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Inner versus Outer Sphere Metal-Monoamide Complexation: Ramifications for Tetravalent & Hexavalent Actinide Selectivity

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11 Abstract

Oxidation of americium to the hexavalent state could streamline used nuclear fuel management 12 through a group hexavalent actinide separation process. Monoamides, N,N-dialkyl amides, are 13 being considered in this work due to their selectivity towards hexavalent, over tetravalent, 14 actinides. Hexavalent selectivity arises when the monoamides contain a branched acyl chain. 15 While this selectivity has been known since its preliminary studies by Siddall, structures of the 16 extracted species have only recently been investigated. This study expands on other research 17 efforts by examining the structure-extraction functionality of straight and branched monoamides 18 with Pu^{4+} and PuO_2^{2+} . In both Pu oxidations states, the effect of acyl chain length was 19 investigated by comparing Pu extraction and UV-Vis spectra of Pu complexes with N,N-20 dihexylbutyramide, N,N-dihexylvaleramide, and N,N-dihexylhexanamide. Furthermore, the 21 22 effects of alkyl chain branching was investigated by comparing N,N-dihexyl(2methyl)butyramide and N,N-dihexyl(2-methyl)valeramide, as well as ethyl branched N,N-23 dihexyl(2-ethyl)butyramide and N,N-dihexyl(2-ethyl)hexanamide. These structure-extraction 24 relationships were characterized by collecting UV-Vis spectra of the metal-monoamide extracted 25 species and tracer distribution studies. The UV-Vis analysis was found to match distribution 26 values collected under radiotracer conditions and indicated Pu was extracted as the tetra- and 27 hexanitrato monoamide complex for Pu^{4+} and the bis- or trisnitrato species for PuO_2^{2+} . The 28 monoamides' ability to recover Cu³⁺ periodate oxidized Am was also studied using radiotracer 29 methods. Initial efforts with nitric acid pretreated monoamides, salting agents, and synergistic 30 studies with di-(2-ethylhexyl)phosphoric acid (HDEHP) were ineffective. Pretreatment with 31 32 sodium bismuthate was found to improve Am recovery, and distributions above one were achieved with straight chain monoamides at 3 M HNO₃. 33

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1 Introduction

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2 Used nuclear fuel arising from commercial nuclear power reactors can generally be managed by using open, partially closed, or fully closed nuclear fuel cycles. In an open nuclear 3 fuel cycle, used nuclear fuel is disposed of in a geological repository without any chemical 4 processing. Open nuclear fuel cycles have several limitations, including million year waste 5 management timelines, lack of viable repository sites and limited demonstration of safe waste 6 7 disposal, and only 5% energy consumption of the nuclear fuel originally placed in the reactor. A partially closed nuclear fuel cycle seeks to recover the remaining energy available in the nuclear 8 9 fuel by separating deleterious fission products from U and Pu. The recovered Pu can be reprocessed into MOX (Mixed Oxide) fuel, which increases the energy recovered from the 10 original nuclear material. More aggressive, fully closed, fuel cycles are designed to recover and 11 fission neptunium and americium to decrease the waste storage timelines and high level waste 12 (HLW) repository capacity. While fully closed nuclear fuel cycle would have several waste 13 management benefits, the separations technology necessary to enable implementation of a closed 14 fuel cycle requires further development to decrease costs and increase proliferation resistance. 15

Industrial scale separations of use nuclear fuel necessary to enable closed nuclear fuel 16 cycles have, by in large, remained unchanged since 1954.¹ In this year, the Plutonium Uranium 17 Reduction Extraction (PUREX) was launched at the Savannah River Site in South Carolina. The 18 PUREX process uses tributyl phosphate (TBP) dissolved in an organic diluent to recover 19 hexavalent uranium, UO₂²⁺, and tetravalent plutonium, Pu⁴⁺, from nitric acid solution containing 20 fission products. In a partially closed fuel cycle, the PUREX process, or a comparable 21 22 commercial derivative, is the only separation step. In a fully closed fuel cycle, the selective recovery of Am and Np is necessary to enable their transmutation to shorter lived isotopes. This 23 transmutation process significantly shortens nuclear waste management timelines and typically 24 requires one or two additional separation steps beyond the PUREX process to complete Am and 25 Np recovery. 26

Since neptunium's chemistry readily parallels that of U or Pu, the PUREX process can be 27 adjusted to recover neptunium. Recovery of Am is non-trivial due to the similar chemistry Am 28 shares with lanthanide fission products. Both Am and the lanthanides share a common trivalent 29 oxidation state, have similar atomic radii, and tend towards ionic interactions due to the 30 contraction of the 4f and 5f orbitals with the 6s and 7s valence shells. Americium - lanthanide 31 separation methods under development use soft donor, such as nitrogen, ligands to selectively 32 complex Am over the lanthanides since actinides participate in limited covalent interactions with 33 soft donor ligands.²⁻⁶ These approaches are non-ideal since they require the removal of U, Np, 34 and Pu, via a PUREX derivative prior to the Am – lanthanide separation. This increases the cost 35 36 associated with used nuclear fuel management through additional capital and operating costs for the Am-lanthanide separation. A more streamlined process, where Am is co-recovered with U, 37 Np, and Pu, would be preferred to minimize reprocessing cost. 38

A potential means of achieving the selective group recovery U, Np, Pu, and Am centers on the common availability of the hexavalent oxidation state. Actinides readily form the unique linear dioxo cation geometry upon oxidation to the pentavalent (AnO_2^+) or hexavalent (AnO_2^{2+})

oxidation state.⁷⁻¹⁰ Uranium generally forms the linear dioxo cation under the PUREX operating 1 conditions, and neptunium and plutonium can be readily oxidized to the hexavalent state.¹¹ 2 Americium, on the other hand, requires the use of strong oxidants, such a sodium bismuthate or 3 Cu³⁺ periodate, that can overcome the AmO₂²⁺/Am³⁺ 1.68 V standard reduction potential.¹² 4 Recent studies have demonstrated the oxidation of Am to the hexavalent state and recovery by 5 organophosphorus extractants, TBP or diamyl amylphosphonate.^{8,10,13,14} The over sixty years of 6 operational precedent associated with the PUREX process have demonstrated the viability of 7 TBP as an actinide extractant, however, the use of TBP has two major drawbacks. As a 8 phosphorus based ligand, TBP cannot be incinerated which leads to completely gaseous 9 byproducts which leads to a secondary low-level radioactive waste stream. Secondly, the 10 radiolytic degradation products of TBP decrease metal stripping efficiency. To circumvent 11 TBP's shortcomings, monoamides (Table 1) have been studied due to their innocuous 12 degradation products and incinerability as a CHON (carbon, hydrogen, oxygen, nitrogen) based 13 ligand.¹⁵ 14

Extraction studies of UO_2^{2+} and Pu^{4+} using monoamides have shown the chemistry of the 15 acyl group effects the monoamide's extraction capabilities. Namely, straight chain monoamides 16 will effectively extract tetravalent and hexavalent actinides. When the alpha carbon off the acyl 17 oxygen group becomes more substituted the monoamide becomes more selective for hexavalent 18 actinides over tetravalent actinides.^{15–17} Selective recovery of the hexavalent state, over the 19 tetravalent state, is unusual since the favorability of actinide recovery usually trends as An^{4+} > 20 $AnO_2^{2^+} >> An^{3^+} > AnO_2^+$ due to the decrease in charge density.^{18,19} While previously reported 21 literature compared the structural effects to hexavalent U to tetravalent Pu and Th, this 22 manuscript uses the same metal, Pu, to study structural effects of synthesized straight chained 23 N,N-dihexylhexanamide, N,N-dihexylvaleramide, N,N-dihexylhexanamide and branched N,N-24 25 dihexyl(2-methyl)butyramide, N,N-dihexyl(2-ethyl)butyramide, N,N-dihexyl(2methyl)valeramide, and N,N-dihexyl(2-ethyl)hexanamide (Table 1). 26

Hexavalent selectivity of branched monoamides is advantageous when considering a 27 hexavalent group actinide separation process. Oxidation of Am³⁺ to the hexavalent state (1.68 V 28 vs. SCE)^{20,21} and extraction by solvating ligands from molar nitric acid has been demonstrated 29 using strong oxidants such as sodium bismuthate⁹ and Cu³⁺ periodate.¹⁰ The strong oxidants are 30 capable of oxidizing other metals encountered in the back end nuclear fuel cycle, i.e. Ce^{3+} to 31 Ce^{4+} . Oxidation of Ce^{3+} to the tetravalent state would cause Ce to be extracted by solvating 32 ligands, such as diamyl amylphosonate or tri-butylphosphate, instead of remaining with the 33 trivalent lanthanides.¹³ Straight chain and hexavalent selective branched monoamides have been 34 shown to extract AmO_2^{2+} oxidized by sodium bismuthate.²² The sodium bismuthate study 35 demonstrated that group hexavalent actinides can be extracted by straight or branched 36 monoamides, but branched are preferred when considering the presence of Ce⁴⁺. The manuscript 37 also showed hexavalent U and Np had different solvation number (~1.5) compared to Pu and Am 38 (~2.0). This manuscript assesses the ability for monoamides to extract AmO_2^{2+} using Cu^{3+} 39 periodate as an oxidant. Furthermore, UV-Vis spectra of Pu⁴⁺ and PuO₂²⁺ monoamide species are 40 presented, and provide insight into the structure of the extracted species based off variations in 41 the monoamides structure and plutonium oxidation state. 42



Table 1: Structure, name, and abbreviation of straight (left column) and branched (middle and right column) of monoamides studied in this manuscript. Chain length increases moving down.

2 Experimental

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3 Monoamide Synthesis

All monoamides were synthesized using nucleophilic attack of dialkylamines with acyl 4 chlorides.²³ To make N,N-dihexylbutyramide, 0.131 moles dihexylamine (Acros Organics, 5 99+%) was diluted with 45.00 mL chloroform (Sigma-Aldrich, HPLC Plus) and 17.00 mL 6 7 triethylamine (Alfa Aesar, 99+%) in a 250 mL round bottom flask with a stirbar, reflux condenser and addition funnel attached. In the addition funnel, 0.150 moles butyryl chloride 8 (Alfa Aesar, 98%) were diluted with 18.4 mL chloroform. The reaction apparatus was purged 9 with nitrogen gas. The round bottom flask was chilled in an ice bath to prevent the reaction from 10 exceeding 10° C during dropwise addition of butyrl chloride to the dihexylamine solution. The 11 12 addition funnel was replaced with a stopper after addition of solutions, and flask was purged with 13 nitrogen. The solution was heated to 60° C, the boiling point of chloroform, and refluxed for 2 hours. The product was filtered, and the filtrate was washed with 10 weight percent Na₂CO₃, 1 M 14 HCl, and distilled water to remove triethylamine chloride and unreacted triethylamine. The 15 16 solution was dried with sodium sulfate overnight. To purify the product, chloroform was removed using a rotovap and finally purified via vacuum distillation. The final product was 17 determined to be 99% pure via ¹H NMR and had a 71% yield. In total, N,N-dihexylvaleramide, 18

- 1 N,N-Diheylhexanamide, N,N-dihexyl(2-methyl)butyramide, N,N-dihexyl(2-ethyl)butyramide,
- 2 N,N-dihexyl(2-methyl)valeramide, and N,N-dihexyl(2-ethyl)hexanamide were synthesized by
- 3 following the same procedure with the desired acyl chloride substituent. All products were 99%
- 4 pure by ¹H NMR (JEOL 500MHz) and percent yield ranged from 53% to 77%. Monoamides
- 5 were also characterized using Bruker Alpha (ATR) FTIR, **SI Figure 1 and 2**.
- 6 ^{$^{1}}H NMR Results:$ </sup>

7 N,N-dihexylbutyramide: (CDCl₃, 500 MHz), $\delta = 0.69 - 0.91$ (9H, m, CH₃), 1.1 - 1.3 (12 H, br, 8 CH₂), 1.33 - 1.50 (4H, br, CH₂), 1.50 - 1.64 (2H, m, CH₂), 2.15 (2H, t, OCH-CH₂), 3.01 - 3.26 9 (4H, 2 t, N-CH₂)

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

12 N,N-dihexylhexanamide: (CDCl₃, 500 MHz), $\delta = 0.76 - 0.93$ (9H, m, CH₃), 1.15 - 1.35 (16H, 13 br, CH₂), 1.39 - 1.68 (6H, m, CH₂), 2.22 (2H, t, CH₂), 3.06 - 3.33 (4H, 2 t, N-CH₂)

14 N,N-dihexyl(2-methyl)butyramide: (CDCl₃, 500 MHz), $\delta = 0.71 - 0.88$ (9H, br, CH₃), 0.95 - 1.06 (3H, m, CH₃), 1.1 - 1.7 (18H, m, CH₂), 2.44 (1H, m, CH), 3.02 - 3.34 (4H, m, N-CH₂)

16 N,N-dihexyl(2-ethyl)butyramide: (CDCl₃, 500 MHz), $\delta = 0.75 - 0.91$ (12H, m, CH₃), 1.16 - 1.34 17 (12H, br, CH₂), 1.34 - 1.67 (8H, m, CH₂), 2.31 - 2.39 (1H, m, CH), 3.14 - 3.32 (4H, 2 t, N-CH₂)

18 N,N-dihexyl(2-methyl)valeramide: (CDCl₃, 500 MHz), $\delta = 0.73 - 0.90$ (9H, m, CH₃), 0.96 -19 1.06 (3H, d, CH₃), 1.12 - 1.66 (20H, m, CH₂), 2.47 - 2.62 (1H, m, CH), 3.04 - 3.36 (4H, m, N-20 CH₂)

21 N,N-dihexyl(2-ethyl)hexanamide: (CDCl₃, 500 MHz), $\delta = 0.72 - 0.90$ (12H, m, CH₃), 1.0 - 1.64 22 (24H, m, CH₂), 2.31 - 2.45 (1H, m, CH), 3.08 - 3.33 (4H, m, N-CH₂)

23 Extraction Studies

Extraction studies were completed on ²³⁹Pu⁴⁺ and ²³⁹PuO₂²⁺ in HNO₃ (Fisher, optima grade) with 24 1.0 M monoamide in n-dodecane (Sigma-Aldrich). The organic phase was pre-equilibrated with 25 HNO₃ prior to Pu extraction. The ²³⁹Pu stocks were prepared by adding 30% H₂O₂ dropwise to 26 25 mM Pu 2 M HNO₃ solution to reduce any oxidized species and generate 99.6% Pu⁴⁺ solution, 27 determined using UV-Vis spectroscopy on a Spectral 420 CCD Array UV-Vis 28 Spectrophotometer (SI Figure 3). The PuO_2^{2+} solution was generated by addition of HClO₄ to 29 oxidize Pu mixed species to PuO_2^{2+} . To remove HClO₄, the solution was slowly evaporated until 30 $PuO_2^{2^+}$ residue was nearly dry. The residue was dissolved with 0.5 M HNO₃. The 31 evaporation/dilution process was repeated two additional times. The final PuO_2^{2+} concentration 32 was 48 mM in 0.5 M HNO₃, and was determined to be 100% PuO_2^{2+} by visible absorbance 33 spectroscopy (SI Figure 3). To complete tracer level extractions, Pu was added to 2 M HNO₃ for 34 a final concentration of 0.21 mM Pu^{4+} or 0.40 mM PuO_2^{2+} , 5.0 µL of either stock was spiked into 35 500.0 mL of the respective nitric acid solution for triplicate samples. Extractions were completed 36 by contacting 1 - 5 M HNO₃ Pu containing solutions with an equal volume of pre-equilibrated 1 37 M monoamide. The solutions were shaken by hand for 30 seconds, and centrifuged to disengage 38

the two phases. Each phase was subsampled, added to LSC cocktail (PerkinElmer, Ultima Gold 1 AB) and quantified using PerkinElmer LSC Tri-Carb 3110 TR. Organic phase visible absorbance 2 spectra were also collected after contacting 1.0 M monoamide (pre-equilibrated with the 3 appropriate HNO₃ solution) with 4.0 mM Pu^{4+} and 3.0 mM PuO_2^{2+} in 4.5 and 4.7 M HNO₃, 4

respectively. All visible absorbance spectra are presented as the average of triplicate readings. 5

Americium extractions were done using ²⁴¹Am (Eckert & Ziegler, 1 M HCl), and followed 6 previous extraction studies that used Cu^{3+} periodate to obtain $AmO_2^{2+,9,13}$ The stock was diluted 7 in 2 M HNO₃, and was slowly evaporated until dry and redissolved in 4 M HNO₃. The solution 8 was evaporated until almost dry and diluted with 0.1 M HNO₃. The process was repeated a third 9 time, and final ²⁴¹Am solution was in 0.1 M HNO₃. The 1.0 M monoamide in n-dodecane 10 organic phase was pre-equilibrated with the corresponding HNO₃ prior to Am extraction. To 11 oxidize Am, 20 mg of Cu³⁺ periodate (synthesized as previously reported)⁹ was added to 2 mL 12 vial and 500 µL²⁴¹Am in respective HNO₃ was added to the vial. An equal volume of HNO₃ pre-13 equilibrated 1.0 M monoamide was added, and was shaken by hand for 5 seconds and 14 centrifuged to disengage the two phases. Each phase was subsampled and added to LSC cocktail 15 (PerkinElmer, Ultima Gold AB) and quantified using PerkinElmer LSC Tri-Carb 3110 TR. 16

Results and Discussion 17

Tetravalent and Hexavalent Pu-Monoamide Extraction 18

Distribution values of Pu⁴⁺ with DHBA, DHVA, and DHHA were collected to determine the 19 effect of acyl chain length on extraction efficiency. As shown in Figure 1, the Pu⁴⁺ distribution 20 values are above 1 at 2 M HNO₃ and increase up to the 5 M HNO₃ measurement. The increase in 21 distribution ratio is consistent with monoamide reagents being solvating extractants that require 22 nitrate to encourage metal recovery.^{24,25} As the concentration of nitric acid increases the 23 partitioning of plutonium into the organic phase by two monoamide ligands increases.¹⁵ The 24 extraction of Pu⁴⁺ by straight chain monoamide ligands from an acyl chain length 4 carbons 25 (DHBA) to 6 carbons (DHHA) does not show an overall trend. At 5 M HNO₃ the Pu⁴⁺ 26 distribution value is 25 ± 3 for DHBA, 15.1 ± 0.5 for DHVA, and 20 ± 2 for DHHA. While the 27 DHBA extracts Pu⁴⁺ more efficiently than the longer acyl chain monoamides, DHVA shows 28 lower distribution values in general than the six carbon DHHA. It should be noted the range in 29 distribution values differs from roughly 96.2% DHBA extraction to 93.8% with DHVA, a 30 31 difference of only 2.4%.

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Figure 1: Distribution values of Pu^{4+} at various HNO_3 concentrations for straight chain monoamides (sky blue) DHBA (circle), DHVA (square), DHHA (diamond). Distribution with methyl branched monoamides (navy blue) DH2MBA (circle) and DH2MVA (diamond) as well as ethyl branched monoamides (green) DH2EBA (square) and DH2EHA (triangle).

2 When the carbon adjacent to the carbonyl group is changed from a secondary (straight chain) to tertiary carbon (branched) the distribution values of Pu⁴⁺ drop significantly across all acid ranges 3 as shown in Figure 1. The type of branching, i.e. methyl versus ethyl, resulted in a specific 4 grouping across all acid ranges as well. The methyl branched DH2MBA and DH2MVA 5 molecules show nearly identical distribution values of 1.09 ± 0.03 and 1.0 ± 0.1 , respectively, at 6 7 5 M HNO₃. Similarly, the DH2EBA and DH2EHA molecules produced distribution values of 0.81 ± 0.06 and 0.77 ± 0.04 . The proximity of the distribution values indicates the length of the 8 9 primary alkyl chain does not greatly affect the distribution values. On the other hand, when comparing DH2MBA vs. DH2EBA, where the primary alkyl chain lengths are equivalent, the 10 distribution values drop from 1.09 to 0.81 for methyl vs. ethyl branching and equates to a 7.4% 11 change in extraction efficiency. To better understand changes in the extracted species visible 12 absorbance spectra were collected on Pu⁴⁺ extracted by the various monoamides. 13

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Figure 2: Absorbance spectra of Pu^{4+} extracted from 4.5 M HNO₃ by 1 M DHBA (sky blue), DH2MBA (navy blue), and DH2EBA (green) in n-dodecane.

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The visible absorbance spectrum of Pu⁴⁺ extracted by the straight chained DHBA from 4.5 M 2 HNO₃, Figure 2, bears a striking resemblance to plutonium hexanitrate, $Pu(NO_3)_6^{2-}$, absorbance 3 spectra.²⁶ A spectrum of Pu⁴⁺ in 10 M HNO₃, producing Pu(NO₃)₆²⁻ species, was overlayed on 4 the Pu⁴⁺-DHBA spectrum (Figure 3). The two spectra have identical spectral signatures and 5 show only slight variation in peak intensity at 609, 445, and 405 nm as well as a slight blue shift 6 7 with 10 M HNO₃ Pu⁴⁺ spectrum around 492 nm. Acher et. al. made a similar observation at elevated nitric acid concentrations, and used EXAFS to determine plutonium hexanitrate was 8 being extracted by two protonated N,N-di(2-ethyl)hexylbutyramide ligands via an outer-sphere 9 coordination as Pu(NO₃)₆(HL)₂.²⁷ The results presented here support the extraction of plutonium 10 hexanitrate species by the straight chain monoamides. The reason why the three peaks between 11 580 and 730 nm are prominent in this work at 4.5 M HNO₃ compared to Acher's 5 M HNO₃ 12 spectra in which the three peaks are present but less defined is not obvious. Nonetheless, in 13 14 Figure 2 the 609 nm peak has a lower intensity than the 650 and 746 nm peaks for all three 15 monoamides. A more intense 609 nm peak relative to 650 and 746 nm would indicate a pure plutonium hexanitrate species is present (Figure 3).²⁸ Therefore, the spectra indicate another 16 species, plutonium tetranitrate, is present. 17

18 The observations in this manuscript and by Acher contrast the common understanding that Pu^{4+}

19 would be recovered as the charge neutral $Pu(NO_3)_4$ species, where the nitrates bind in a bidentate

20 fashion to $Pu^{4+,25,26}$ The previous assignment of Pu^{4+} recovery as a $Pu(NO_3)_4L_2$ species was

21 based on radiotracer distribution studies that did not account for the nitrate activity or the

2 ability for commonly available visible spectroscopy to corroborate previous EXAFS findings of 3 the $Pu(NO_3)_6(HL)_2$ extracted species suggests that this extracted species should be considered as

4 the primary mechanism for Pu^{4+} , and possibly tetravalent actinide recovery, by straight chain

5 monoamide reagents.



Figure 3: Absorbance spectrum of Pu^{4+} in 10 M HNO₃ which takes the form of plutonium hexanitrate species, $Pu(NO_3)_6^{2-}$ (dark blue) and spectrum of 4.5 M HNO₃ Pu^{4+} (green) extracted by 1 M DHBA in n-dodecane (light blue).

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In the Pu⁴⁺ 1 M DHBA spectrum (Figure 2), the 650 nm peak is more intense than 609 and 746 7 nm. This peak intensity pattern indicates some inner-sphere Pu(NO₃)₄L₂ species are present in 8 solution or a dual inner/outer species, Pu(NO₃)₅L(HL).^{27,29} Similarly, the most prominent of the 9 three peaks between 580 - 730 nm spectral region for DH2MBA and DH2EBA occurs at 649 10 11 nm. All three peaks are broadened in both branched monoamides with DH2EBA peaks being the broadest. The broadening is an indication that Pu⁴⁺ extracted species is more characteristic of 12 inner-sphere species, Pu(NO₃)₄L₂.²⁷ Furthermore, the peak intensity at 746 nm decreases relative 13 to the 580 – 730 nm peaks, and the 495 nm peak broadens when moving from the straight to 14 methyl to ethyl branched monoamide. The experimental uncertainty based off triplicate spectral 15 16 measurements showed the monoamide's spectra were significantly different. The spectra reveal that the branched monoamides show an increase in inner-sphere species, such as $Pu(NO_3)_4L_2$ or 17 the dual inner/outer species, Pu(NO₃)₅L(HL).²⁹ An increase of inner-sphere extracted species for 18 branched monoamides is peculiar as the branching on monoamides induces an increase in steric 19 hindrance and has been ascribed as the reason tetravalent actinide extraction decreases.^{15,16,29,30} 20 Further work should consider assessing the complex speciation that seems to persist in these 21

The Pu⁴⁺ distribution values were calculated by measuring the Pu⁴⁺ concentration at the 476 nm 7 aqueous phase peak before and after extraction, example shown in SI Figure 4. For 1 M DHBA, 8 the Pu⁴⁺ concentration was below limit of quantitation after mixing owing to its 96% extraction 9 efficiency measured in Figure 1 by LSC. The 1 M DH2MBA and DH2EBA distribution values 10 11 were 1.12 ± 0.05 and 0.79 ± 0.04 respectively and match the values measured in Figure 1. The decrease in distribution values correlates to a decrease in outer-sphere extraction character as 12 DHBA > DH2MBA > DH2EBA. Intuitively, the branched monoamide would experience less 13 steric hindrance with an outer-sphere species since the extractant is sitting further from the metal 14 center. The decrease in monoamide protonated outer-sphere species, Pu(NO₃)₆(HL)₂, with 15 branched monoamides for Pu⁴⁺ extraction under similar HNO₃ concentration suggests branched 16 monoamides are less apt to protonation than their straight chain homologues. While monoamide 17 protonation has not been directly measured, Condamines determined HNO₃ K₁₁ constant was 18 N,N-di(2-ethylhexyl)butyramide Μ in TPH 19 0.135 for 1 while N.N-di(2ethylhexyl)isobutyramide had a lower K₁₁ constant of 0.086.²⁴ Condamines' results support the 20 protonation hypothesis. Therefore, steric hindrance as well as availability of protonated 21 monoamides could be contributing to the decreased distribution values observed with branched 22 monoamides. 23

Extraction of hexavalent plutonium, PuO_2^{2+} , by straight chain monoamides displayed a trend 24 across all acid concentrations with increasing acyl chains. Shown in Figure 4, the distribution 25 values decrease with increased acyl chain length as $7.9 \pm 0.3 > 6.1 \pm 0.1 > 5.4 \pm 0.1$ for DHBA > 26 DHVA > DHHA from 5 M HNO₃. The extraction efficiency is approximately 88.8% for DHBA 27 and decreases to 84.4% for DHHA. The extraction efficiency is lower than that observed with 28 Pu^{4+} , but is to be expected due to Pu^{4+} having a higher charge density than PuO_2^{2+} . Conversely, 29 branched monoamides extract PuO_2^{2+} to a greater extent than Pu^{4+} , Figure 4. The branched 30 monoamides show distribution values approach 1 at 3 M HNO₃ for PuO₂²⁺, while Pu⁴⁺ 31 distribution values approach 1 at 5 M HNO₃ with the same monoamides. At 5 M HNO₃, the 32 $PuO_2^{2^+}$ distribution values reach 2.27 ± 0.01, 2.5 ± 0.3, 2.8 ± 0.1, and 2.60 ± 0.07 for DH2MBA, 33 DH2EBA, DH2MVA, and DH2EHA respectively. The values fall within experimental 34 uncertainty of each other; therefore, no overall trend could be deduced. 35

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Figure 4: Distribution values of $PuO_2^{2^+}$ extracted from various HNO₃ solutions by 1 M DHBA (circle), DHVA (square), and DHHA (diamond) in n-dodecane (sky blue). Values for methyl branched monoamides (navy blue) DH2MBA (circle) DH2MVA (diamond) and ethyl branched (green) DH2EBA (square) and DH2EHA (triangle) compared to Pu⁴⁺ extracted by DH2MBA (grey star).

1 The organic phase absorbance spectra of PuO_2^{2+} extraction from 4.7 M HNO₃ shows a multitude 2 of peaks compared to the PuO_2^{2+} aqueous HNO₃ spectrum, Figure 5. Several peaks are present 3 between 450 and 670 nm, and five distinct peaks are observed at 789, broad 801, 809, broad 824, 4 and 849 nm. The monoamide spectra bear a stark resemblance to UV-Vis collected by Keder et. 5 al. of PuO_2^{2+} extraction from 4 M HNO₃ by tri-n-octylamine in o-xylene - particularly in the 450 6 -670 nm region and with 789 - 824 nm peaks.²⁸ Keder et. al. deduced PuO₂²⁺ was extracted as a 7 trinitrate species, $PuO_2(NO_3)_3$, by comparing the PuO_2^{2+} tri-n-octylamine spectrum to a 8 9 tetraethylammonium trinitratodioxoplutonate(VI) spectrum. Both spectra are consistent with the aforementioned peaks observed in this work with the exception of the 849 nm peak. Absence of 10 the 849 nm peak in the tetraethylammonium trinatodioxoplutonate(VI) spectrum suggests 11 another species is being extracted by the monoamides. Correlating with Keder's research, one 12 species could be the plutonyl trinitrate species which would be extracted by a protonated 13 monoamide as, PuO₂(NO₃)₃·HL.^{22,25} The second could be the charge neutral dinitrate plutonyl 14 species, PuO₂(NO₃)₂(L)₂, that gives rise to the 849 nm peak.³¹ These assignments would be 15 further supported by collecting EXAFS or infrared spectra. 16



Figure 5: Absorbance spectra of PuO_2^{2+} extracted from 4.7 M HNO₃ by 1 M DHBA (dashed), DH2MBA (dark green), DH2MVA (light green), DH2EBA (navy blue), and DH2EHA (light blue) in n-dodecane.

The presence of two species contradicts 1:2 metal:ligand ratio previously reported for 2 monoamide extraction from 6.5 M HNO₃.²² However, the slope analysis method used to 3 determine the metal: ligand ratio revealed a slope lower than 2. A slope of 2 would be indicative 4 5 of ideal conditions where only one extracted species exists, but the less than 2 value indicates a 1:1 species can exist which absorption spectra in this study indicate. Changes of Pu 6 concentration in the aqueous phase were measured before and after extraction, and showed 2.2 7 $mM PuO_2^{2+}$ was extracted into the organic phase for all branched monoamides. Given the same 8 $PuO_2^{2^+}$ concentrations in each monoamide study, the spectra are distinct from each other based 9 off the type of branching. The methyl branched monoamides exhibit similar relative peak 10 intensities compared to the ethyl branched monoamides between 450 and 670 nm. In the 780 – 11 860 nm range the 789, 801, and 809 peaks are similar. The 824 nm peak, however, shows a 12 broader intensity for the methyl branched while the ethyl branched come to more of a point 13 around 821 nm. The reason for slight differences in the 824 nm spectral region is not obvious. 14 The possibility of a protonated outer sphere 1:1 metal:ligand species instead of a inner sphere 1:1 15 16 species could be considered. Research by Acher et. al. indicated the presence of a protonated 17 monoamide ligand. Since protonated monoamides with a 1:2 metal:ligand ratio have been 18 observed, and a PuO₂(NO₃)HL has not been observed with monoamides or other types of 19 solvating ligands, the possibility of a non-protonated single ligand extracted species is unlikely. 20 Future studies, using EXAFS, could explicate the type of extracted species and the fine structure differences observed in the UV-Vis. 21

22 Hexavalent Americium Extraction

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Extraction efficiency for hexavalent actinides decreases as one moves across the actinide series (i.e., increasing Z) due to the decrease in charge density.²² Therefore, it was interest to see if the synthesized monoamides were strong enough to effectively extract hexavalent americium,

 AmO_2^{2+} . Prior to studying AmO_2^{2+} the extraction of Am^{3+} by 1 M DHBA was measured for 1 – 1 5 M HNO₃ solutions. Trivalent americium was not extracted by DHBA in quantifiable amounts 2 3 from any acid concentration. This is a favorable result as it indicates trivalent lanthanides will not be extracted in appreciable amounts by monoamides if employed in fuel reprocessing. The 4 Cu^{3+} periodate oxidized Am did show extraction, Figure 6, with 1 M DHBA, DHVA, and 5 DHHA, however, the distribution values are below 1, or less than 50%' was extracted. The 6 distribution values increased from 1 to 3 M HNO₃, but decreased at higher nitric acid 7 concentrations. The trend is similar to that observed with diamyl amylphosphonate (DAAP), and 8 further studies have revealed the decreased values are a result of incomplete Am³⁺ oxidation as 9 well as reduction of AmO_2^{2+} in higher nitric acid concentrations.¹⁰ Reduction of AmO_2^{2+} also 10 occurs in the organic phase and produces AmO_2^+ and Am^{3+} species which are poorly extracted 11 by monoamides.²² Comparing the monoamide chain length, DHBA shows the highest 12 distribution while DHVA and DHHA extract comparatively. Considering PuO₂²⁺ had similar 13 distribution values for all three straight chain monoamides it is thought that AmO_2^{2+} experienced 14 a higher degree of reduction with DHVA and DHHA due to the presence of trace reducing 15 agents. 16



Figure 6: Distribution values of Cu^{3+} periodate oxidized Am in 1 – 5 M HNO₃ extracted by 1 M DHBA (blue squares), DHVA (grey diamonds), and DHHA (green triangles) in n-dodecane.

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18 Several parameters were adjusted in attempts to obtain greater than 50% extraction efficiency for 19 AmO_2^{2+} with straight chain monoamides. Salting agents can be used to increase the ionic 20 strength of aqueous phase and promote metal extraction. Using the acid concentration with 21 highest distribution, 3 M HNO₃, distribution values were determined with the addition of 0.1 to 22 1.0 M LiNO₃ and Al(NO₃)₃ (SI Figure 5). In the absence of LiNO₃ distribution value was 0.75 ±

0.02. In the presence of 0.1 M LiNO₃, the distribution value increased slightly to 0.81 ± 0.08 and 1 steadily decreased to 0.71 ± 0.03 at 1 M HNO₃. All distribution values fell within experimental 2 3 uncertainty of each other; therefore, LiNO₃ had no effect on the distribution values. A small effect was observed when Al(NO₃)₃ was added to 3 M HNO₃ solutions. The distribution 4 increased from 0.69 ± 0.09 in absence of Al(NO₃)₃ to 0.86 ± 0.04 with 0.30 M Al(NO₃)₃. The 5 6 distribution values then fell to 0.75 ± 0.8 at 1 M Al(NO₃)₃. The addition of 1 M Al(NO₃) results in a 3 mole equivalent addition of NO3 . The increased NO3 concentration would promote 7 formation of the charge neutral AmO₂(NO₃)₂ extracted species, but the high concentration of 8 NO_3 at 1 M Al(NO_3)₃ could promote formation of anionic species which are only extracted by 9 protonated monoamides that exist at high molar acid concentrations.^{22,27} Although Al(NO₃)₃ 10 showed some improvement the distribution values did not increase in appreciable amounts. 11

Mixed ligand separations such as a neutral extractant, diglycolamide (T2EHDGA), and the acidic 12 extractant 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (HEH[EHP]) in the ALSEP 13 system promote higher metal extraction than when the extractants are used individually. The 14 increased extraction is referred to as a synergistic effect. It was of interest to see if the neutral 15 monoamide extractants would experience synergism with the acidic extractant di-(2-16 ethylhexyl)phosphoric acid, HDEHP. On its own, HDEHP does not extract Am³⁺ at high nitric 17 acid concentrations (SI Figure 6). Extraction of Cu^{3+} periodate oxidized Am resulted in 18 distribution values as high as 3.43 ± 0.03 at 2 M HNO₃ with 0.5 M HDEHP in n-dodecane, SI 19 Figure 6. The HDEHP result in and of itself is promising. When compared to 1 M diamyl 20 amylphosphonate (DAAP) studies, a 2.0 ± 0.1 distribution value was achieved, and corresponded 21 to a AmO₂²⁺/Am³⁺ separation factor of 6.1 at 2 M HNO₃ (Am³⁺ as a Ln³⁺ surrogate).¹⁰ At 2 M 22 HNO₃ a AmO₂²⁺/Am³⁺ separation factor of 1150 was achieved with 0.5 M HDEHP and 3249 at 3 23 M HNO₃. Even higher distribution values were envisioned with a HDEHP-monoamide 24 synergistic effect. Since the highest monoamide distribution value occurred at 3 M HNO₃, the 25 distribution of oxidized Am was measured at 3 M HNO₃ by maintaining an extractant 26 concentration of 1 M while changing the ratio of DHBA and HDEHP. The results are shown as 27 a Job's plot in Figure 7. When no HDEHP is present the distribution is 0.66 ± 0.03 and the 28 distribution increases with the inclusion of 0.1 and 0.3 M HDEHP. At 0.5 M HDEHP/0.5 M 29 DHBA the distribution value is 1.7 ± 0.4 which lies within experimental error of the 2.0 ± 0.7 30 distribution value obtained with 0.5 M HDEHP individually. The similar distribution value 31 indicates no synergistic effect is observed for HDEHP with DHBA. Based on comparisons with 32 other solvating reagents,³²⁻³⁶ the inability for monoamide reagents to participate in a synergistic 33 metal extraction mechanism with HDEHP was unanticipated. In other synergistic systems the 34 extractants can orient to have a polar head (oxygen donor) and nonpolar tails, akin to a 35 shuttlecock. The monoamide extractants do not share a similar ability, and the acyl group's 36 vicinity to the nonpolar nitrogen alkyl chains could be inhibiting the synergistic coordination. 37

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Figure 7: Distribution values of Cu^{3+} periodate oxidized Am in 3 M HNO₃ extracted by varying the ratio of HDEHP and DHBA. Extractant concentration was maintain at 1 M in n-dodecane while the amount of DHBA decreased from 1 M DHBA (ratio value of 0) to 0.5 M with 0.5 M HDEHP (ratio value of 1) to generate the Job's plot. Distribution of oxidized Am in 3 M HNO₃ extracted by 0.5 M HDEHP n-dodecane is included for comparison (green square).

The presence of trace reducing species in the organic phase was considered as contributing to the 2 low extraction since AmO_2^{2+} would be readily reduced to poorly extracted AmO_2^{+} and Am^{3+} 3 species. To decrease the amount of reducing species, NaBiO₃ was added to HNO₃ during the pre-4 equilibration step. Although Cu³⁺ periodate is used to oxidize Am³⁺ in the actual extractions, 5 Cu³⁺ periodate quickly reduces in the presence of organic phase.¹⁰ Due to Cu³⁺ periodate's short 6 7 lifetime, NaBiO₃ was used during pre-equilibration because it persists for the longer time durations used to pre-equilibrate the solutions (2 hours) and has been used elsewhere in 8 literature.²² The results, shown in **Figure 8**, show the same trend observed with Am³⁺ where the 9 10 distribution values increase between 1 and 3 M HNO₃ but decrease at 4 and 5 M HNO₃. Although the same trend occurs, the distribution values are higher compared to non-oxidative 11 12 pre-treatment samples. The distributions are noticeably higher between 3 and 5 M HNO₃. This suggests the NaBiO₃ did behave as a scavenger to eliminate reducing agents in the organic phase. 13

Less of a difference between pre-treatments with and without NaBiO₃ is observed at 1 and 2 M HNO₃ solutions since less Am recovery occurs in the presence of lower nitric acid concentrations. Higher nitric acid concentrations increase the concentration of $AmO_2(NO_3)_2$ species causing the increase in distribution values. The sensitivity of AmO_2^{2+} towards reduction prevented deduction of an observable trend in distribution values for the increasing monoamide acyl chain. Distribution values were within close proximity to each other at 3 M HNO₃ as $1.03 \pm$ 0.02, 1.16 ± 0.03 , and 1.08 ± 0.07 with DHBA, DHVA, and DHHA respectively. At other acid concentrations, the values were not statistically different. As seen with $PuO_2^{2^+}$, distribution values with branched monoamides are lower than straight chained for hexavalent actinides. Although NaBiO₃ was used to pretreat 1 M DH2MBA and DH2EBA solutions, the extraction efficiency did not exceed 50%. Previous research has shown that distribution values with monoamides increase up to 6.5 M HNO₃ for NaBiO₃ oxidized Am³⁺.²² If more efficient oxidation, with less reduction could be achieved at 4 and 5 M HNO₃ with Cu³⁺ periodate, the distribution values should also increase above 3 M HNO₃ concentrations.



Figure 8: Distribution values of Cu^{3+} periodate oxidized Am over 1-5 M HNO₃ acid range. The 1 M monoamide in n-dodecane solution were pre-equilibrated with 60 mg/mL NaBiO₃ in the respective acid concentration. Oxidized americium extraction by straight chain monoamides (light blue) 1 M DHBA (circle), DHVA (square), and DHHA (diamond) are compared to branch chain DH2MBA (navy blue circle) and DH2EBA (green triangle).

8

9 **Conclusion**

Extraction of Pu^{4+} and PuO_2^{2+} with synthesized straight and branched monoamides was 10 demonstrated. As expected, Pu⁴⁺ and PuO₂²⁺ was efficiently extracted (96% and 89% 11 respectively) by straight monoamides. No trend was observed over increasing acyl chain length 12 for Pu^{4+} extractions, but PuO_2^{2+} extractions decreased with increasing acyl chain length from 13 butyramide to hexanamide. Branched monoamides demonstrated the selective extraction of 14 $PuO_2^{2^+}$ over Pu^{4^+} . No trend was observed with $PuO_2^{2^+}$ extractions, but Pu^{4^+} extraction was 15 grouped based off the branch being either methyl or ethyl branched monoamide. The monoamide 16 UV-Vis spectra showed a decrease in the outer-sphere extracted species, Pu(NO₃)₆(HL)₂, in the 17 order of straight > methyl branched > ethyl branched and indicated $Pu(NO_3)_4(L)_2$ or 18

 $Pu(NO_3)_5L(HL)$ was also extracted. The PuO_2^{2+} monoamide UV-Vis spectra indicated a plutonyl 1 trinitrate species, mostly likely as PuO₂(NO₃)₃(HL), was extracted as well as PuO₂(NO₃)₂(2L). 2 3 Slight variations were observed in the Pu(NO₃)₃(HL) region between methyl and ethyl branched 4 monoamides indicating fine structural effects which should be investigated in future studies. Oxidized americium distribution values were below one for acid pretreated monoamide 5 6 solutions. Salting agents LiNO₃ and Al(NO₃)₃ did not significantly improve extraction, and no 7 synergistic extracted effect was observed with addition of HDEHP. However, 0.5 M HDEHP itself showed promising results having achieved a 3.43 ± 0.03 distribution value and 1150 8 separation factor at 2 M HNO₃. The use of HDEHP as an extractant for hexavalent group 9 actinide separations has not been considered in previous oxidized Am studies, and should be 10 investigated in future studies. Monoamide distribution values above one were achieved in 3 M 11 HNO₃ when straight chain monoamide solutions were pretreated with NaBiO₃ to remove 12 reducing species, but values decreased at 4 and 5 M HNO₃ due to incomplete Am³⁺ oxidation 13 and rapid AmO₂²⁺ reduction. Future studies should focus on determining the structure of 14 hexavalent monoamide species, which could provide further insight on the branched monoamide 15 selectivity. 16

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Extraction of tetravalent and hexavalent plutonium by straight and branched chained monoamides was studied using UV-Vis spectroscopy. It was determined that anionic species tended to be extracted, indicating outer-sphere species formed. Branched monoamides showed more inner-sphere type behavior. Distribution values calculated from UV-Vis analysis were compared to tracer level LSC measurements, and were found to agree. Distribution values of hexavalent Am were also assessed. Good distribution values were achieved with straight monoamides while branched showed room for improvement.