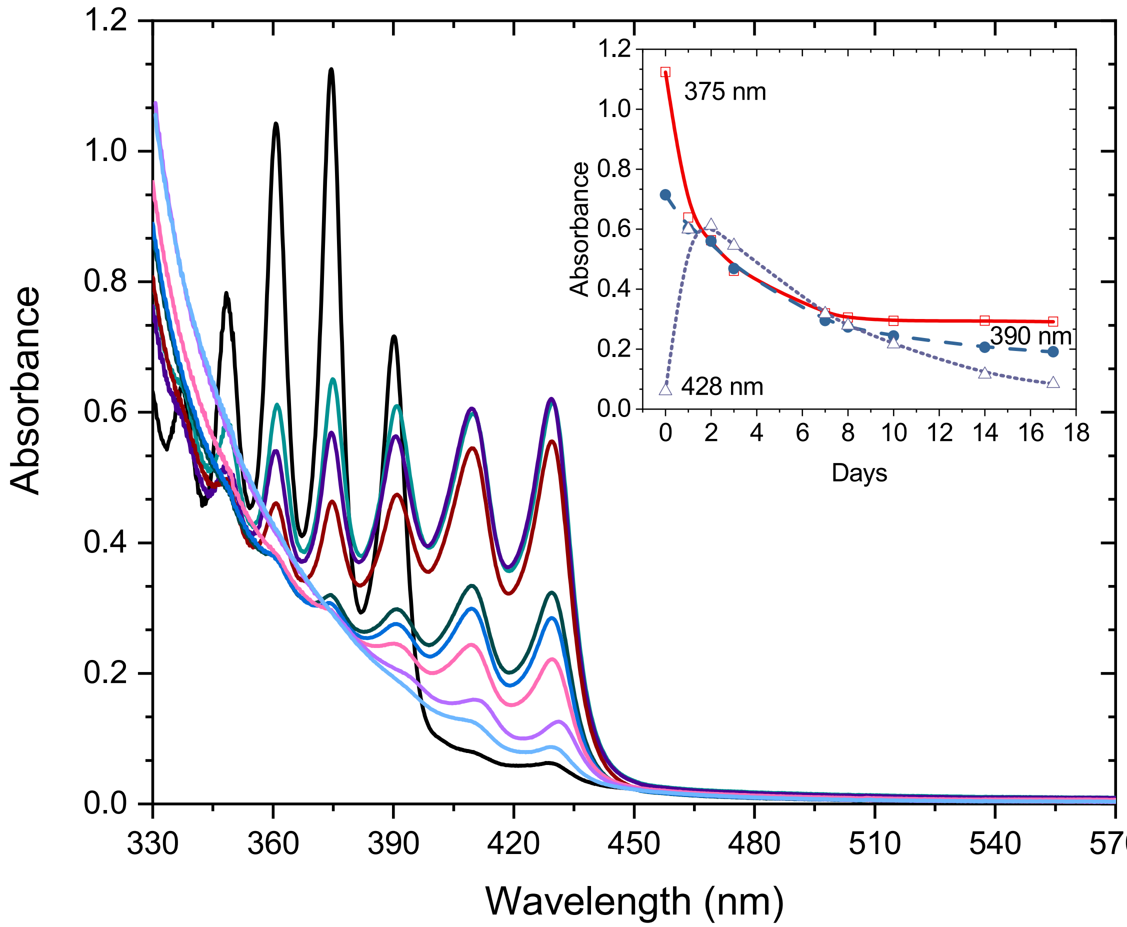


Figure 5.7: Nitrous acid decomposition in 6 M HNO_3 pre-equilibrated 0.85 M DHBA. Days 0, 1, 2, 3, 7, 8, 10, 14, and 17 correspond to 390 nm peaks decreasing over time (Day 0 is black, Day 1 is cyan, Day 3 is dark blue, etc.). Inset shows the absorbance over time for 375, 390, and 428 nm.

The rapid growth rate with a subsequent slow decay rate of compound-X is perplexing because the reaction of nitrous acid in high acidic conditions with a monoamide has not been previously reported. While most primary amides readily react with nitrous acid to form carboxylic acids [154], the monoamides used in this study are tertiary amides. The N in a tertiary amide is surrounded by three carbon chains, whereas a primary amide has one carbon chain with two hydrogens. Since nitrous acid is reacting with the extractant differently depending if the acidity is low or high, this phenomenon was investigated with TBP.

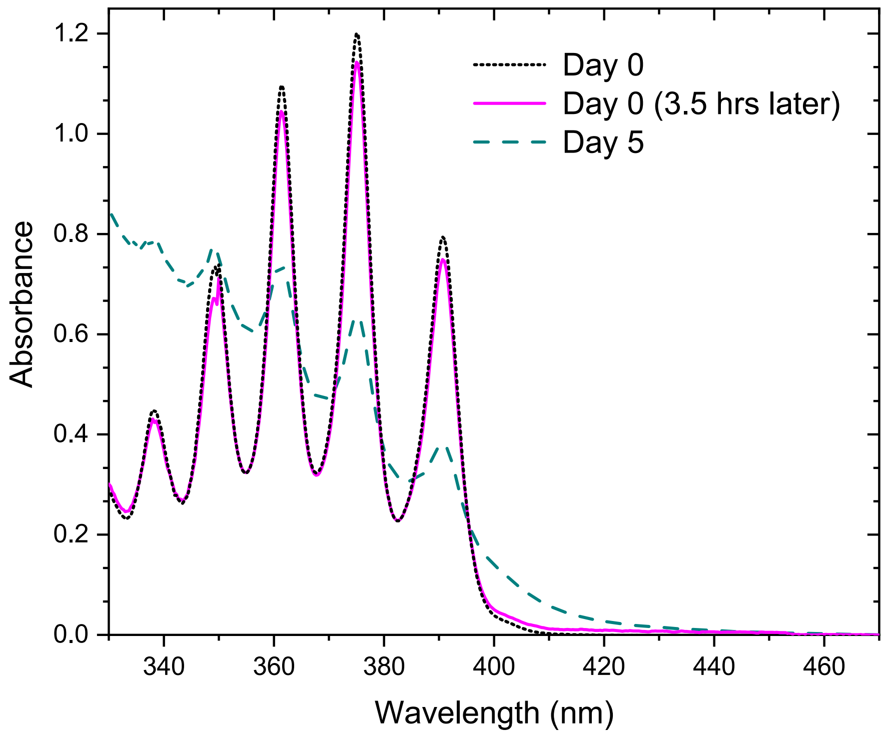


Figure 5.8: 20 mM nitrous acid in 6 M HNO_3 in 1 M TBP/dodecane, pre-equilibrated with 6 M HNO_3 initial (dot), 3.5 hours later (solid), and five days later (dash).

Even though previous studies with TBP-HNO_2 complexes were done at low HNO_3 concentrations, none mention that a separate compound forms in the organic phase at the higher acidities. Figure 5.8 confirms that there are no peaks forming at 409 and 428 nm in the time frame of a few hours to five days later in 1 M TBP/dodecane. The absence of a new complex forming with pre-equilibrated 6 M nitric acid TBP and nitrous acid suggests that the nitrous acid, catalyzed by high acidity, is reacting with the nitrogen or the carbonyl group of the monoamide. Nitrous acid decomposition in high nitric acid can form multiple gases in addition to the ones shown in Equation

5.8. Equation 5.8 shows the relevant one electron standard reduction potentials associated with decomposition of aqueous nitrous acid are shown at 1 M acidity [155]. It is probable that a nitrous acid gas is forming compound-X.

$$NO_3^- \xrightarrow{0.79} NO_2 \xrightarrow{1.12} HNO_2 \xrightarrow{0.996} NO \xrightarrow{1.59} N_2O \xrightarrow{1.77} N_2 \qquad (5.8)$$

5.3.4 Nitrous Acid Interacting with *N,N*-Dialkylamides at High Acidity

As observed in Figure 5.6, the reaction of nitrous acid with monoamides that produces compound-X takes place in highly acidic conditions. In addition to the characteristic HNO_2 peaks, the peaks from compound-X are present when the monoamide solution (not pre-equilibrated with nitric acid) is exposed to only the gas from a 6 M nitric (or 5 M sulfuric) and nitrous acid mixture in a closed system with the organic and aqueous phases in separate glass vials (Figure A.10). The absorbance from the peaks in the gas experiment are considerably lower than in the previously described experiments where the solutions were vigorously mixed. This phenomenon would suggest that the gas forming from the nitrous acid decomposition is not particularly stable and dependent on concentration of H^+.

In addition to the nitrous acid pathway in Equation 5.8, it is possible for several other side reactions to occur. The following compounds can form from mixtures of nitric and nitrous acids: nitrosonium ($H_2NO_2^+$), nitronium (NO^+), dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2), nitrogen tetraoxide (N_2O_4), nitric oxide (NO), and nitrous oxide (N_2O) [141, 156-158]. Due to reports from previous studies that the gaseous radical NO will readily react with the nitrogen in primary or secondary amides [130, 159], it seemed that NO would be the primary cause of forming compound-X. However, recall that the monoamides used in this study are tertiary amides. It is unknown if the carbon chains branching off the amide center of *N,N*-dialkylamides shelter the complex from reacting with NO. The gas NO can readily form via the following reactions.

$$4HNO_2 \leftrightarrow 2H_2O + 4NO + O_2 \tag{5.9}$$

$$2HNO_2 \leftrightarrow NO + NO_2 + H_2O \tag{5.10}$$

It is possible that one of the other mentioned compounds could also be participating in the reaction with the monoamide, such as nitrosonium that forms at higher acidities [156]. It is unlikely that the mentioned HNO_2 derivatives bind directly to the monoamide because most of these compounds have spectroscopic signatures outside of the 400 - 450 nm range [151]. The major exception is the gas NO_2. However, unless a catalyst is present, NO_2 will not react or complex with the alkyl chains on the monoamide [160, 161]. Ascertaining the structure of compound-X or the combination of monoamide and nitrous acid degradation products by correlating the UV-Vis analysis with NMR or mass spectroscopy is difficult. The maximum concentration of compound-X using 20 mM nitrous acid is at most ca. 2 % of the total monoamide concentration.

NMR of DH2EHA with ^{13}C (Figure A.11 and Figure A.12) was used to try and determine the compound-X structure. The carbon center of the carbonyl group in a *N,N*-dialkylamide structure has ca. 180 ppm signature in ^{13}C NMR. The inset in Figure A.12 confirms that HNO_3, and most likely HNO_2 are binding to the carbonyl group due to the ^{13}C shift. Interestingly, as the monoamide sits with nitric and nitrous acid over time, the new peak grows but does not shift as evident by comparing Figure A.11 and Figure A.12. The ^{1}H NMR of DH2EHA, Figure A.13, shows overlap in the spectrum from pre-equilibrated 6 M HNO_3 with 20 mM HNO_2 in 6 M HNO_3 that has sat for 24 hours. The NMR results indicate that compound-X does not noticeably impact

^{1}H NMR. On the other hand, the variations in the ^{13}C NMR suggest overall structural changes of the monoamide or the growth of a monoamide degradation product.

Monoamides will degrade at high nitric acid concentrations (e.g. 6 M HNO_3). Even though the percentage of the degradation products formed is quite small [75], nitrous acid and its decomposition products (specifically nitric oxide) readily reacts with amines and non-tertiary amides [141]. Therefore, the two proposed pathways for forming compound-X is that as the monoamide degrades from either high nitric acid or a nitrous acid decomposition gas, the nitrous acid and nitric oxide react with a monoamide degradation product.

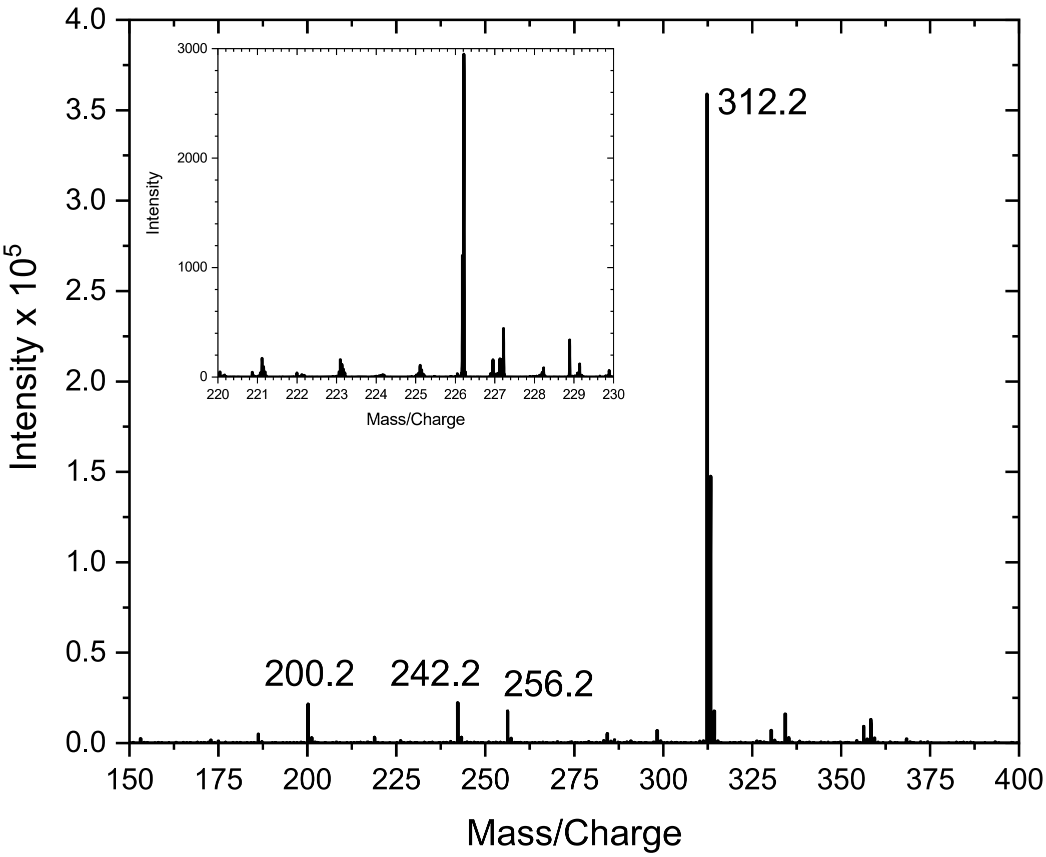


Figure 5.9: Mass spectrometry analysis of DEHBA in Exxsol D60 with 6 M HNO_3 and 20 mM HNO_2 for 24 hours. The values are the protonated mass/charge (m/z) of prominent compounds. Inset zooms in for EHBA-NO peak.

The results from mass spectrometry show the compounds that are forming in a 6 M HNO_3 solution with nitrous acid, Figure 5.9. Since mass spectrometry is an extremely sensitive technique and the monoamides are not 100 % pure (greater than 98 %), it is possible that the degradation products might be in addition to impurities remaining from monoamide synthesis. Also, it is quite difficult to ionize acids using electron spray mass spectrometry and consequently troublesome to analyze acidic compounds. The hydrogen bond is easily severed during the nebulizing process. Three of the prominent peaks in the mass spectrum are the protonated forms of DEHBA (312.2 m/z), di-2-ethylhexylamine (DEHA = 242 m/z), and mono-2-ethylhexylbutanamide (EHBA = 200.2 m/z). The occurrence of the fourth peak (256.2 m/z) is peculiar. A possible compound that can form is when a double bound oxygen takes the place of two alkyl protons in DEHA, as part of an oxidative reaction [75].

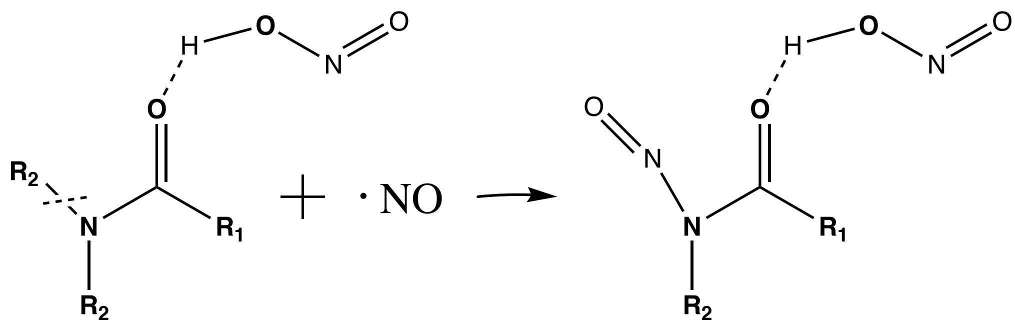


Figure 5.10: Proposed reaction pathway to form compound-X with a simplified monoamide. R_1 and R_2 represent alkyl chains.

An amine like DEHA can readily react with HNO_2 to form a yellowish oil [141, 162], a color that is observed in the organic solution over time. The other main possibility is the secondary amide EHBA reacting with nitric oxide. The inset in Figure 5.9 shows a unique peak that indicates the formation of the adduct (EHBA-NO) at 226.2 m/z. The reaction scheme in Figure 5.10 indicates the proposed reaction pathway [163] of the adduct forming and then binding to HNO_2. (As explained, hydrogen bonded nitrous acid to EHBA-NO would be difficult to see with mass spectrometry.) Either of the two complexes formed could give rise to the two additional peaks seen in the UV-Vis spectra. Isolating the compounds from the monoamides is difficult because it was verified spectroscopically that monoamide-HNO_2 and compound-X are fairly stable even when washed with water, Figure A.14.

Considering that the goal is to use a monoamide as a replacement for TBP in PUREX, it was investigated to see if compound-X would have an effect on the uptake of an actinide at a trace level metal concentration. Little to no variation was found in the distribution ratios of trace U(VI) between pre-equilibrated 1 M DHOA (used immediately), two-week old pre-equilibrated 1 M DHOA with 6 M HNO_3, and two-week old pre-equilibrated 1 M DHOA with 6 M HNO_3 and 20 mM HNO_2 (Figure A.15). This observation indicates that compound-X is innocuous and does not interfere with actinide extraction by a monoamide.

5.4 Conclusions

The various *N,N*-dialkylamides used in this study demonstrate that their structure does not appreciably impact the extraction nor the stoichiometry of HNO_2. Also, monoamides extract HNO_2 similarly to TBP. As the concentration of HNO_3 increases there is a steady decrease in the amount HNO_2 being extracted. The dominant stoichiometric complex of monoamides to HNO_2 seems to be 1:1 at less than 2 M HNO_3. However, at a higher acidity (4 M HNO_3), a 1:2 monoamide-HNO_2 seems to be forming.

While the spectra of TBP-HNO_2 and monoamide-HNO_2 complexes are similar in the organic phase at low acidities, there is a distinct change in the monoamide-HNO_2 complex at higher acidities. The growth of separate peaks suggests that a HNO_2 degradation product is reacting with the amide center of the monoamide or a degradation product because the new peaks are not observed with a TBP-HNO_2 complex.

While compound-X does not affect distribution ratios for trace metal conditions, it is uncertain what effect HNO_2 would have on monoamides for a full-scale process such as PUREX. Drastically increasing the nitrous acid concentration to form a corresponding amount of compound-X could cause other side reactions that do not occur at the low nitrous acid concentration. On the other hand, nitrous acid is generally employed at low acidities, which might prevent complications that would occur from nitrous acid or its decomposition products.

CHAPTER 6

CONCLUDING REMARKS AND FUTURE POSSIBILITIES

6.1 Summary

The *N,N*-dialkylamides, specifically DHOA, DHHA, DEHBA, and DEHiBA, were investigated, evaluated, and tested to determine their adequacy to replace TBP or HDEHP for Np(VI)/Pu(IV) and Np(VI)/Th(IV) separations. Three of the monoamides, DHOA, DHHA, and DEHBA, are promising extractants for Np(IV, VI) and Pu(IV, VI). While DHHA and DHOA slightly surpass DEHBA in extraction, any of the three can feasibly be used for an efficient Np(VI)/Pu(IV) separation (MAPNEX). Since DEHiBA extracts Np(VI) considerably greater than the tetravalent actinides, that monoamide would be ideal for Np purification from actinide contaminants that could be selectively adjusted to the tri-, tetra-, or pentavalent oxidation states in the presence of Np(VI).

The MAPNEX study used DHHA to coextract Np and Pu and then separate them using selective redox agents. That study also reflects the separation results if DHOA (and conceptually DEHBA) were used instead of DHHA. Extracted Np(VI) is first reduced to Np(V) in separate low acidity stripping stages and then reduction of Pu(IV) to Pu(III) is required for purification of both actinides since neither Np(V) nor Pu(III) are extracted well at the low acidities. Low acidities are necessary because at higher HNO_3 concentrations Np(V) and Pu(III) will be oxidized to extractable states. Unfortunately, controlling the oxidation states with a mix of metals was observed to be difficult even at tracer concentrations, resulting in an inefficient purification of either actinide in this study. However, the selective stripping stages might be improved by using significantly higher metal concentrations, which would substantially decrease the experimental uncertainty due to counting error for the later stages and may enable isolation of the effect the reducing agents have on the monoamides.

Studies with the monoamides revealed distinct differences in their ability to extract various actinides in their different oxidation states. Purification of Np and Pu oftentimes requires manipulating their oxidation states to achieve an efficient separation, especially when using a single extractant. There are two possible alternatives that deviate from the overall TBP-based Np/Pu process used at ORNL. The first scheme is a monoamide-mediated Np(IV)/Pu(IV) separation. This process would adjust Np and Pu to their tetravalent states for coextraction. Hydroxylamine would be added to first reduce Pu(IV) in the organic phase to be stripped as Pu(III). The Np(IV) can then be recovered in dilute nitric acid.

The second scheme is an alternative based on a previous study by Condamines and Musikas [46]. They suggested using a mixture of DEHBA and DEHiBA to partition the actinides, Pu(IV) and U(VI). Since U(VI) and Np(VI) are extracted similarly, this attractive concept of using two monoamides might work for MAPNEX. This is possible because as the concentration of HNO_3 decreases, the Pu(IV) will readily strip from DEHiBA whereas Np(VI) would stay in the organic phase because of the presence of DEHBA. A key difference though is the substantially higher percentage of Pu to Np in this process vs. the Pu to U in PUREX which would impact the solvent loading effects. However, using DEHiBA with one of the other studied monoamides could be an interesting configuration to explore when finalizing a process for MAPNEX monoamide represented in Figure 6.1.

I found the other separation process of interest, the purification of Np(VI)/Th(IV) mixtures, could be successful using the branched monoamides. The steric hinderance of the ethyl branching on the nitrogen substituents of DEHBA and DEHiBA make them ideal for separating Np(VI) from

Th(IV). As mentioned earlier, the isobutyl group in DEHiBA is effective in preventing the efficient extraction of any tetravalent actinide (Th, Np, and Pu). This extraction behavior is useful if there are Pu contaminants, along with the Th, in the initial Np stockpile as Pu(IV), like Th(IV), would not be extracted with the Np(VI).

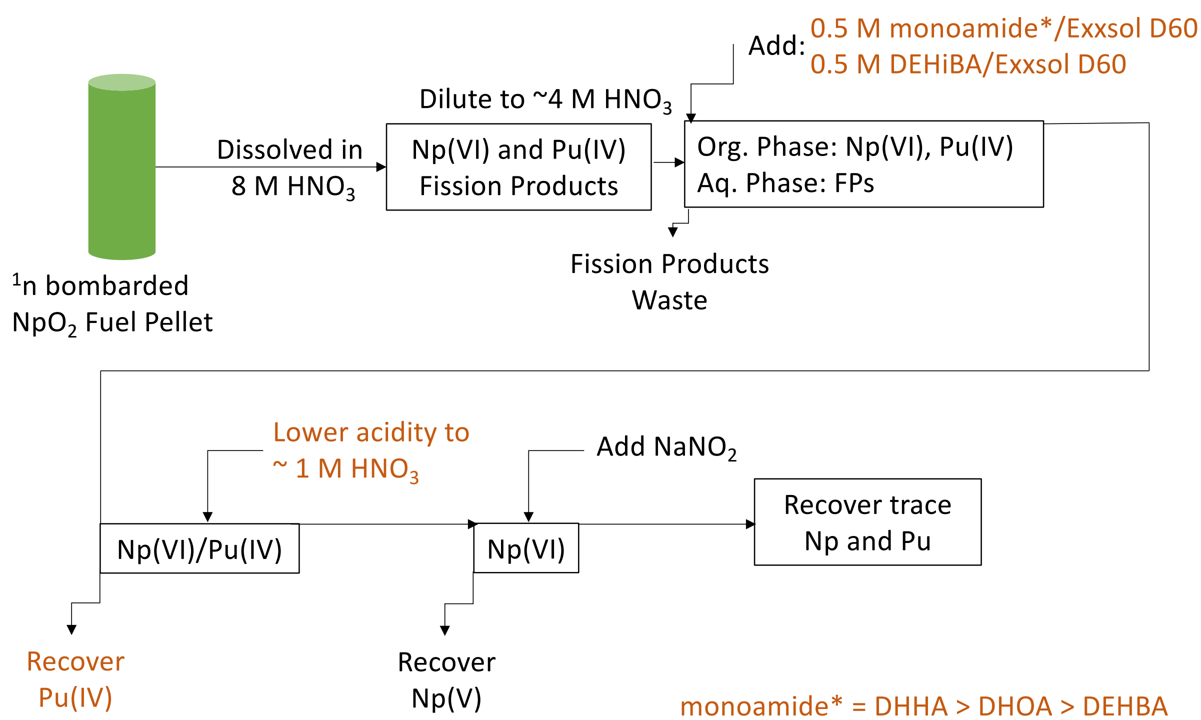


Figure 6.1: Slightly modified MAPNEX parameters from Figure 1.14, modifications are indicated with orange text.

6.2 Future Work

There are multiple components to consider in substituting a new extractant into a full-scale process. This study considered a few of those components such as the extraction potential at trace and non-trace scale metal concentrations, stoichiometry of Np and Pu with monoamides, and some redox effects. Omitted factors include the effect of macro concentrations of a ^{237}Np and ^{238}Pu mixture (which include radiation effects), extraction mechanisms for Th(IV) and pentavalent actinides (specifically Np and Pa), and interference from fission products.

6.2.1 Macro Np/Pu Separations

It is ideal to study the possible metal loading, radiation, and redox effects on monoamides for process scale $^{237}Np/^{238}Pu$ separations. Comparing the results of the distribution ratios for semi-macro Np in Chapter 3 and trace Np in Chapter 4 shows a depression in distribution ratio values going from trace to semi-macro. The direct cause is uncertain because the monoamide concentration is much greater than the Np concentration for both studies. In other words, the metal concentration should not have affected the distribution ratios due to the large excess of unbound monoamide present in solution. Impurities formed during the monoamide synthesis or complexes that interact with the Np that would then interfere with effective binding to the monoamide carbonyl group are possibilities. However, experiments with macro ^{238}U with a ^{233}U spike indicate that no contaminant capable of extracting the Np more strongly than the monoamide was present in the organic phase. Nevertheless, the semi-macro Np experiments show that even by slightly scaling the process to higher concentrations of metals will complicate the separation.

The other major effects that are introduced from increased metal concentration, radiolysis and thermal degradation, could impact the Pu purification as well [44, 63, 75, 77]. While monoamides are generally resistant to degradation and their degradation products do not cause noticeable deleterious side effects, those studies were done under PUREX conditions. Comparatively, the two dominant extracted nuclides $^{238}Pu/^{237}Np$ have an overall significantly higher radioactivity than the actinides extracted in PUREX (especially the ^{238}Pu). Therefore, the radiolysis of the monoamides from alpha decay would be considerably higher for a MAPNEX separation.

The effects of nitrous acid on monoamides (Chapter 5) was observed to not change the distribution ratios for ^{233}U at the trace scale. Since the exact nature of the complex is unknown, it is possible that unintentional side effects will occur at higher metal and nitrous acid concentrations. The decomposition products of nitrous acid are well known and it would be prudent to experiment with those gases (e.g. NO, NO_2. N_2O_4, N_2O_3) separately on the monoamides to determine if there are consequential effects for actinide extraction.

6.2.2 *N,N*-Dialkylamide-Actinide Structures

While the structures of monoamides binding to Pu(IV) and U(VI) have been recently explored, it would be interesting to also probe the structures of monoamides with actinide ions that are poorly extracted (specifically Th(IV), Pa(V), and Np(V)). Comparing multiple monoamide-actinide complexes may illuminate some of the reasons why Th(IV) is not extracted as well as the other tetravalent actinides (Np and Pu) or why Pa(V) is extracted noticeably better than Np(V). My preliminary measurements of the Th(IV):monoamide stoichiometric ratio, described below, offer a possible reason for poor Th(IV) extraction, but structural studies would illuminate this further.

The general extraction equilibrium of neutral actinide-monoamide complexes are represented in Equation 6.1, as referenced earlier. There is general agreement that the extractant equilibrium for Th(IV) contains at least a 1:3 Th:monoamide complex (n = 3). It is believed that the 3rd monoamide binds to the inner coordination sphere of Th(IV), instead of the outer coordination sphere like Pu(IV), because the Th(IV) ion is sufficiently large to accommodate more than two monoamides [46, 54, 164].

$$\mathrm{An}^{4+} + 4\mathrm{NO}_3^- + \overline{n\mathrm{Monoamide}} \leftrightarrow \overline{\mathrm{An(NO_3)_4(Monoamide)}_n} \qquad (6.1)$$

However, my preliminary experiments find an extractant dependence slightly lower than 2 (n = 2), Figure 6.2. This extractant dependence study (experimental details in Chapter 4) was done using the nonbranched amides (DHHA and DHOA) instead of branched monoamides due to the low distribution ratios of Th(IV) with branched monoamides even at high acidity. This work agrees with two separate studies that looked at the stoichiometry of the extracted Th(IV) complexes. Those studies found extractant dependence slope of ca. 1.66 and ca. 1.5 at low concentrations (less than 0.02 to 0.1 M) of DEHBA and DEHiBA, respectively [46, 165]. Note that the other studies used a nitrate salt to boost extraction.

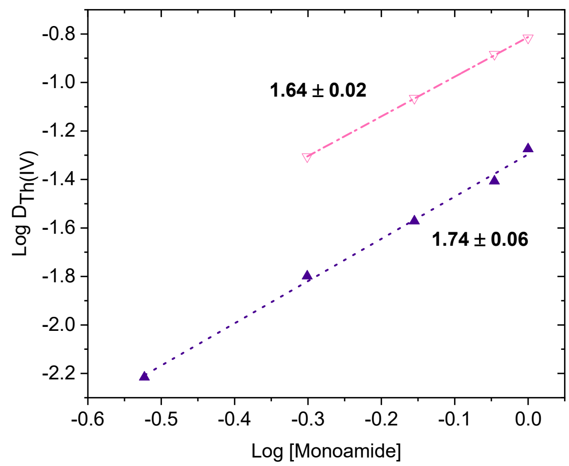


Figure 6.2: Th stoichiometric ratios DHHA (triangle), DHOA (inverse triangle) at 4 M HNO_3.

The same group that found DEHBA to have an extractant dependence of ca. 1.66, also found a 1:3 (Th(IV):monoamide) complex using higher monoamide concentrations (up to 2 M) [54]. They concluded that the discrepancy was due to di-solvate complexes being favored at extremely low concentrations of extractant. Regardless, there seems to be discrepancies on whether a 1:3 or 1:2 complex is dominant for a given set of conditions [46, 110]. These discrepancies are interesting because of the observations that other tetravalent actinides, Np and Pu, can form an anionic complex that is extracted by two protonated monoamides at higher acidities (Equation 6.2) [91].

$$\mathrm{An}^{4+} + 2\mathrm{H}^{+} + 6\mathrm{NO}_3^{-} + \overline{2\mathrm{Monoamide}} \leftrightarrow \overline{\mathrm{An(NO_3)_6(H \cdot Monoamide)_2}} \tag{6.2}$$

However, it is unknown if Th(IV) can also form anionic complexes, which is another pathway to extract Th(IV). Comparing the absorption spectra of the organic monoamide complexes with organic Th(IV) nitrate salts can help isolate specific Th(IV) complexes that are being extracted by monoamides. Studying a range of acidic concentrations and monoamide concentrations with extended X-ray absorption fine structure (EXAFS) could prove if Th(IV):monoamide are formed as 1:2 or 1:3 complexes depending on conditions and also determine if the 3rd monoamide binds to the inner coordination sphere of Th(IV) or if Th(IV) forms anionic complexes with monoamides. The poor extraction of Th(IV) might be ascertained once the extraction mechanisms are better understood.

The other poorly extracted actinide compounds, the pentavalent actinides Np and Pa, present an intriguing puzzle due to the lack of studies into the structure and stoichiometry of monoamide-An(V) complexes. Even though the Pa(V):monoamide is reported to have a 1:1 metal:extractant stoichiometry [122], the nature of the extracted Pa(V) compound is uncertain. On the other hand, the extracted Np(V) compound is probably $NpO_2(NO_3)$ [166] but there has not been a study with monoamides to confirm a 1:1 stoichiometric ratio. Although, it is necessary to point out that the chemistry of the stable Np(V) and Pa(V) complexes differ. For instance, Pa(V) can easily form hydrolyzed compounds in acidic solutions whereas Np(V) does not [167]. The hydrolyzed Pa(V) compounds tend to 'stick' to glass surfaces [168], which could interfere with solvent extraction studies. A study of extractants with Np(V) is complicated because Np(V) can disproportionate even in the organic phase [100, 169]. If these problems could be overcome, important and useful information for understanding these complexes and why Pa(V) is better extracted than Np(V) over a range of acidities would be available from looking at their structures using EXAFS.

6.2.3 Separation of Fission Products

Major metals that were omitted from this extraction study are the cladding materials (mainly aluminum) and fission products from Np and Pu. As shown in Figure 1.4, the process of irradiating the ^{237}Np to form ^{238}Pu will create fission products. Separate studies examined using monoamides to extract fission product metals (e.g. Ru, Cs, Sr, Eu, Fe, Zr), showed that only Zr(IV) was appreciably extracted [48, 76, 136, 170]. While a couple of those studies simulated process scale conditions to see the effects that other metals could have for PUREX or THOREX [48, 170], there has not been a Pu/Np study that simulated process conditions with fission products. Fortunately, the radioactivity of the chemically problematic fission products, ^{95}Zr ($t_{1/2}$ = 64 days) and ^{95}Nb ($t_{1/2}$ = 35 days) in the ^{238}Pu product greatly diminish while in storage [12]. While it is unlikely that fission products would have a different impact on the solvent extraction system, it would be beneficial to ensure efficient separation of the Np/Pu from the fission products with monoamides.

6.3 MAPNEX Revisited

The reason for this work was to assess the potential for monoamides to replace TBP or HDEHP in the separation and purification of ^{237}Np and ^{238}Pu. The four monoamides that were chosen showed considerable promise towards this goal. This research has contributed to understanding the extraction behavior of a variety of actinides using the aforementioned monoamides, directly comparing well-studied actinides (e.g. Th(IV), U(VI), and Pu(IV)) to understudied actinides (e.g. Am(III), Pu(VI), Np(IV-VI)). In fact, another key aspect of these studies was to greatly expand the available literature about Np monoamide extraction and to propose Np(VI) separation strategies from Pu(IV) and then Th(IV). Even though manipulating the redox chemistry of Np and Pu within MAPNEX was problematic in my tests of the MAPNEX concept. This is an issue for any extractant, even TBP [14], and it is certainly a surmountable problem for MAPNEX.

The ability to be completely incinerated and the relatively innocuous nature of the degradation products are crucial advantages that monoamides have over TBP. Another benefit that DHHA, DHOA, DEHBA, and DEHiBA have is their resistance to third phase formation in Exxsol D60 and with the metal concentrations used at ORNL. The particularly high activity of the Np/Pu stream (compared to a used fuel stream) will cause radiolytic degradation of the monoamides. However, the resulting degradation products have not been observed to noticeably impede the separation of either actinide. With these benefits in mind, the following important studies are needed before these monoamides can be fully implemented for ^{238}Pu purification in space applications. First, is fully understanding what occurs with monoamides when they are mixed with in concentrated nitric acid containing nitrous acid. Second, a simulated Np/Pu separation close to process scale metal concentrations is needed, as detailed in the previous section. After the favorable results from experimentation with close-to-process conditions the monoamides could be ready pilot-scale demonstration and then use in ^{237}Np/^{238}Pu purification.

6.4 Scientific Advances

Compared to their initial inception, *N,N*-dialkylamides have gained substantial renewed interest in recent years as a replacement for TBP in PUREX and THOREX. My work broadens the application of DHHA, DHOA, DEHBA, and DEHiBA for their possible use in ^{237}Np and ^{238}Pu purification. The principle motivation for this study was to circumvent the excessive phosphorus contamination that is currently present in ^{237}Np and ^{238}Pu products by using an incinerable extractants that do not contain phosphorus, specifically *N,N*-dialkylamides.

The studies into *N,N*-dialkylamide-Np chemistry within this dissertation support the feasibility of *N,N*-dialkylamides for Np/Pu separations. The best extractant for Np(VI) and Pu(IV), DHHA, has been previously overlooked, most likely due to concerns about high metal loading causing a third phase, which is not an issue for ^{238}Pu purification considering that DHHA does not approach the heavy metal loading limit within the Np/Pu purification process. DEHiBA has been proposed to be useful for extracting U(VI) from a mix of other metals [171, 172] but no published study has proposed and demonstrated its potential for Np(VI) purification as shown in this dissertation. In the course of ascertaining the optimal *N,N*-dialkylamide(s) to be used for Np/Pu purification, this research has additionally compared the behavior of Np(IV) and Np(VI) against An(IV) and An(VI) with four different *N,N*-dialkylamides. This in turn allows general predictions to be made for the separation chemistry of Np(IV) and Np(VI) with other *N,N*-dialkylamides that have only been studied for uranium and plutonium extraction.

N,N-dialkylamides extract metals and acids similarly to TBP, but a combination of nitrous acid with high concentrations of nitric acid causes a decomposition reaction in *N,N*-dialkylamides that cannot occur for TBP. This research indicates that possible effects on actinide extraction from the decomposition product are minimal to non-existent at low nitric acid concentrations. However, the difficult to remove decomposition product could impact the extraction power of *N,N*-dialkylamides in a full scale process that prolongs the exposure of the organic phase to nitric acid (acid hydrolysis) and to the high radiolytic activity of the ^{237}Np/^{238}Pu mixture. The combination of these two degradation modes also could facilitate other unintended side reactions to occur with the decomposition product. These findings and the preliminary studies of the decomposition pathway has contributed to understanding the distinctive chemistry of *N,N*-dialkylamides with an important Np redox agent.

APPENDIX A

SUPPLEMENTARY DATA

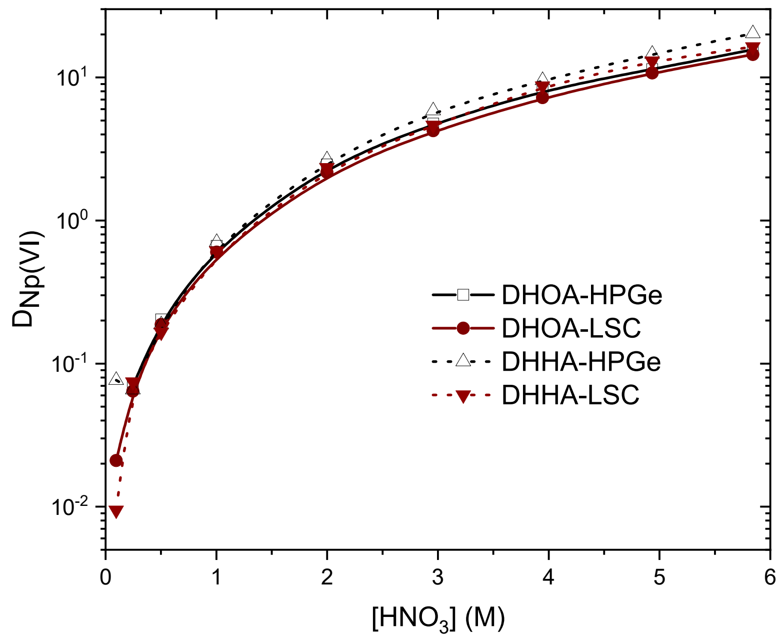


Figure A.1: Comparison of the distribution ratios calculated from the γ-counts using an HPGe detector and the α-counts determined by liquid scintillation counting using 1 M DHOA and 1 M DHHA diluted in Exxsol D60 to extract Np(VI). Lines are plotted as a visual guide.

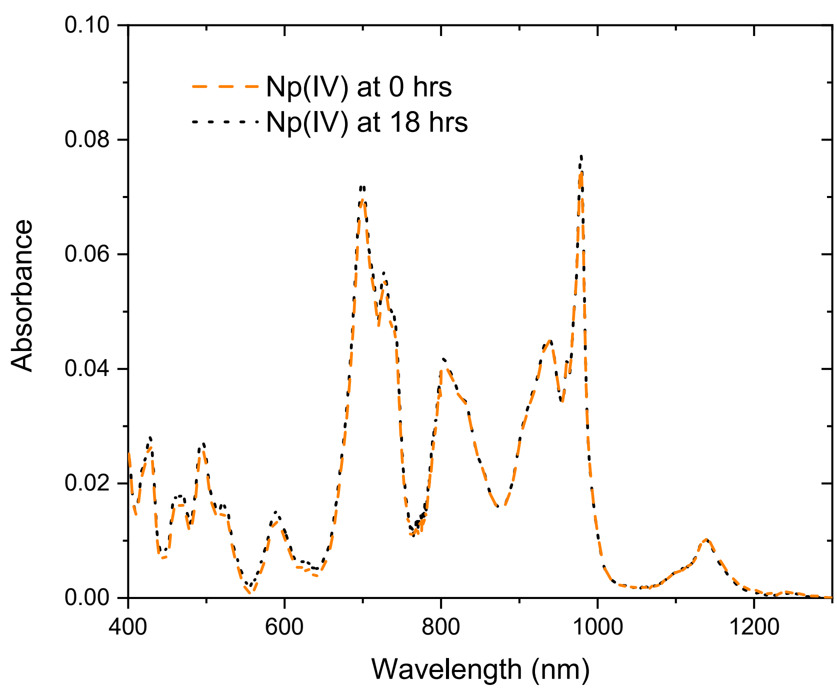


Figure A.2: Np(IV) stability in 4 M HNO_3 over 18 hours in the presence of 4 x 10^{-4} M ferrous sulfamate.

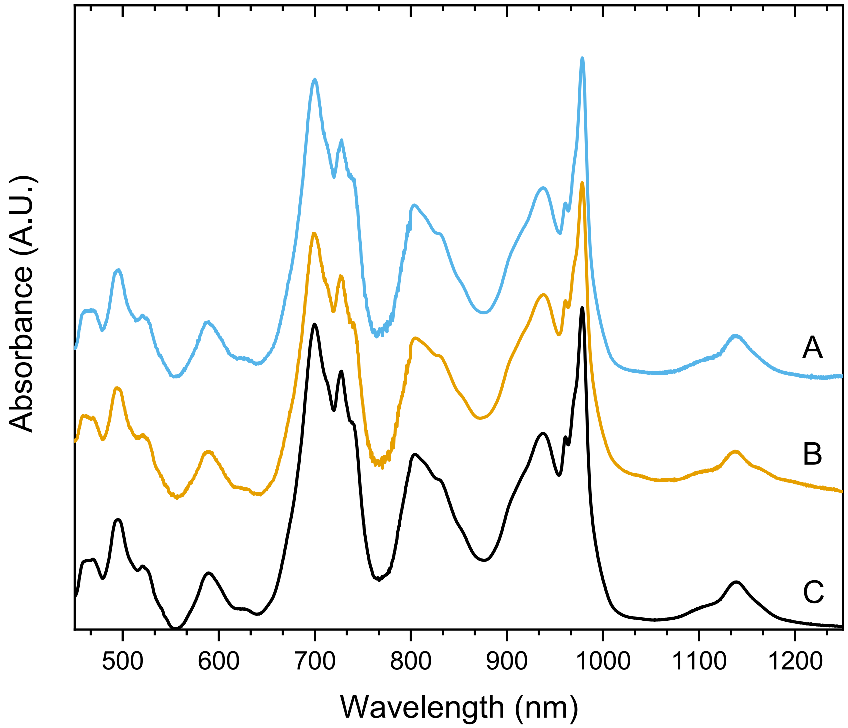


Figure A.3: Comparison of the absorption spectra of Np(IV) solutions in 4 M HNO_3: (A) Np(IV) in 4 M HNO_3/ 4 x 10^{-4} M ferrous sulfamate, (B) Aqueous Np(IV) in 4 M HNO_3/1.3 x 10^{-3} M ferrous sulfamate after contact with 1 M DHOA/Exxsol D60 (C) Aqueous Np(IV) in 4 M HNO_3/1.4 x 10^{-3} M ferrous sulfamate before contact with DHOA. Lines are offset for clarity.

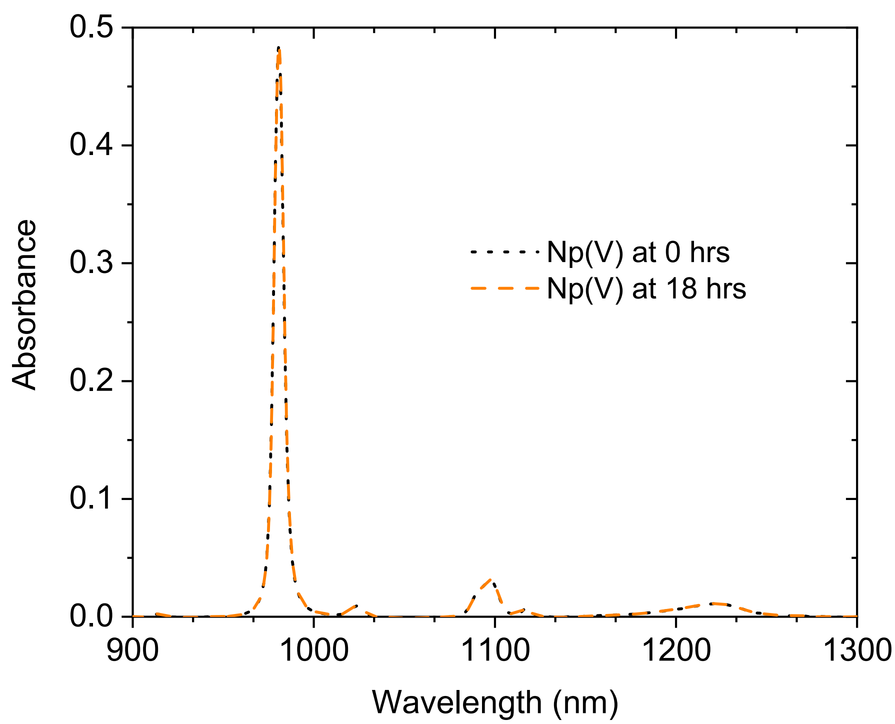
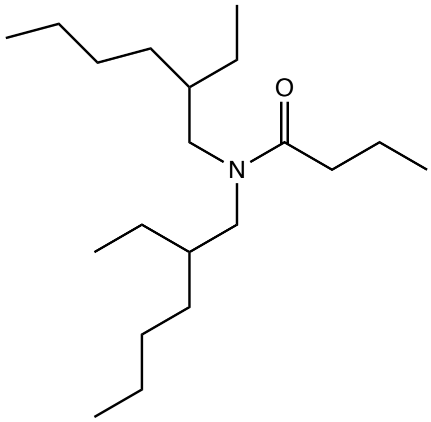
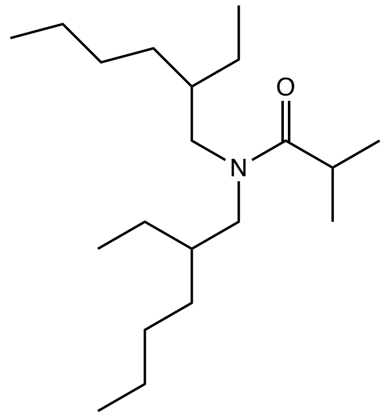


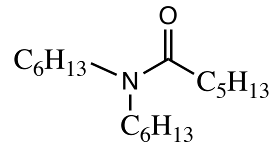
Figure A.4: Stability of Np(V) in 0.1 M HNO_3 over 18 hours.



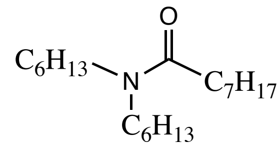
DEHBA



DEHiBA



DHHA



DHOA

Figure A.5: Monoamide Structures: DHHA and DHOA are abbreviated for clarity Carbon chains off the N is the dialkyl side and the carbon chain off the carbonyl is the acyl side.

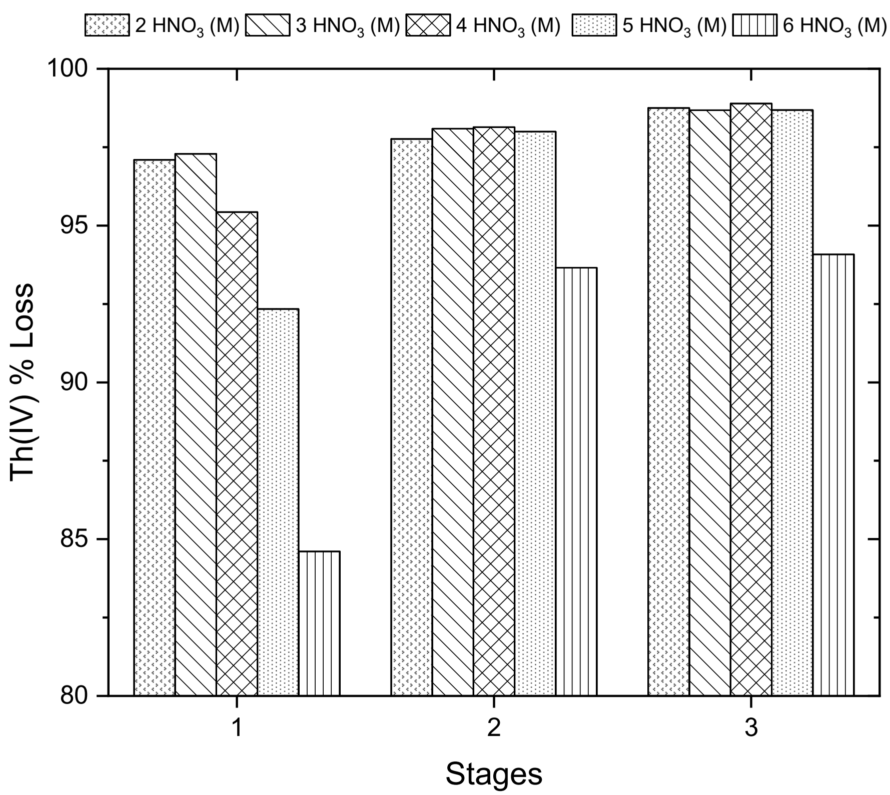
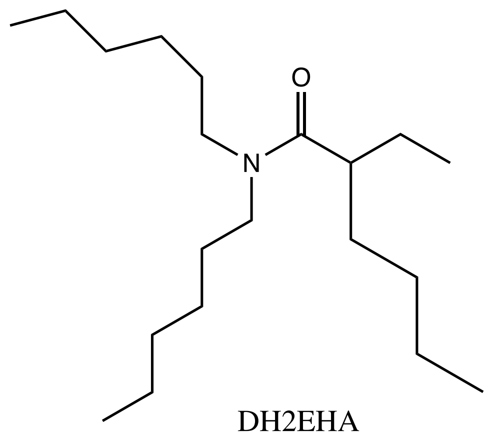


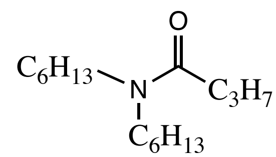
Figure A.6: The legend denotes the initial acidic concentrations that were used in Stage 1 and then to scrub (Stage 2). The acidic concentration for Stage 3 was 2 M HNO_3. Each stage reflects the total percentage loss of the initial Th(IV) concentration from a mixture of Np(VI) mixed with 4 mM Th(IV) using 1 M DEHBA/Exxsol D60. Data for Np(VI) are omitted for clarity.

Table A.1: The column HNO_3 denotes the initial acidic concentrations that were used in Stage 1 and then to scrub (Stage 2). The acidic concentration for Stage 3 was 2 M HNO_3. Each stage reflects the total percentage loss of the initial Th(IV) concentration from a mixture of Np(VI) mixed with 4 mM Th(IV) using 1 M DEHiBA/Exxsol D60.

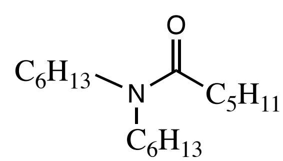
HNO_3 (M)	Stage 1	Stage 2	Stage 3
5	99.68	99.90	99.96
6	99.53	99.92	99.98



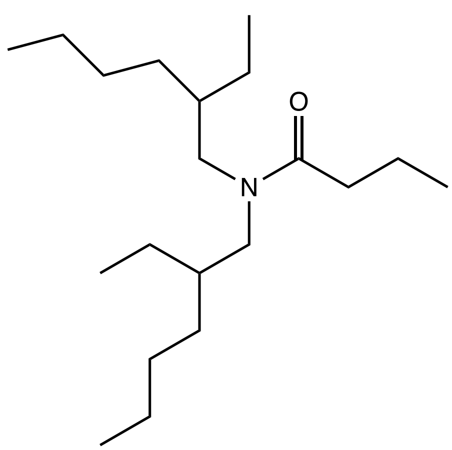
DH2EHA



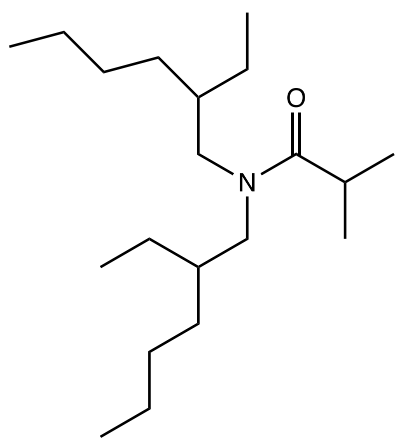
DHBA



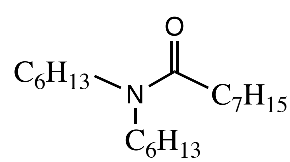
DHHA



DEHBA



DEHiBA



DHOA

Figure A.7: Monoamide Structures

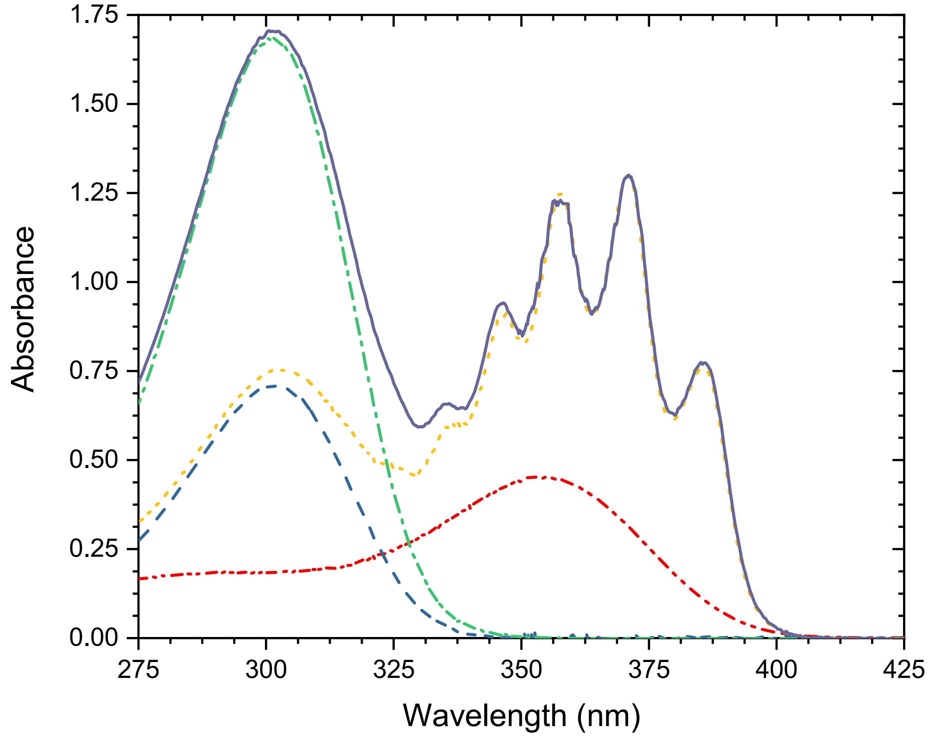


Figure A.8: Spectral comparison of $NaNO_2$ in solution, nitric acid peaks and nitrous acid at different nitric acid acidities: 20 mM $NaNO_2$ ( ), 0.1 M HNO_3 ( ), 0.1 M HNO_3 with 20 mM $NaNO_2$ ( ), 0.25 M HNO_3 ( ), 0.25 M HNO_3 with 20 mM $NaNO_2$ ( ).

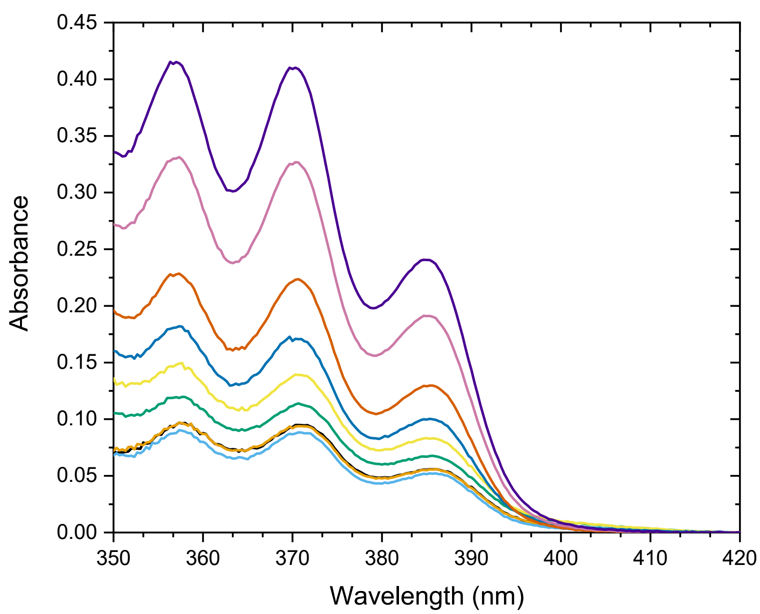


Figure A.9: Spectra of nitrous acid in aqueous phase after contact with 1 M DHOA in Exxsol D60. The decreasing acidities correspond directly with decreasing absorbance: 6, 5, 4, 3, 2, 1, 0.5, 0.25, and 0.1 M HNO_3.

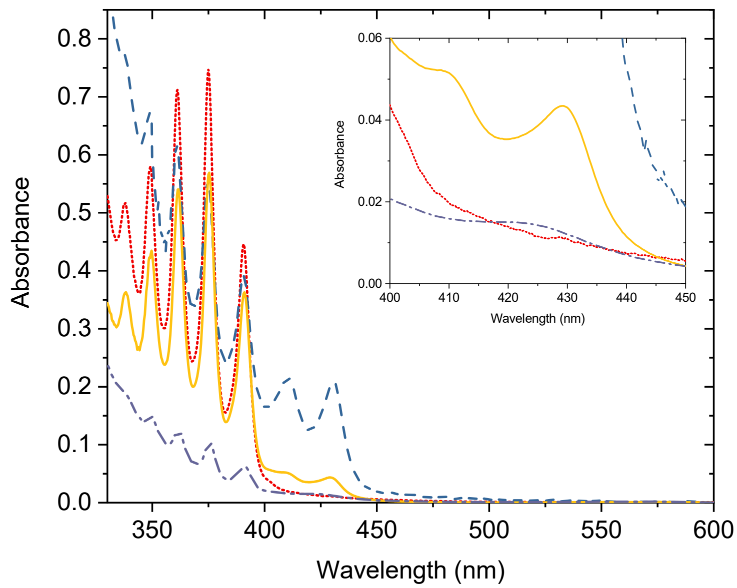


Figure A.10: Spectra of non-pre-equilibrated monoamide in Exxsol D60 exposed to gas under various conditions. 1 M DH2EHA exposed to gas from 20 mM HNO_2 in 0.1 M HNO_3 (dot) and 6 M HNO_3 (dash). 1 M DHBA exposed to gas from 20 mM HNO_2 in 5 M H_2SO_4 (solid) and 1M DHBA mixed with 20 mM $NaNO_2$ exposed to gas from 6 M HNO_3 (dash dot).

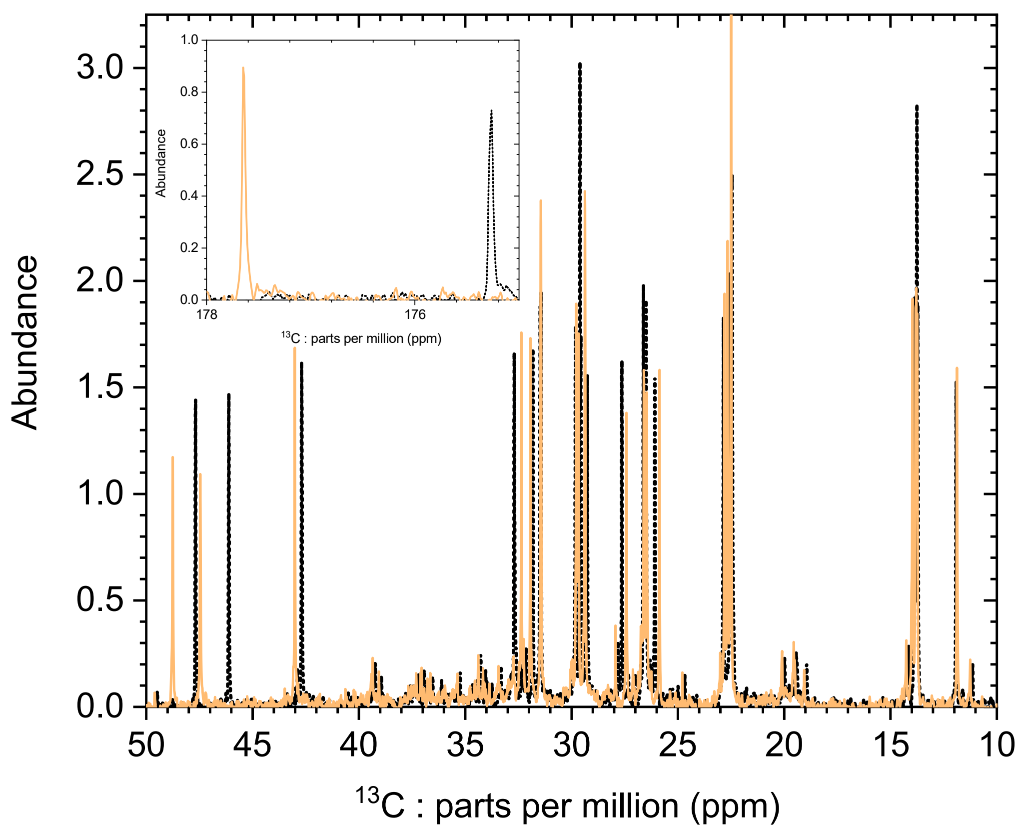


Figure A.11: ^{13}C NMR of 1 M DH2EHA (dot) and 24 hours with 20 mM HNO_2 and 6 M HNO_3 (solid).

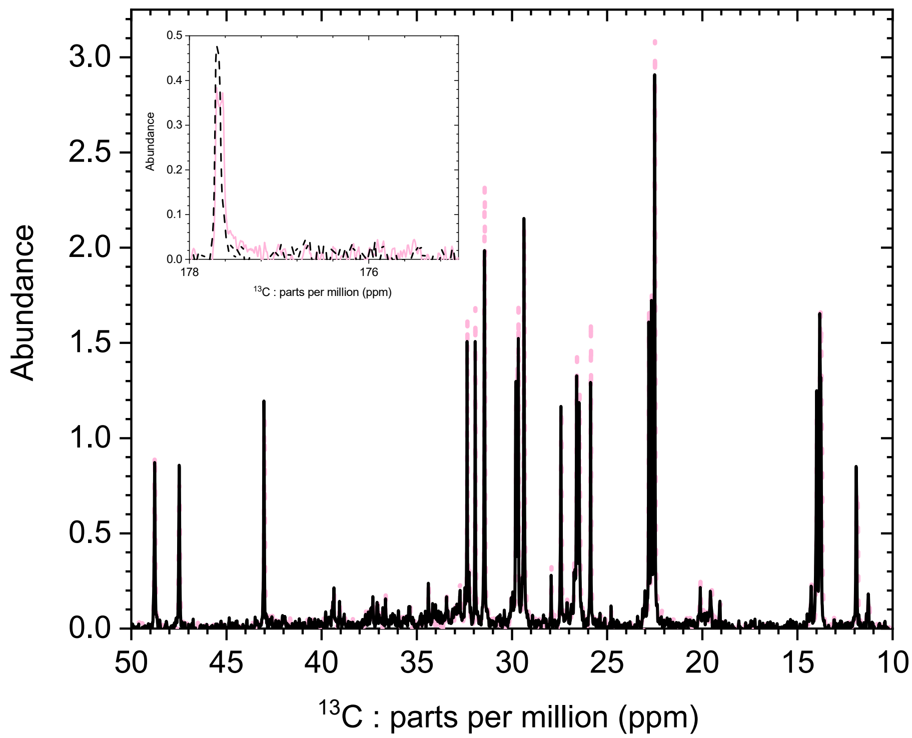


Figure A.12: ^{13}C NMR of 1 M DH2EHA pre-equilibrated with 6 M HNO_3 (dash), 45 minutes with 20 mM HNO_2 and 6 M HNO_3 (solid).

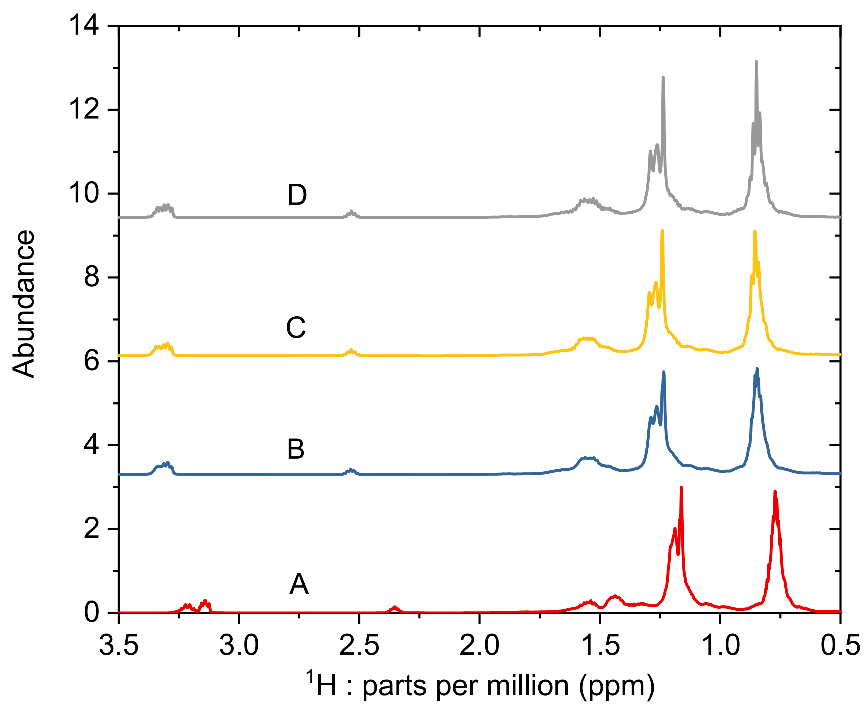


Figure A.13: ^{1}H NMR of: 1 M DH2EHA (A), pre-equilibrated with 6 M HNO_3 (B), 45 minutes with 20 mM HNO_2 and 6 M HNO_3 (C), 24 hours with 20 mM HNO_2 and 6 M HNO_3 (D). Lines are offset for clarity.

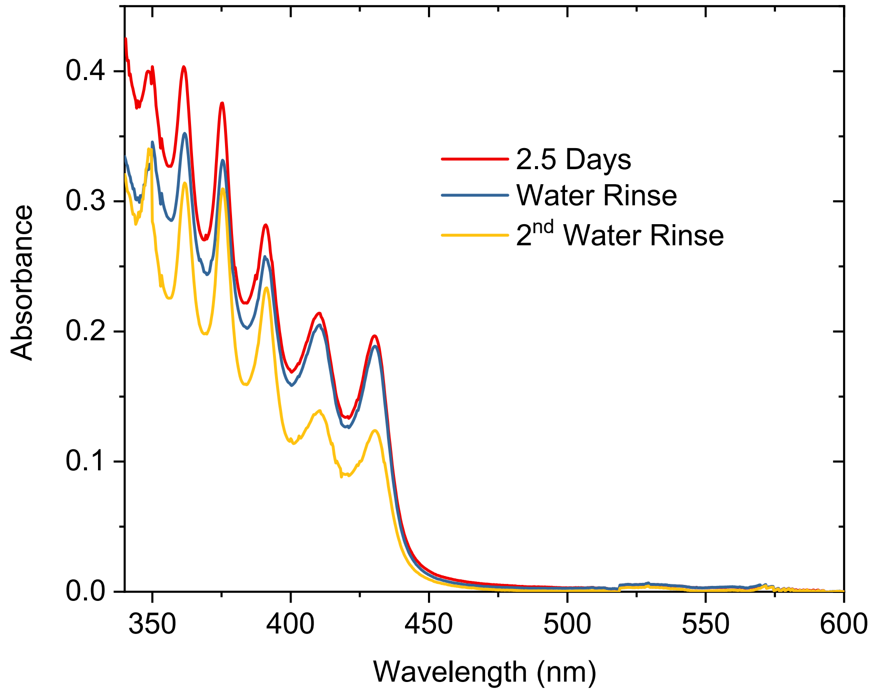


Figure A.14: Spectra of 1 M DEHBA in Exxsol D60 after mixing with 20 mM HNO_2 and 6 M HNO_3 that has sat for 2.5 days to allow monoamide-X to build-up. The organic phase was rinsed with pure H_2O once (blue) and twice (yellow).

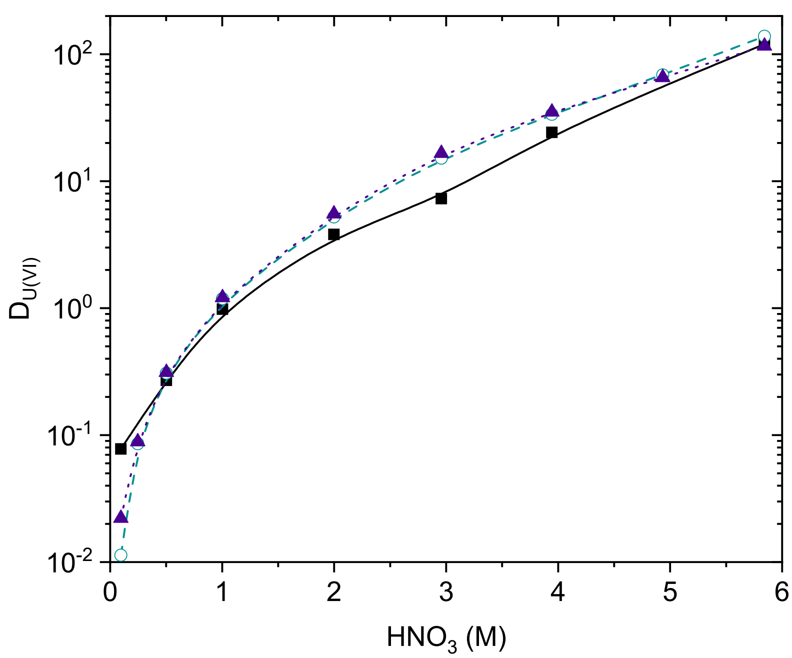


Figure A.15: Distribution ratios of ^{233}U with 1 M DHOA with no nitrous acid (square), HNO_3 pre-equilibrated 1 M DHOA sat for two weeks (circle), HNO_3 and 20 mM HNO_2 preequilibrated 1 M sat for two weeks (triangle). Lines are plotted as a visual guide.

APPENDIX B

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