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Hexavalent Actinide Extraction Using N,N-Dialkyl Amides

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ABSTRACT

Recently, efforts towards closing the nuclear fuel cycle have considered oxidizing americium to a hexavalent, linear-dioxo cation for co-recovery with hexavalent U, Np, and Pu from molar nitric acid using solvating extraction ligands such as tri-*n*-butyl phosphate or diamyl amylphosphonate. This work assesses solvent extraction recovery of sodium bismuthate oxidized americium by N,N-di-(2-ethylhexyl)butyramide (DEHBA), N,N-di-(2-ethylhexyl)isobutyramide (DEHiBA), and N,N-dihexyloctanamide (DHOA). Extraction efficiency between the monoamides was found to increase in the order of DEHiBA < DHOA < DEHBA. For all monoamides, oxidized americium extraction was less than 50% from 4 M HNO_3 and below. Extraction efficiency above 50% was obtained using concentrations of 5 M HNO_3 or higher. The DEHBA extractant provided the highest distribution value of 5.4 at 7 M HNO_3. Distribution values were found to be stable for up to 45 seconds aqueous/organic phase mixing times and indicated decreased reduction of hexavalent americium relative to separations completed with organophosphorus extractants. The simultaneous co-extraction of U, Np, Pu, and Am was demonstrated using DEHiBA, and was found to decrease with increasing atomic number ($D_U > D_{Np} > D_{Pu} > D_{Am}$). Interestingly, a break in recovery was observed where ligher actinides, U and Np, were better recovered relative to the heavier actinides, Pu and Am, in this study. This observation seems to be related to differences in the extracted metal complex for light actinides compared to heavy actinides. The metal:ligand stoichiometry was found to be mixed 1:1 and 1:2 species for U and Np while Pu and Am displayed 1:2 stoichiometry..

INTRODUCTION

Concepts for closing the nuclear fuel cycle typically include separating select actinides (U – Am) from other fuel components to allow for their fissioning in light water reactors (e.g., U, Pu, and possibly Np) or in fast spectrum nuclear reactors (all actinides). In such an advanced fuel cycle, radioactive fission products and activation products would be deposited into geological storage for several hundred years to allow for their decay to stable isotopes. Partitioning and transmutation of actinides substantially reduces the long term radiotoxicity and the volume of high level waste relative to a once-through fuel cycle. Advanced fuel cycles considered to date typically involve two or three post-irradiation separations. The first separation would recover U, Pu and perhaps Np from Am, Cm and fission products. Subsequent steps seek to separate Am from the lanthanide fission products.

Closing the nuclear fuel cycle would be simpler if (after removing bulk U via UREX or equivalent) the actinides Np through Am could be recovered as a group from fission products and Cm. Such an approach would offer improved proliferation resistance because Pu would not be separated from the other transuranic elements (except for Cm). In light of the significant redox instability of U^{3+}, Np^{3+} and Am^{4+} and the weak extraction of pentavalent actinides, AnO_2^{+}, the search for a common oxidation state for U-Am leads to the hexavalent state (AnO_2^{2+}). The linear dioxo cation geometry is unique to hexavalent and pentavalent actinides; this characteristic geometry impacts both redox chemistry and patterns of stability of actinide complexes. Because this geometry is not seen elsewhere in the mix of fission and activation products found in dissolved used fuel, this feature of actinide chemistry could be exploited to separate these ions from all other species using liquid-liquid extraction technology.

These motivations have led to a renewed interest in hexavalent americium extraction for nuclear fuel cycle applications. Americium is difficult to oxidize, though once achieved, americium has comparable solvent extraction chemistry to other actinyl ions. Strong chemical oxidizing agents such as sodium bismuthate[1] or copper periodate,[2,3] as well electrochemical oxidation using novel, surface functionalized electrodes[4] have been used to prepare Am(VI) in nitric acid solution. Only sodium bismuthate and copper periodate have demonstrated americium oxidation followed by its recovery as a hexavalent cation in solvent extraction processes.[3,5–7] The recovery of hexavalent actinides (U- Am) in the presence of either copper periodate or sodium bismuthate produces decreasing extraction efficiency with increasing atomic mass.[5] The most viable extractant for these separations has been diamyl amyl phosphonate (DAAP), but DAAP will recover both tetravalent and hexavalent elements and contains phosphorus that can complicate low-level waste management after DAAP's use in an extraction. An extractant with selectivity for just hexavalent actinides and that adheres to the CHON principal (reagents containing carbon, hydrogen, oxygen and nitrogen) would be preferential.

Monoamides have been proposed as extractants for nuclear fuel cycle applications, with advantages over phosphorus containing reagents that include greater selectivity for uranium over fission products and possibly higher radiolytic stability.[8] The selectivity of a given monoamide for both hexavalent and tetravalent actinide recovery, versus just hexavalent actinide recovery, depends on the alkyl chain substitution at the carbonyl carbon. The *n*-alkane substituted amides have overall higher extraction efficiencies while branch-chain alkanes are used for selection of U(VI) over Th(IV), Pu(IV) and Zr(IV).[9,10] For example, N,N-di-(2-ethylhexyl)butyramide (DEHBA) extracts U(VI) and Pu(IV), while N,N-di-(2-ethylhexyl)isobutyramide (DEHiBA) selectively extracts U(VI), although with lower D_U than for the unbranched amide.[11] Thus, for applications involving U/Pu co-extraction, DEHBA would be preferred and for applications involving selective extraction of U, DEHiBA would be preferred. The structures of these compounds are shown in **Figure 1**.

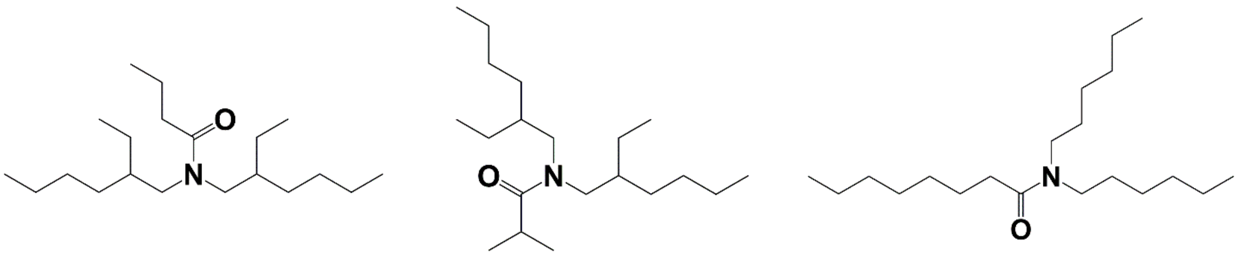

Figure 1 Monoamide structures discussed in this study: DEHBA (left), DEHiBA (middle) and DHOA (right).

Since the monoamide ligands can recover hexavalent uranium, they may be able to recover other hexavalent actinides – including americium. This could make them ideal candidates for group actinide recovery of hexavalent actinides. This report considers the solvent extraction-based recovery of bismuthate-oxidized americium using *n*-alkane substituted DEHBA, the branched alkane DEHiBA, and also N,N-dihexyloctanamide (DHOA), a monoamide that has received extensive previous investigation as a TBP replacement compound.[12] The utility of the monoamides in the simultaneous co-extraction of U, Np, Pu and Am is also demonstrated.

EXPERIMENTAL METHODS

The monoamides DEHBA and DHOA were synthesized via nucleophilic attack of acyl chloride by secondary amines containing the desired alkyl chains.[8] A 1.2:1 molar ratio of butyryl chloride or 1: 1 octanoyl chloride, diluted in chloroform, was added dropwise to a mixture of the secondary amine, bis(2-ethylhexyl)amine or di-*n*-hexylamine, diluted in chloroform and triethylamine. The dropwise addition was done in a nitrogen atmosphere at 5°C under vigorous stirring. Once mixed, the solution was refluxed for 2 hours at 60° C. The solution was then filtered and washed with water, 10 wt % sodium carbonate, and 1 M HCl to remove unreacted triethylamine as well as residual alkyl chlorides. The solution was dried with sodium sulfate overnight. To purify the product, chloroform was removed by rotary evaporation followed by vacuum distillation. Characterization by H-NMR showed the product to be greater than 99% pure. DEHiBA was purchased from Technocom (Edinburgh, UK). The product was also characterized by NMR upon receipt and found to be greater than 99% pure.

Solvent extraction experiments were completed using equal organic:aqueous phase volumes. The aqueous phase of appropriate acidity was traced with 30 uM uranium, 2 uM neptunium, 20 uM plutonium, and/or 10 uM americium, as appropriate. The radiotracers used were natural uranium, ^{237}Np, ^{239}Pu, and ^{243}Am, from stocks on-hand at INL. A two hour pre-equilibration of the organic phase with an acidic bismuthate-containing aqueous phase was completed prior to the extraction contact. The aqueous phase was also treated for two hours with 60 mg mL^{-1} sodium bismuthate powder to oxidize the actinides to their actinyl valence state. After these pre-treatments, the extraction was completed with a 10 sec contact at 23 ± 2 ^{o}C of an organic phase consisting of 1 M monoamide in dodecane. Short contact times are necessary to prevent Am(VI) reduction by reaction with the ligands themselves. The phases were separated with 1 min centrifugation, and then aliquots were removed for analysis. ***Caution!*** *The isotopes ^{237}Np, ^{239}Pu, ^{243}Am, and natural uranium are radioactive. All radioactive materials were handled in radioactively controlled facilities that are equipped with personal safety equipment.*

Distribution ratios were measured as the concentration or activity of the actinide metal in the organic phase, over the concentration or activity in the aqueous phase. Post extraction americium characterization for both phases was completed by γ-ray counting, using the ^{243}Am 74.7 keV line. Uranium, Np, and Pu were determined in both phases using a Thermo X series 2 ICP-MS with a Teflon sample introduction system and platinum cones. During analysis of organic solutions, 0.2 L/min of 20 % oxygen in argon was added to the spray chamber to aid in combustion of the organic material and to reduce build up on the cones. Organic solutions were emulsified with Triton TX100 into the normal 1 % nitric acid solution used to dilute samples prior to analysis. The aqueous phases were also treated with the surfactant to ensure consistency between sample matrices.

RESULTS AND DISCUSSION

Am(VI) extraction by DEHBA, DEHiBA and DHOA

The solvent extraction distribution ratios for bismuthate-oxidized americium from nitric acid solution using 1 M solutions of DEHBA, DEHiBA or DHOA in dodecane are shown in **Figure 2**. The extraction of Am(III) using DEHBA is also presented and shows no significant extraction of trivalent americium at any acid concentration. The average D_{AmIII} was 0.002. The extraction of oxidized americium (nominally Am(VI)) was evident for all three ligands. Increasing D_{Am} occurs with nitric acid concentration and possibly reaches a maximum at 7 M HNO_3. This behavior is consistent with that previously reported for the extraction of bismuthate-oxidized americium by DAAP, where extraction attributable to Am(VI) increased with acid concentration.[6] This was attributed to a combination of low solubility of the oxidant at the lower acid concentrations,[13] and also the necessity of forming the neutral ligand complex for solubility in the organic phase.

Figure 2 also shows that DEHBA offers the highest D_{Am} of nearly 5.5 at 7 M HNO_3, versus approximately 2.1 for the other monoamides. For the comparison between DEHBA and DEHiBA, these results are consistent with those previously measured for the extraction of U(VI), where higher extraction efficiency was reported for the *n*-alkane substituted monoamide.[11] The longer-chain DHOA behaved similarly to the branch-chain DEHiBA with regard to americium extraction efficiency. The highest D_{Am} of 4.5–5.5 occurred for DEHBA extraction of oxidized americium from 6–7 M HNO_3, and is consistent with DAAP extraction where D_{Am} of 3–4 are typically reported at this high acidity. Thus, the single-stage extraction efficiency for bismuthate-oxidized americium is slightly higher for DEHBA (85 %) than for DAAP extraction (80 %), using the same ligand concentration.[6,7]

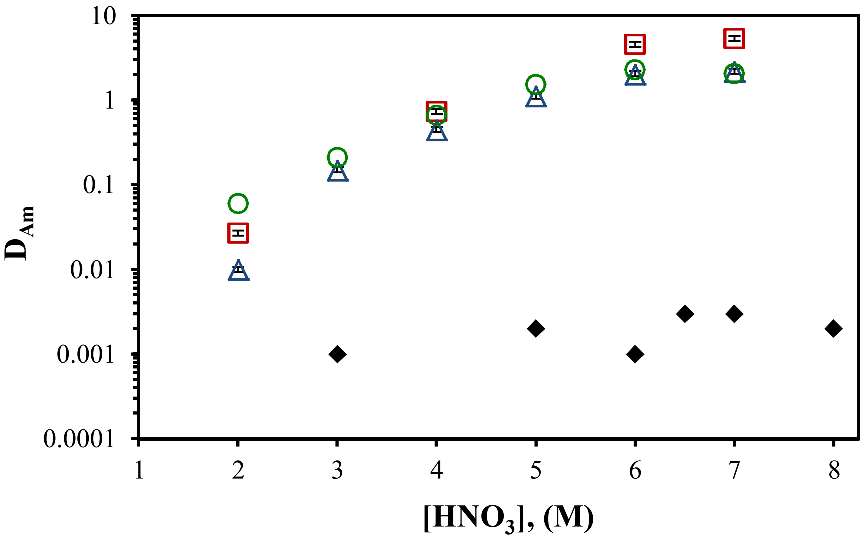

Figure 2 The solvent extraction distribution ratios for nominally Am(VI) over a range of nitric acid concentrations using 1 M DEHBA (squares), DEHiBA (triangles), and DHOA (circles). The extraction of non-oxidized Am(III) using DEHBA is shown for comparison (filled diamonds). The error bars shown represent ± 7% uncertainty based on repetitive extractions (N = 5 for DEHiBA and N = 2 for DEHBA). Other data shown are for a single extraction.

Effect of contact time

Previous work with TBP[5] and DAAP[6] extractants have shown that short contact times were necessary to ensure adequate extraction of americium. This is presumably due to reduction of the Am(VI) by the organic phase, though more rigorous studies regarding the species responsible for reduction or the reduction mechanism have not been outlined. The effect of contact time on Am recovery by DEHBA was considered for extraction from 6.5 M HNO_3. Contact times varied from 8–45 seconds. **Figure 3** shows extraction values with a 68% confidence interval (one sigma, 10% error) and 95% confidence interval (two sigma, 20%). For less than 30 second contact times no change occurs within the one sigma values, and D_{Am} decreases slightly at 45 seconds. When two sigma values are included, there is no loss in extraction efficiency from 8 to 45 second contact times. By comparison, the D_{Am} decreased by one-third with increased DAAP contact time from 15 to 30 sec for extraction from 6.5 M HNO_3.[6]

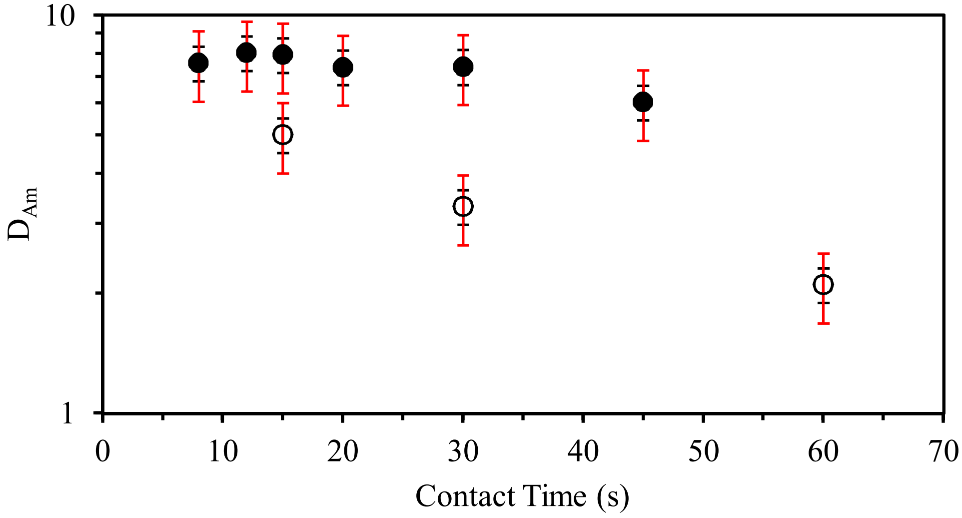

Figure 3 The effect of contact time on distribution ratios for the extraction of bismuthate oxidized americium from 6.5 M HNO_3 at different contact times with DEHBA (closed circles) and DAAP data from reference #6 (open circles). Black error bars encompass values within one sigma (10%) and red error bars account for values within two sigma (20%).

Ce (IV) extraction using DEHBA and DEHiBA

Among the lanthanides, only cerium is oxidized by sodium bismuthate. During oxidation for actinide co-extraction, Ce(IV) extractable by DAAP.[6,7] The potential extraction of Ce(IV) by monoamides DEHBA and DEHiBA was also investigated here. **Figure 4** shows the distribution ratios for the extraction of tetravalent cerium were high for DEHBA, but the extraction of cerium was inefficient for the branched-chain DEHiBA. This result is consistent with those reported by others for Zr(IV), Th(IV), and Pu(IV).[9–11] Due to the high cerium extraction efficiency using DEHBA, a separation of Am(VI) from Ce(IV) in nitric acid concentrations of 6–7 M would require DEHiBA as a ligand, and a separation factor between Am and Ce of ~ 2 is obtained using 1 M DEHiBA. Efficient extraction of both americium and cerium using DEHBA might be preferable, followed by selective stripping of the americium with dilute hydrogen peroxide, as was previously demonstrated using DAAP.[6]

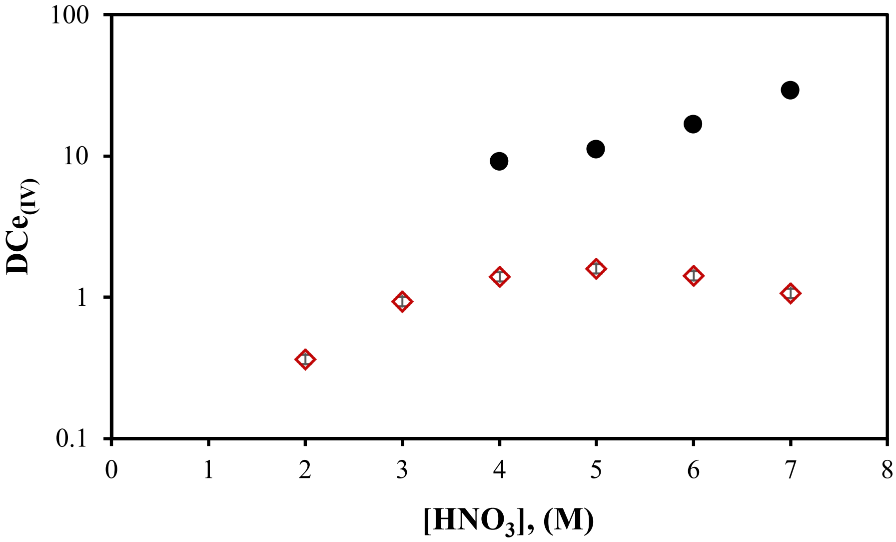

Figure 4 The solvent extraction distribution ratios for Ce(IV) extraction using 1 M DEHiBA (open diamonds) with ± 7 % error bars for duplicate extractions; and a single set of 1 M DEHBA extractions (closed circles).

Co-extraction of the actinyl ions using DEHBA and DEHiBA

Any oxidant sufficient to oxidize Am(III) to Am(VI), with its standard redox couple of 1.72 V,[14] should also oxidize neptunium and plutonium to the hexavalent state. Uranium already exists as U(VI) under acidic aqueous conditions. Thus, treatment of an actinide containing acidic solution with sodium bismuthate is expected to prepare a solution containing U(VI), Np(VI), Pu(VI) and Am(VI), all as their hexavalent AnO_2^{2+} cations, to enable a group hexavalent actinide extraction. Here acidic solutions containing all four actinides in tracer amounts were oxidized with sodium bismuthate and subjected to 1 M DEHiBA extraction. The results in **Figure 5** indicate that americium was extracted with the same efficiency as shown in **Figure 2**, when in the presence of these additional actinides.

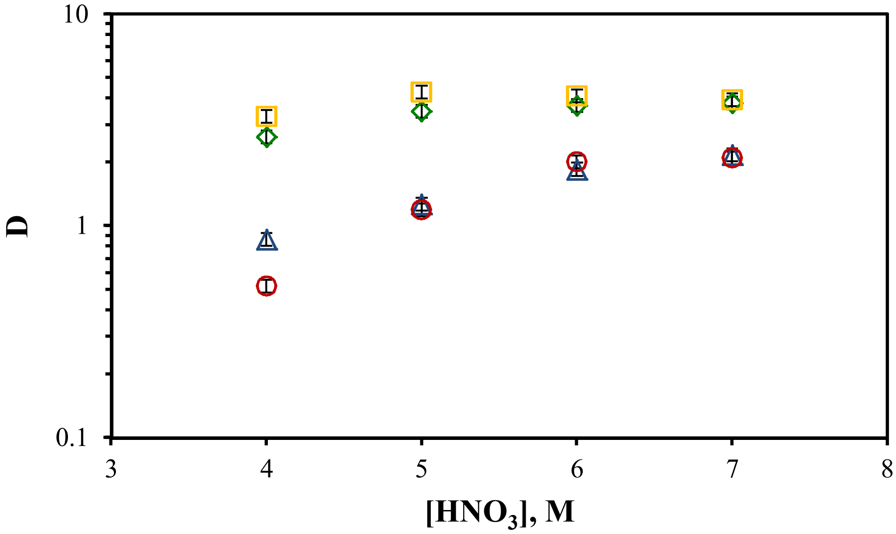

Figure 5 The solvent extraction distribution ratios for nominally U(VI) (squares), Np(VI) (diamonds), Pu(VI) (triangles) and Am(VI) (circles) over a range of nitric acid concentrations using 1 M DEHiBA/dodecane extraction. All data are the means of duplicate co-extractions with error bars shown of ± 7%.

Previously reported co-extraction experiments using TBP as the extractant produced data with a regular decrease in extraction efficiency across the actinide series, with americium being the least well recovered.[5] The same pattern, $D_U > D_{Np} > D_{Pu} > D_{Am}$, is shown for DEHiBA extraction in **Figure 5**; however, the actinides appear in two groups with D_{U} and D_{Np} being similar, and D_{Pu} and D_{Am} being similar. To further investigate this result, the extraction stoichiometry was assessed for all four metals by varying the DEHBA (0.1-0.5 M) concentration in the presence of 6.5 M HNO_3, as shown in **Figure 6**. Although DEHiBA and DEHBA have slightly different structures, the same pattern is observed for the straight chain monoamide, with $D_{\mathrm{U}} > D_{\mathrm{Np}} > D_{\mathrm{Pu}} > D_{\mathrm{Am}}$ and again forming the two groups.

The solvation numbers, possibly reflecting ligand stoichiometry, increased across the series with a range of 1.4–1.9. However, these also fell into two groups with a mean value of 1.5 ± 0.2 for U/Np, and 1.9 ± 0.1 for Pu/Am. This suggests a change in stoichiometry from mixed 1:1 and 1:2 metal:ligand complexes for U/Np to predominantly 1:2 complexes for Pu/Am. Recent studies have suggested high nitric acid concentration increases the amount of protonated monoamide ligands (HL) in the organic phase, bringing about an outer-sphere coordination environment.[15,16] Similarly, elevated nitric acid conditions give rise to anionic trinitrate uranyl species, $[UO_2(NO_3)_3]^-$.[17,18] The mixed 1:1 and 1:2 stoichiometry could be due a protonated monoamide complexing with anionic uranyl ($UO_2(NO_3)_3HL$) and neptunyl species while the 1:2 ratio is synonymous with two ligands extracting the neutral hexavalent actinide dinitrate species ($UO_2(NO_3)_2L_2$). For comparison to these DEHBA results, the solvation number was also measured for Am(VI) using the branch chain DEHiBA and a value of 1.9 ± 0.2 was obtained (data not shown), consistent with the results in **Figure 6**.

It is acknowledged that the proper determination of a solvation number relies on low ligand and metal concentrations, such that ligand aggregation effects and/or substantial changes in free ligand concentration do not perturb the stoichiometry under investigation. Low acid concentrations are also preferred. Here the acid concentration was kept at 6.5 M to dissolve sufficient oxidizing agent, and higher than desirable ligand concentrations of 0.1–0.5 M were necessary to ensure measurable D_{Am}. While the solvation numbers reported here may not represent actual stoichiometry, they should be adequate to reveal comparative trends in stoichiometry as discussed above.

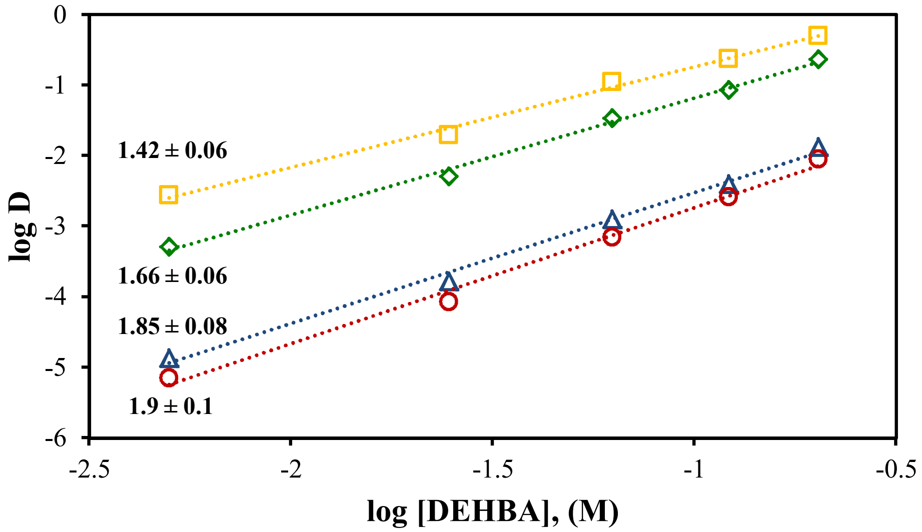

Figure 6 Solvation number study for U(VI) (squares), Np(VI) (diamonds), Pu(VI) (triangles) and Am(VI) (circles) using a range of DEHBA concentrations from 0.10–0.50 M in dodecane.

CONCLUSIONS

The monoamide DEHBA is a promising ligand for use in hexavalent americium extraction. As expected, DEHBA provides increased extraction efficiency for Am(VI) over DEHiBA and DHOA. Interestingly, the recovery of hexavalent americium using DEHBA is somewhat greater than achieved using DAAP or TBP, and appears to be less reducing toward Am(VI) than those ligands. In co-extraction of hexavalent uranium, neptunium, plutonium and americium, the actinides fall into two groups with behavior of the two light and two heavy actinides being similar. This is true both for distribution ratios and for solvation numbers, as illustrated by extractions with DEHiBA and DEHBA. The magnitude of the solvation number increases across these actinyl ions from 1.4–1.9, indicating a higher ligand to metal ratio in the extracted complex for the higher z-numbers. The reason for the shift in coordination number is not completely obvious currently, but could be related to a protonated monoamide extracting anionic trinitrato uranyl and neptunyl species. Future work should further examine the possibility of trinitrato actinyl recovery, characterize americium oxidation states in the organic phase using spectrophotometry and study actinide recovery in the presence of used nuclear fuel simulants.

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