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Abstract: *Implementation of a closed loop nuclear fuel cycle requires the utilization of Pu-containing MOX fuels with the important side effect of increased production of the transplutonium actinides, most importantly isotopes of Am and Cm. Because the presence of these isotopes significantly impacts the long-term radiotoxicity of high level waste, it is important that effective methods for their isolation and/or transmutation be developed. Furthermore, since transmutation is most efficiently done in the absence of lanthanide fission products (high yield species with large thermal neutron absorption cross sections) it is important to have efficient procedures for the mutual separation of Am and Cm from the lanthanides. The chemistries of these elements are nearly identical, differing only in the slightly stronger strength of interaction of trivalent actinides with ligand donor atoms softer than O (N, Cl, S). Research being conducted around the world has led to the development of new reagents and processes with considerable potential for this task. However, pilot scale testing of these reagents and processes has demonstrated the susceptibility of the new classes of reagents to radiolytic and hydrolytic degradation. In this project, separations of trivalent actinides from fission product lanthanides have been investigated in studies of 1) the extraction and chemical stability properties of a class of soft-donor extractants that are adapted from water-soluble analogs, 2) the application of water soluble soft-donor complexing agents in tandem with*

conventional extractant molecules emphasizing fundamental studies of the TALSPEAK Process. This research was conducted principally in radiochemistry laboratories at Washington State University. Collaborators at the Radiological Processing Laboratory (RPL) at the Pacific Northwest National Laboratory (PNNL) have contributed their unique facilities and capabilities, and have supported student internships at PNNL to broaden their academic experience. New information has been developed to qualify the extraction potential of a class of pyridine-functionalized tetraaza complexants indicating potential single contact Am-Nd separation factors of about 40. The methodology developed for characterization will find further application in our continuing efforts to synthesize and characterize new reagents for this separation. Significant new insights into the performance envelope and supporting information on the TALSPEAK process has also been developed.

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Principal Investigator: Kenneth L. Nash, Chemistry Department, Washington State University, Pullman, WA 99164-4630

Accomplishments:

In addition to the tangible scientific accomplishments to be discussed below, the following highlights arising from this project can be enumerated:

- Dr. Mark D. Ogden completed a Ph.D. dissertation in the Chemistry Department at Washington State University entitled ***THE EFFECT OF STRUCTURAL HINDRANCE ON THE COMPLEXATION OF ACTINIDES AND LANTHANIDES BY LIGANDS CONTAINING SOFT NITROGEN DONORS***; 3 open literature publications supported under this project are in preparation based on the results discussed in this dissertation. A fourth review paper remains in preparation.
- An open literature publication reviewing the literature of the TALSPEAK process has been published in the open literature Nilsson, Mikael, Nash, Kenneth L. **A Review of the Development and Operational Characteristics of the TALSPEAK Process**, *Solvent Extr. Ion Exch.* **25(6)** 665-701 (2007)
- An open literature publication examining selected features of the TALSPEAK process has been published in the open literature **Trans-lanthanide Extraction Studies in the TALSPEAK System: Investigating the Effect of Acidity and Temperature**. M. Nilsson, K. L. Nash, *Solvent Extr. Ion Exch.*, **27(3)** 354-377 (2009)
- This research continues in a NERI-C project: AWARD NUMBER: ID14896 Advanced Aqueous Separation Systems for Actinide Partitioning
- A Postdoctoral Associate who worked on this project, Dr. Mikael Nilsson, is now a Chemical Engineering Professor at the University of California at Irvine
- A Postdoctoral Associate who worked on this project Dr. Leigh Martin, is now an Assistant Scientist at the Idaho National Laboratory

Project Objective: Implementation of a closed loop nuclear fuel cycle requires the utilization of MOX fuels containing plutonium. The use of MOX fuel, combined with longer irradiation times for fuel, results in increased production of trans-plutonium actinides, most significantly, isotopes of americium and curium. Furthermore, long-stored spent fuel suffers the steady increase in the relative amount of ^{241}Am resulting from the β^- decay of ^{241}Pu . Because the presence of these isotopes significantly impacts the long-term radiotoxicity of high-level waste, it is important to

develop effective methods for their isolation and/or transmutation. Whether by thermal reactor, fast spectrum reactor, or accelerator irradiation, transmutation is most efficiently done in the absence of lanthanide fission products, as some of the lanthanides are important neutron poisons. Because the lanthanide content is 100 fold higher than Am/Cm (on a molar basis) in freshly discharged spent fuel, it is very important that effective procedures for their mutual separation be developed. The most useful and versatile separations of these species are accomplished using reagents containing donor atoms “softer” than O (N or S in particular, but chloride ion (Cl⁻) has been used as well), which interact more strongly with actinides than lanthanides. Reagents that have been advanced in recent years in research being conducted around the world show promise, but suffer various weaknesses, many relating to their instability in a radiation field or strongly acidic solutions. This project investigates new chemical methods (or the improvement of existing methods) for selective separation of transplutonium actinide isotopes from fission product lanthanides using the proven techniques of aqueous processing. Of greatest relevance are those processes that employ soft donor atoms, in this context, those exhibiting less ionic bonding character than oxygen (N, Cl⁻, S, specifically). One thrust seeks to promote the development of poly-nitrogen donor extractant molecules; the second thrust, which arose from applications development work being done elsewhere within the Advanced Fuel Cycle Initiative program, is on the characterization of the basic chemistry of the TALSPEAK process, wherein group separation is derived from the presence of a polyaminopolycarboxylic acid in the aqueous phase.

Project Narrative:

Despite decades of research, the selective separation of the minor actinides Am and Cm from fission product lanthanides (predominantly La-Dy) with decontamination factors of $> 10^4$ remains an elusive target. However, several new extractant systems have been identified and characterized during the past decade. Some of these systems promise to yield such separation performance. In addition, there are several notable examples of successful approaches to trivalent actinide/lanthanide separations that have been brought forward and in some cases extensively characterized though never deployed in spent fuel processing ^[1]. The most important among these earlier studies involve ternary or quaternary amine extractants contacted with concentrated lithium chloride solutions (the TRAMEX process ^[2]) and aminopolycarboxylic acid complexants used in combination with acidic organophosphorus extractants (the TALSPEAK process ^[3]). The basic principals of these processes are the foundation of ongoing investigations, as in the SETFICS process ^[4-6] proposed by Japanese scientists. TRAMEX is an essential component of the production of transplutonium actinides for research application and the preparation of ²⁵²Cf neutron irradiation sources carried out at the High Flux Isotope Reactor (HFIR) and Radiological Engineering Development Center (REDC) at Oak Ridge National Lab ^[2].

All successful aqueous processing options for group separation of fission product lanthanides from trivalent actinides have relied on the applications of ligand donor atoms “softer” than oxygen (N, S, Cl⁻) ^[1], following the lead of the earliest reports of this effect from Diamond et al. ^[7]. The slightly greater strength of the complexation of trivalent actinides with these donor atoms than that exhibited by the corresponding lanthanides (believed to be derived from a greater covalent contribution to the bonding in the actinide systems) provides adequate thermodynamic driving force for the separation to occur. Though the effects are difficult to quantify, an apparent correlation exists between the numbers of soft donor atoms that can be coordinated to the trivalent cation and the separation factors. However, the appearance of hard donor oxygen atoms

(resulting from degradation of the soft-donor extractant molecule) has been shown to significantly degrade the effectiveness of many soft donor separation systems^[8].

Various protocols based on the application of soft donor ligands containing nitrogenous (amines, pyridines, imidazole, triazine,...) functional groups have been developed recently^[9] that achieve single stage mutual separation factors of 10 to 100. Am/Eu separation factors of more than 5000 have been reported for selected dithiophosphinic acid extractants^[10, 11]. Other derivatives of this general class of extractant molecules bearing aromatic substituents sacrifice some separation efficiency for a higher degree of radiation stability and the ability to conduct separations operations in more acidic solutions^[12-14]. The success of separation processes based on either of these classes of reagents in pilot scale demonstrations has been limited by extractant purity problems and by unacceptable radiation or hydrolytic stability of the reagents^[15-17]. It can be inferred from this observation that reagent stability is as important an aspect of ligand design for nuclear fuels processing as is the configuration of the cation binding site or control of ligand/complex solubility in the extractant phase.

For spent fuel separations applications, the design of chelating agents and the development of processes for their use must emphasize equally complex stability (derived from the creation of a binding site compatible with the structural requirements of the target metal ion), organic phase compatibility (derived from adjustment of the nature and positioning of the attached alkyl groups) and radiation/hydrolysis resistance. It is possible to build radiation tolerance into extractant molecules, though this may come at the expense of either or both of the other two elements of ligand design. Rather than focusing on a large scale program to develop new extractant formulations (which would require substantially greater amounts of effort and a longer time frame than was available in this program), this project emphasized ligand binding sites known to distinguish between trivalent lanthanides and actinides. The initial objectives of this program included a significant emphasis on radiation stability studies; developments in the science and in the larger Global Nuclear Energy Program (GNEP) and Advanced Fuel Cycle Initiative (AFCI) led to a shift in emphasis from some aspects of the original scope of this work. The two primary tasks completed in this investigation focused on the preparation and characterization of tetraaza complexing agents and fundamental studies of the TALSPEAK Process. Scoping experiments were done on the planned work on radiation stability of the complexants, but ultimately the bulk of this work was postponed due to the perception that focusing on nitrogen-based ligand design and TALSPEAK studies were higher priority activities.

Most of the studies of metal ion partitioning were done using radiotracer techniques. Trans-lanthanide studies were greatly facilitated by the ICP-MS facilities residing on the WSU campus in the School of Earth and Environmental Sciences. Synthesis of the tetraaza complexants was accomplished in our laboratory facilities and those of colleague Prof. G. P. Meier at WSU. Lanthanide studies (both those involving radiotracers and non-radioactive materials) were conducted both at WSU and at PNNL. Studies involving spectrophotometry of Am(III) were conducted by Ogden and Nilsson working in conjunction with G. Lumetta and S. Sinkov at PNNL. Radiotracer lanthanides were conducted using materials activated in the WSU Nuclear Radiation Center 1 MW TRIGA reactor. Working supplies of ²⁴¹Am for the radiotracer studies conducted at WSU were obtained from the supplies of our collaborators at PNNL.

Task 1: Selectivity derived from water-soluble complexants: Features of the TALSPEAK process

The TALSPEAK process, developed in the 1960's, relies on acidic organophosphorus extractants (liquid cation exchangers like bis(2-ethylhexyl)phosphoric acid, HDEHP) for phase transfer and uses a combination of concentrated lactic acid and lower concentrations of aminopolycarboxylic acids. This combination retains Am/Cm selectively in the aqueous phase, while lanthanides are preferentially extracted. The TALSPEAK process has been reported to achieve (Am, Cm)/(Σ Ln) separation factors of about 100 on average in laboratory-scale demonstrations. Reverse TALSPEAK separations involve similar aqueous solutions employed as stripping reagents for selective removal of Am/Cm from an extractant phase loaded with both lanthanides and actinides. The Japanese DIDPA process also employs an aminopolycarboxylate complexant for selective stripping of trivalent actinides away from lanthanides; literature reports indicate that this approach was not fully successful^[18]. The CTH process developed in Sweden is similar, and has been tested to the pilot scale^[19-21]. The SETFICS process (developed in Japan) is reverse TALSPEAK using a neutral organophosphorus extractant. SETFICS separation factors are somewhat lower, though the reasons for the comparative degradation in the separation have not been fully explained.

This portion of the project began with an examination and evaluation of the substantial prior literature on the TALSPEAK Process. The baseline conditions for the TALSPEAK process are 0.3-0.5 M HDEHP in 1,4-diisopropylbenzene equilibrated with an aqueous medium of 1.0 M lactic acid ($\text{CH}_3\text{CH}(\text{OH})(\text{CO}_2\text{H})$) buffer solution also containing 0.05 M DTPA (See Figure 1 for structures). The pH must be maintained at 3.6 and because of the considerable complexity of the application, high concentrations of the buffer are needed. The primary species participating in the phase transfer process are the (primarily) dimeric extractant $(\text{HDEHP})_2$ in which monoacidic dialkylphosphate groups are internally hydrogen bonded, most typically exchanging a corresponding number of H^+ ions needed to satisfy the charge balance requirements of the metal ion in the organic phase. The octadentate, penta-acidic DTPA (diethylenetriamine- $\text{N},\text{N},\text{N}',\text{N}'',\text{N}'''$ -pentaacetic acid, H_5DTPA) serves as the counterbalance to the complexing strength of the HDEHP extractant molecule.

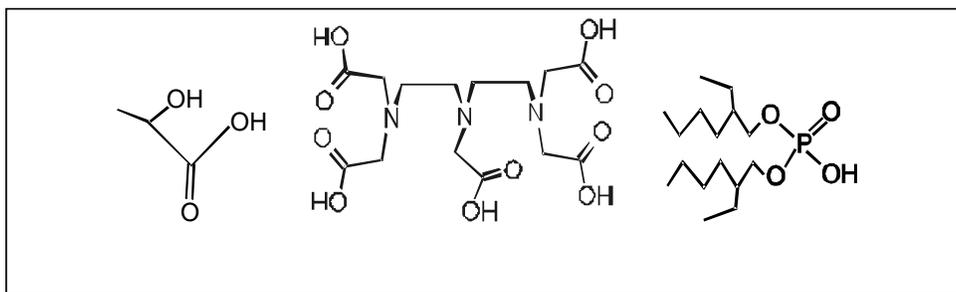


Figure 1. Major components in TALSPEAK, from left to right, lactic acid (HL), diethylenetriamine- $\text{N},\text{N},\text{N}',\text{N}'',\text{N}'''$ -pentaacetic acid (DTPA) and bis-2-ethylhexyl phosphoric acid (HDEHP).

The baseline performance of TALSPEAK is demonstrated by the data shown in Figure 2. For extraction from mineral acid solution, the extractant HDEHP shows regular variation with the

size of the ions, but An/Ln distribution ratios overlap, hence there is no separation. Substituting lactic acid/DTPA for the mineral acid allows greater relative extraction of the light lanthanides, suppresses extraction of trivalent lanthanide and results in separation factors for Am/Cm from Ln of up to 100.

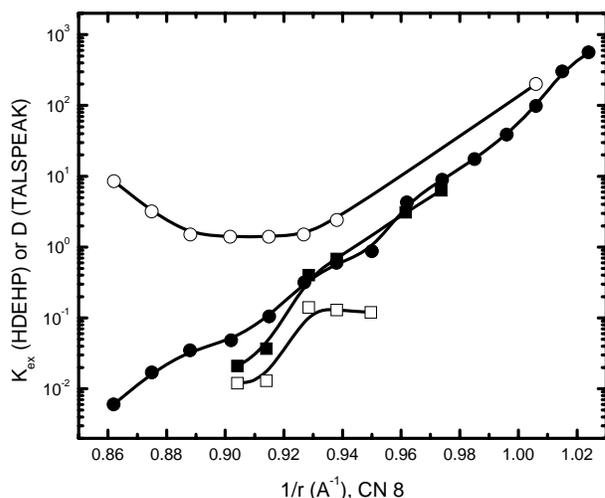


Figure 2. Extraction of trivalent actinides and lanthanides by HDEHP from mineral acid and lactate buffer media containing DTPA: (● (Ln) ■ (An)) Extraction equilibrium constants (K_{ex}) for trivalent f elements ions into HDEHP/toluene from perchloric acid solutions ^[22]; (○ (Ln), □ (An)) Distribution ratios (D) for trivalent f-elements in the TALSPEAK process (0.3 M HDEHP in diisopropylbenzene, 1.0 M lactic acid, 0.05 M DTPA, pH 3) ^[23].

To test the thermodynamics of this extraction system, an internally consistent data base of equilibrium constant information was assembled from the open literature. These equilibrium constants were employed to predict the speciation of the TALSPEAK system as conditions were varied. In Figure 3 the results of speciation calculations are shown for Eu^{3+} and Am^{3+} between $\text{p}[\text{H}^+]$ 2 and 4 for 0.3 M HDEHP, 1.0 M total lactate and 0.05 M DTPA, representative TALSPEAK conditions. Figures 3a and 3b demonstrate that the metal-lactate complexes for these ions are significantly less important than those of HDEHP and DTPA. Parallel calculations for La^{3+} and Ce^{3+} indicate that lactate complexes are more important at low $\text{p}[\text{H}^+]$ for these cations. $\text{Am}(\text{DTPA})^{2-}$ and $\text{AmH}(\text{DTPA})^-$ are the clearly dominant species for Am^{3+} under these conditions, while $\text{Eu}(\text{AHA})_{3\text{org}}$, $\text{Eu}(\text{DTPA})^{2-}$ and $\text{EuH}(\text{DTPA})^-$ are of comparable concentrations. These species predominance diagrams translate into distribution ratios around 1 for Eu^{3+} and about 0.01 for Am^{3+} for a net separation factor ranging from 55 to near 96 as the $\text{p}[\text{H}^+]$ increases from 2 to 4.

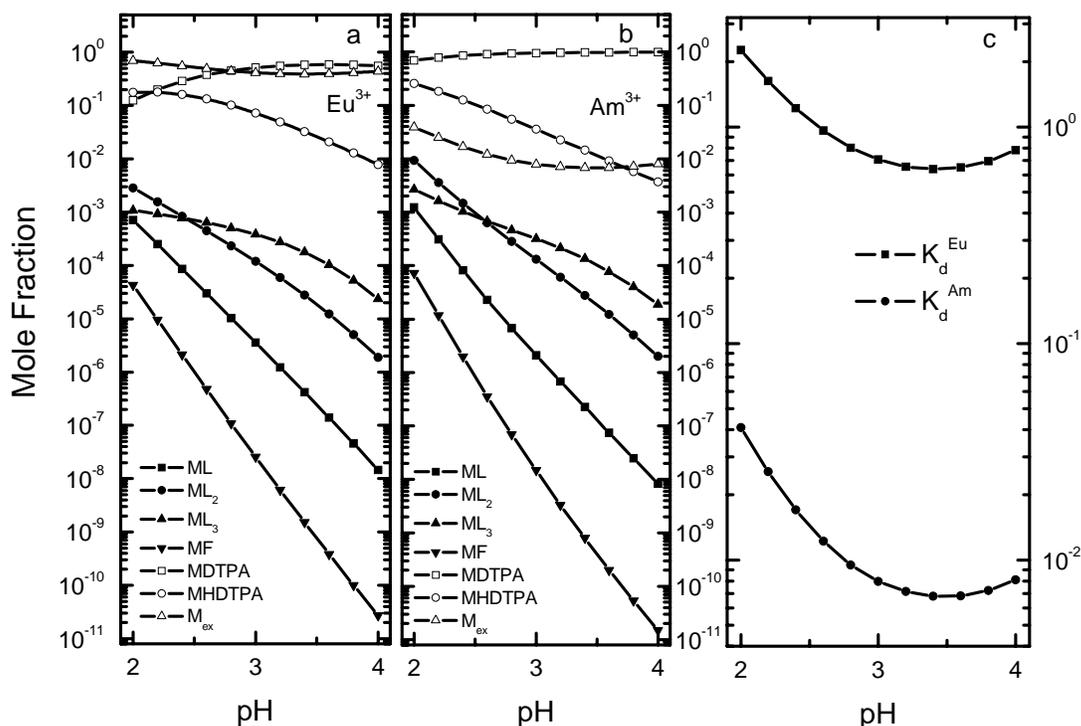
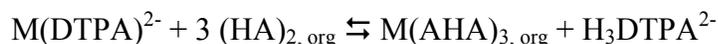


Figure 3. Calculated speciation of Eu³⁺ (a) and Am³⁺ (b) under representative TALSPEAK conditions: 0.3 M HDEHP, 0.05 M DTPA, 1.0 M lactic acid; (c) Calculated distribution ratios. Species calculations based on available set of chemical equilibrium constants at 0.1 M ionic strength, T=25.0°C [12].

In Figure 3c it is noted that the distribution ratios of both Eu³⁺ and Am³⁺ decline to a minimum value at about p[H⁺] 3.6 then rise somewhat at p[H⁺] 3.6 to 4.0. This latter result contrasts with the information reported in Figure 4. Experimentally it is seen that distribution ratios decline as p[H⁺] rises from 2 to 4. The discrepancy between these calculations and experimental observations implies that either the aqueous equilibrium constants increase significantly as the ionic strength increases (the principal contributor to ionic strength in this system is free lactate, which increases significantly above p[H⁺] 3.7), activity coefficients of the reactants are increasing or that additional species are present under these conditions that are not considered in the calculations. These data do not provide a basis for choosing between the three options. The simplest approach is to postulate the presence of ternary complexes (e.g., Am(DTPA)(lac)³⁻) in the aqueous phase. Calculations suggest a steeper descent of D's with increasing p[H⁺] above 3 if such a complex is postulated. Thermodynamic data describing the equilibria of ternary complexes are very rare, though such species might be important in many contexts besides TALSPEAK.

Given this analysis, it is clear that the overall reaction governing metal ion partitioning between HDEHP and DTPA/Lactic acid is:



Under normal operational conditions of the process, i.e., at pH 3.6, this reaction should be almost independent of pH. At pH 3.6, the equilibrium position of the lanthanide metal ions lies to the right in this expression, i.e., they are preferentially extracted; Am^{3+} and Cm^{3+} are to be found in the left side of this equilibrium, thus retained in the aqueous phase. Complexes of lanthanide and actinide metal ions with the lactic acid buffer are known, but based on known thermodynamic parameters describing the stability of the complexes, they are less likely to be important in the operation of this process, due to the much stronger complexes formed with HDEHP and DTPA. Literature data predicts that lactate complexes are much weaker than those of either DTPA or HDEHP. There are suggestions in the literature of the presence of mixed ligand complexes $(\text{Ln}(\text{Lac})(\text{AHA})_2$ in the organic phase or $\text{An}(\text{Lac})(\text{DTPA})$, but these species are inferred rather than the result of direct observation, so must be considered unconfirmed. Experimental work conducted as a part of this program and at other institutions have failed to establish any direct observation of such species.

Previous reports from the literature indicate that pH control is in fact the most challenging aspect of this system, thus the lactate buffer is essential to performance. Our own subsequent analysis of the system has confirmed that the lactate buffer performs several essential functions in the TALSPEAK process ^[25]. It has been reported by several authors that the extraction of trivalent lanthanides and actinides decreases as the pH rises in TALSPEAK, implying that the preference for the aqueous phase increases with this change (Figure 4). A report from Kolarik and Kuhn ^[26] addressed the kinetic features of this system. They established that the phase transfer kinetics of the system are quite slow in the absence of lactic acid. Overall, the phase transfer kinetics of this system are seen to be very challenging, changing in a complex manner with [lactate], [HDEHP], $[\text{H}^+]$ and with the addition of tributylphosphate (TBP) as a phase modifier. The work of Tachimori and coworkers establishes that lactic acid actually provides a measure of radiation protection to DTPA ^[27] (Figure 5).

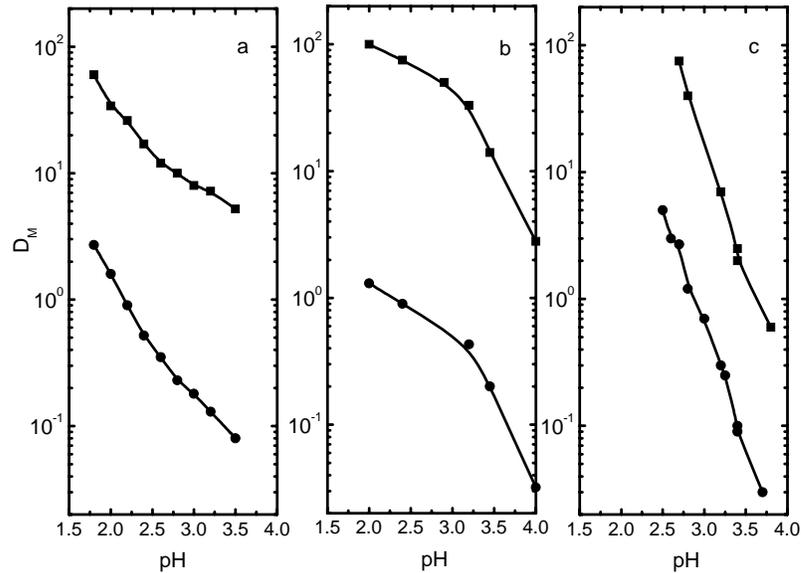


Figure 4. pH dependence of extraction of Am (●), Eu (■ a and b), Nd (■ c.) a. Organic phase: 0.5 M HDEHP in diisopropylbenzene. Aqueous phase: 1 M lactic acid and 0.05 M DTPA. Reproduced from data in [23], b. 0.5 M HDEHP in *n*-decane from 1 M lactic acid and 0.07 M DTPA versus the $p[H^+]$ of the aqueous phase. Reproduced from data in [28], c. Organic phase: 1 M HDEHP in odorless kerosene. Aqueous phase: 1.5 M lactic acid and 0.05 M DTPA. Reproduced from data in [29]

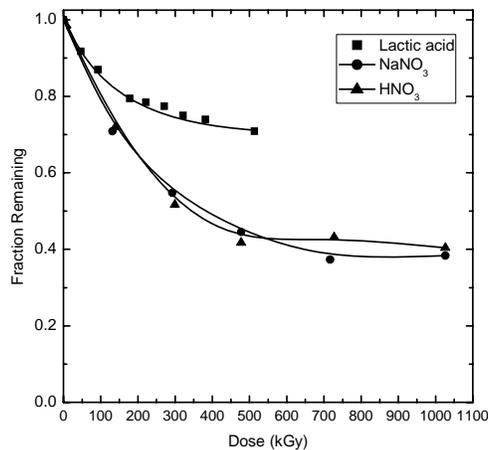


Figure 5. Radiolytic degradation of DTPA in aqueous solutions by gamma irradiation. 0.2 M HNO_3 (▲); 1 M $NaNO_3$, $p[H^+]$ 3.0, (●); 1 M lactic acid, $p[H^+]$ 3.0, (■). Reproduced from data in [27].

Following on from the review of the literature, we noted that the cumulative literature reports provided a wide variety of observations over a wide range of conditions. One objective of the review and subsequent study was to attempt to validate the performance of this system relative to the predictions of an internally consistent set of thermodynamic parameters the basic components of the system. Therefore, subsequent studies addressed several of these issues experimentally, in particular the questions of pH dependence of extraction and of reaction kinetics. The pattern of extraction of the lanthanides as a function of pH is shown in Figure 6. It is seen that the experimental performance of this system is consistent with earlier reports of declining extraction with increasing pH. Separate information indicates that Am/Ln separation factors do not vary substantially with pH. It has been noted above that the available thermodynamic data predict the opposite trend.

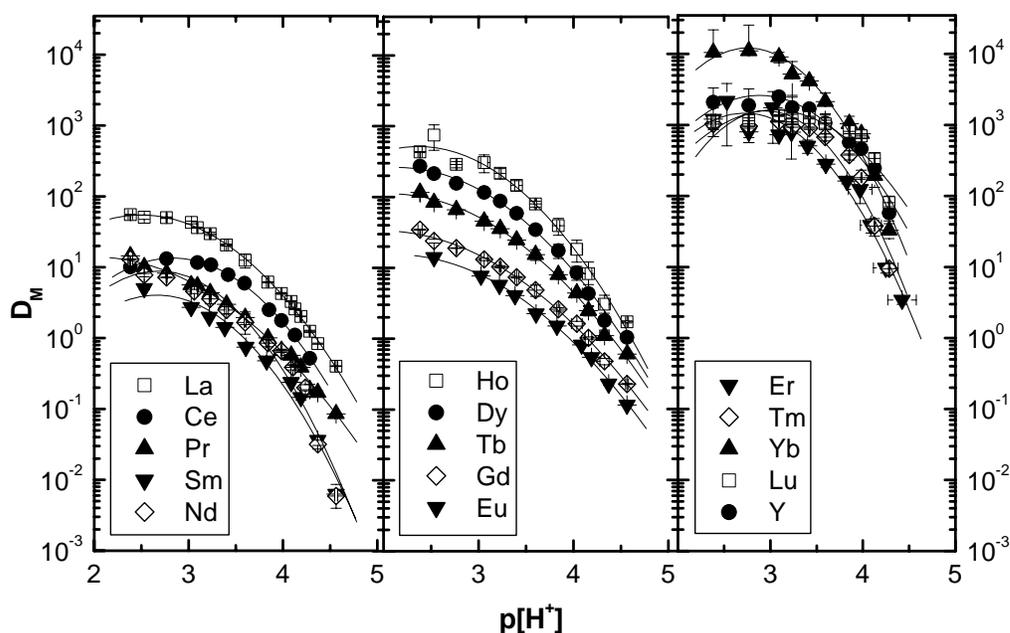


Figure 6. Distribution ratios of the lanthanide series plotted against $p[H^+]$. Extraction from 1 M total NO_3^- , 1 mM total $[Ln] + [Y]$, 1 M lactic acid, 0.05 M DTPA at various acidity. Organic phase was 0.5 M HDEHP in 1,4-DIPB. These experiments were conducted at room temperature. Data correspond to 1st and 2nd run. The lines in the figure represent quadratic fits for each dataset.

One important parameter to study for industrial applications is the temperature dependency of the phase transfer reaction. The temperature in process may be elevated due to decay heat. If the effect is extreme, it can prove necessary to control the temperature to maintain system performance. This information can also indicate opportunities for improving process efficiency by adjusting the temperature into a more efficient range. To investigate this feature of the system, extraction experiments were carried out at different temperatures. Figure 7 demonstrates

the extraction trends as a function of inverse temperature, a typical van't Hoff analysis. All lanthanides show exothermic reactions in the temperature range studied and it can be seen that the heat of extraction changes slightly between different lanthanides.

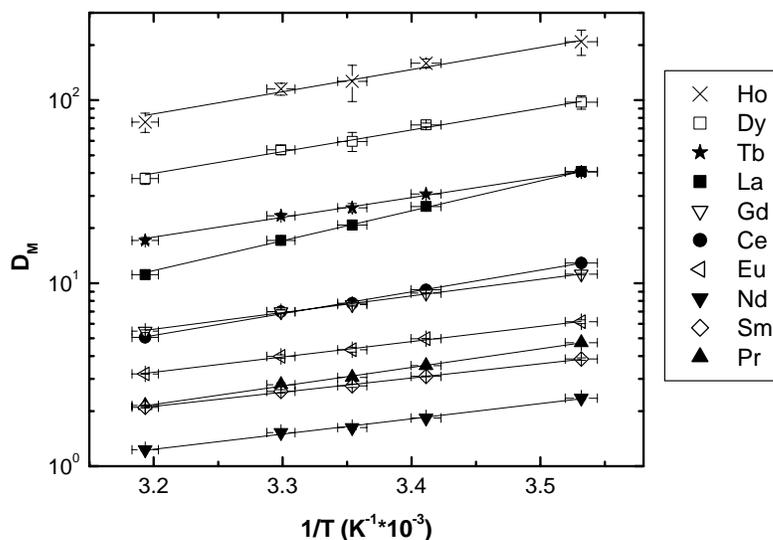


Figure 7. van't Hoff analysis of lanthanide distribution ratios: Experimental conditions (aqueous phase) - 1M total nitrate, 1 M lactic acid, 0.05 M DTPA, 1 mM total [Ln] + [Y], pH around 3.7, (organic phase) - 0.5 M HDEHP in 1,4 DIPB. Temperature of extraction was varied between 10 °C and 45 °C. Data taken from Nilsson and Nash^[25]

Across the lanthanide series (Figure 8), the heat of extraction becomes less exothermic from the lightest lanthanides, reaching the least exothermic value around neodymium/samarium; for the lanthanides heavier than Sm, extraction enthalpy again becomes increasingly exothermic with increasing atom number. This behavior is also observed for HDEHP extraction of lanthanides from mineral acid solutions^[30-32] and thus it may be postulated that HDEHP dominates the enthalpic contribution to the extraction in the TALSPEAK system. Because the observed enthalpies represent the cumulative effect of numerous processes, they can be considered to be strictly relevant only to the conditions of the experiment. Since they parallel enthalpies reported for the extraction of lanthanides by HDEHP reported previously, it is safe to assume that the phase transfer reaction dominates the thermal signature for lanthanide extraction.

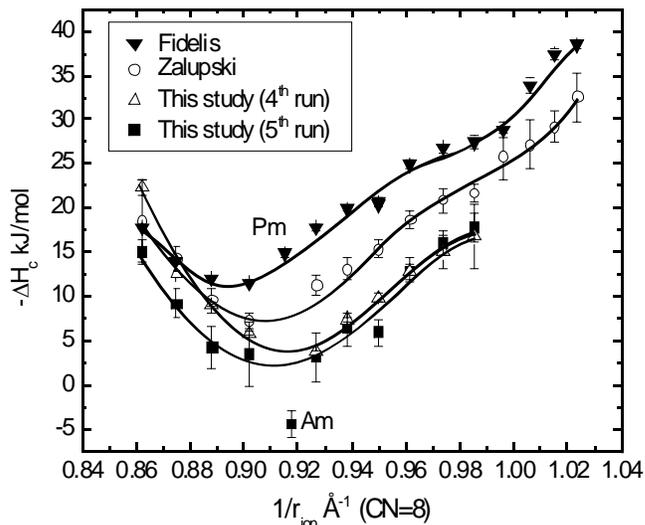


Figure 8. Conditional enthalpies for extraction of lanthanides and Am^{3+} from 1M lactic acid, 0.05 M DTPA, 1mM total Ln + Y, 1 M total nitrate (4th run) or sodium (5th run) into 1,4-DIPB containing 0.5 M HDEHP (4th run) and 0.2 M HDEHP (5th run) at p[H] 3.7 (4th run) and 4.1 (5th run). Results from the literature on the extraction of lanthanides from mineral acid solutions are for HDEHP in n-heptane [30, 31] or n-dodecane [32].

Task 2: Ligand Design for selected new reagents

Our initial plan was to pursue two classes of new reagents for possible application in trivalent actinide/lanthanide separations: lipophilic analogs of EDTA and polyamino ligands, specifically tetradentate species of constrained coordination geometries. It was determined early on in this investigation that there was greater need for increased understanding of polyaza compounds, there for it was determined that a focus on the relationship between the structural arrangement of N-donor atoms in a series of tetraamine ligands was the more productive pathway for study, therefore we elected to focus on the synthesis and characterization of new compounds modeled after previously reported polypyridine donor systems.

The methyl pyridyl complexants are best represented by the complexing agent ethylenediamine-N,N,N',N'-tetramethyl pyridine (TPEN) in which acetate groups of EDTA are substituted by methyl pyridyl binding groups. TPEN has the ability under suitable conditions to engage in f-element coordination through four aromatic and two aliphatic nitrogen atoms, and has been reported to exhibit a 100-fold preference for trivalent actinides over lanthanides of similar radius [33-36]. Because of the general tendency of amine-bearing complexants to partition to the aqueous phase, an acidic co-extractant is required. Takeshita and coworkers [36] have demonstrated this effect using HDEHP (bis(2-ethyl(hexyl))phosphoric acid). We will examine the performance of selected members of these assorted ligands in combination with acidic extractants known to engage in the formation of reverse micelles in the organic phase. This approach has not been previously reported in the actinide/lanthanide separations literature. Synthesis of each class of extractants has been reported to be straight-forward [37].

A limitation of this class of complexants is the comparative weakness of the strength of the interaction between the trivalent actinide ion and nitrogen donor ligands. To amplify the effect, it is important to “tune” the interaction strength by improving the entropic contributions to net bonding strength by improvement of the geometric arrangement of the nitrogen donor atoms. The effect of donor group preorganization is clearly seen in the chemistry of a novel optimized bicyclic diamide^[38]. The difference between the formation constants for a 1:1 complex with Am(III) of N,N'-dimethyl bicyclic diamide (DMBCDA) and tetramethylmalonamide (TMMA) at 0.1 M HNO₃ and 0.9 M NaNO₃ is $\Delta \log \beta = 1.98$ which represents a difference in the Gibbs free energy of formation between TMMA and DMBCDA of $-11.3 \text{ kJ mol}^{-1}$ ^[38]. The energy difference required for a separation factor of 100 in a solvent extraction system is approximately 11.4 kJ mol^{-1} , which is comparable to the energy of a single hydrogen bond^[1]. Even though “soft” donor containing ligands in general have an inherent selectivity for An(III) over Ln(III), the binding constants in general are low. To increase the binding constant of the complexant for metal ions the ligand can be structurally preorganized.

In Figure 9 the ligands synthesized to allow examination of this effect are presented. It can be seen that by changing the steric hindrance of the bridging diamines, (B) N,N'bis(2-pyridylmethyl)-1,2-diaminoethane (BPMDAE), (C) N,N'bis(2-pyridylmethyl)piperazine (BPMPIP), (D) N,N'bis(2-pyridylmethyl)-*trans*-1,2-diaminocyclohexane (BPMDAC), and by replacing the amine bonds with imine bonds (A) N,N'bis(2-pyridylmethylene)-1,2-diiminoethane (BPM DIE), (E) N,N'bis(2-pyridylmethylene)-*trans*-1,2-diiminocyclohexane (BPM DIC), it is possible to preorganize the binding pyridyl nitrogens. It is expected that the necessary structural features required in a complexing ligand that will increase the binding affinity and selectivity for An(III) over Ln(III) can be identified. Potentiometric titrations of the compounds to determine the individual pK_as for the ligands with amine backbones (BPMDAE, BPMDAP, BPMDAC and BPMPIP) follows the corresponding trend in the overall basicity of the free amine^[24], in that; BPMDAP > BPMDAE > BPMDAC > BPMPIP i.e., propane-1,3-diamine > ethane-1,2-diamine > *trans*-cyclohexane-1,2-diamine > piperazine. The values of the last two pK_as for BPMDAE, BPMDAP, BPMPIP, & BPMDAC indicate the more acidic nature of the pyridyl moieties when compared with the aliphatic analogue triethylenetetramine (trien)^[24].

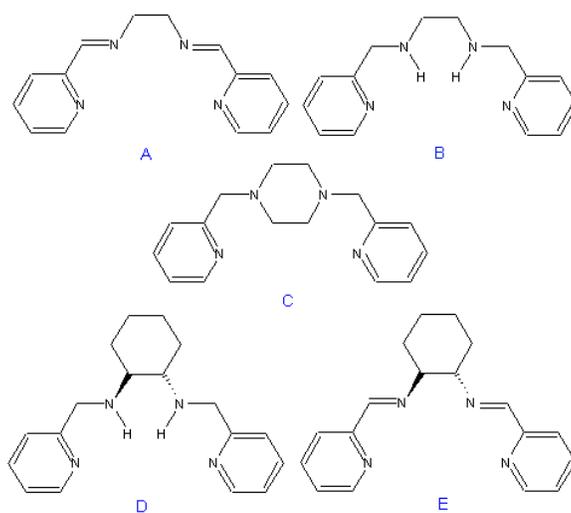


Figure 9: A to E represent the following ligands, BPM DIE, BPMDAE, BPMPIP, BPMDAC and BPM DIC respectively

The pK_1 for both BPMDIE and BPMDIC match that of 2-pyridine carboxaldehyde at 3.8^[39] and indicate that both of these ligands undergo hydrolysis in aqueous solution to form the tridentate ligands *N'*-(1-pyridin-2-ylmethylene)ethane-1,2-diamine (PMED) and *N*-[*trans*-2-aminocyclohexyl]-*N*-pyridin-2-ylmethyleneamine (*trans*-CPMA) respectively. The pK_a 's of the tridentate ligands *trans*-CPMDA and PMED, like the tetradentate amine ligands, follow the trend of the basicity of the free amine used in the backbone.

The stability of Cu^{2+} complexes with these ligands was employed as a preliminary screening method for the relative strength of the complexes. From these studies it has been ascertained that the relative affinity of the ligand for protons does not correlate with its affinity for the divalent copper ion. The stability constants for the tetradentate ligands, containing secondary amines, are exceedingly high. The most preorganized ligand BPMDAC has the highest value of $\log K_{101}$ (19.5) with BPMDAP and BPMDAE running up with values of 18.9 and 17.7 respectively. After the complete hydrolysis of BPMDIE and BPMDIC, *trans*-CPMDA and PMED are still strong complexants for copper, with each having a $\log K_{101}$ of 14.13 and 11.73. The $\log K_{101}$ value for BPMPPI is approximately 10 orders of magnitude smaller than the value for BPMDAE. It is believed that this deficit is partially due to the energy penalty associated with the rearrangement of the piperazine ring from the free ligand chair to metal complex boat configuration.

Contrary to previous distribution studies into nitrobenzene^[40, 41] the distribution of the ligands directly correlates to the lipophilicity of the backbone. It is clear that due to hydrolysis ligands BPMDIE and BPMDIC are not suitable to be used for solvent extraction although the tridentate chelate formed on degradation may extract or be used to retain metal ions in the aqueous phase. What is clear from the distribution study is that extraction experiments must be carried out at higher pH to prevent loss of the ligand to the aqueous phase. Although it can be argued that the K_D values for these ligands are too low to be useful, they may still prove to be effective at separating Am(III) from Ln(III). Much like TPEN under the following conditions, 0.001 M TPEN, 0.1 M NH_4NO_3 , pH 4.16 and nitrobenzene as the organic phase.

Table 1. Stability constants for the complexation of Cu^{2+} by N_4 -Tetradentate ligands determined at 21 °C.

Compound	Acronym	$\log K_{101}$	ΔG (kJmol ⁻¹)
A	BPMDAE	17.7 ± 0.9	-99 ± 5
B	BPMDIE	11.73 ± 0.02	-66.1 ± 0.1
C	BPMPPI	7.41 ± 0.06	-41.7 ± 0.3
D	BPMDAP	18.9 ± 0.2 18.7 ± 0.2 [†]	-106 ± 1 -105 ± 1
E	BPMDIC	14.13 ± 0.03	-79.6 ± 0.1
F	BPMDAC	19.5 ± 0.6	-109 ± 3
G	BPMDIB	4.4 ± 0.3	-25 ± 2

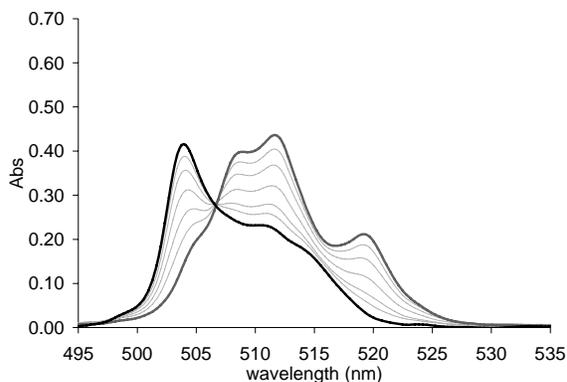
[†]Data fitted using selected pK_a s for BPMDAP at 1.0 M ionic strength from NIST database^[12]

Task 2A: Ligand Design for selected new reagents – Am³⁺ and Nd³⁺ complex strength

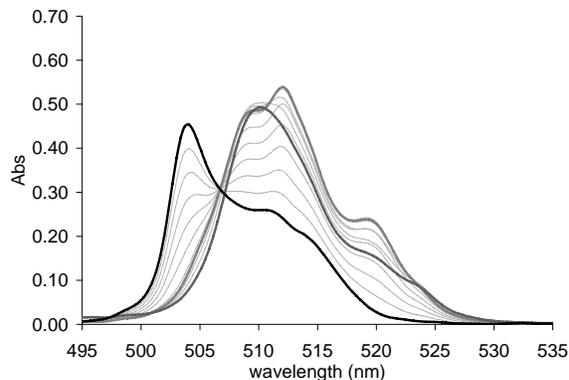
To improve the understanding of trivalent actinide-lanthanide separations, a series of polydentate N-donor ligands have been synthesized and their complexation with americium(III) and neodymium(III) investigated. Conditional stability constants were determined by UV-visible spectrophotometry. The trends in stability constant are similar to those of the terdentate bis(dialkyltriazinyl)pyridine (BTP) molecules and much weaker than those of 2-amino-4,6-di-(pyridin-2-yl)-1,3,5-triazine (ADPTZ). This leads to theoretical separation factors that are similar to those of the BTP systems. This suggests that this series of ligands could lead to an enhanced actinide(III)-lanthanide(III) separation if used in a solvent extraction system.

In this study the stability constants for a series of N₄ tetradentate ligands with Am³⁺ and Nd³⁺ have been reported for the first time. Investigating the metal ion bonding affinity of these metal-ligand systems in methanol solutions allows “simulation” of metal-ligand interactions in polar organic media that might be employed in a separation system based on these ligands, but avoids the competitive bonding complications imposed by working in aqueous media. It is understood that creating a useful solvent extraction reagent based on these chelation geometries would demand additional alteration of the periphery of the ligands. This series of multi-dentate nitrogen donor ligands were prepared to systematically examine the effects of pre-organizing the donor groups on the stability of Nd(III) and Am(III) complexes. For the ligands with bridging diamine groups, the complexation constants followed the order:

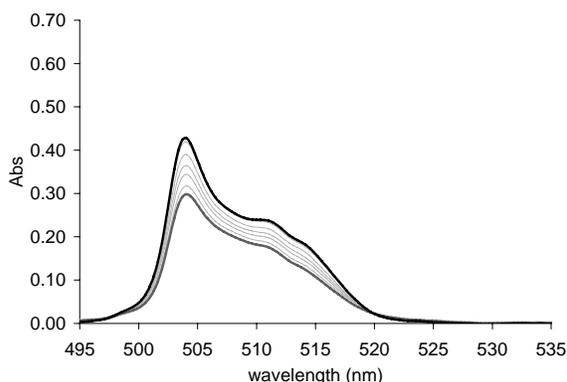




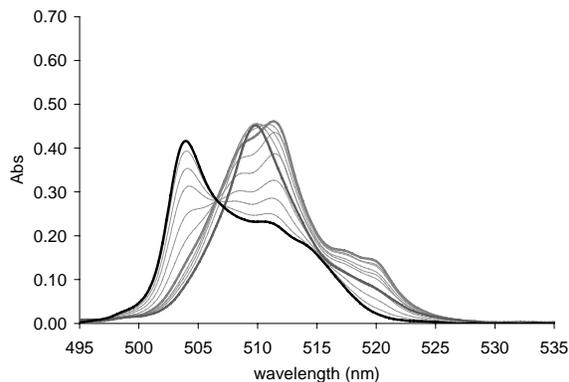
Spectra of Am^{3+} (2.20×10^{-3} M) with incremental additions of BPMDAE (A) (5.00×10^{-2} M). Thick dark grey line is the end point resulting in a M:L ratio of 1:3.0.



Spectra of Am^{3+} (2.20×10^{-3} M) with incremental additions of BPMDAC (F) (5.00×10^{-2} M). Thick light grey line is the primary species formed in solution at a M:L ratio of 1:1.5 and thick dark grey line is the end point resulting in a M:L ratio of 1:7.9.



Spectra of Am^{3+} (2.20×10^{-3} M) with incremental additions of BPMPPIP (C) (5.05×10^{-2} M). Thick dark grey line is the end point resulting in a M:L ratio of 1:10.4.



Spectra of Am^{3+} (2.20×10^{-3} M) with incremental additions of BPMDAP (D) (5.02×10^{-2} M). Thick light grey line is the primary species formed in solution at a M:L ratio of 1:3.0 and thick dark grey line is the end point resulting in a M:L ratio of 1:9.9.

Figure 10. Am(III) spectrophotometric titrations with N_4 -Tetradentate diamine based ligands, using 1 cm cuvette. Black lines represent Am^{3+} in methanolic media and dotted grey lines represent incremental additions.

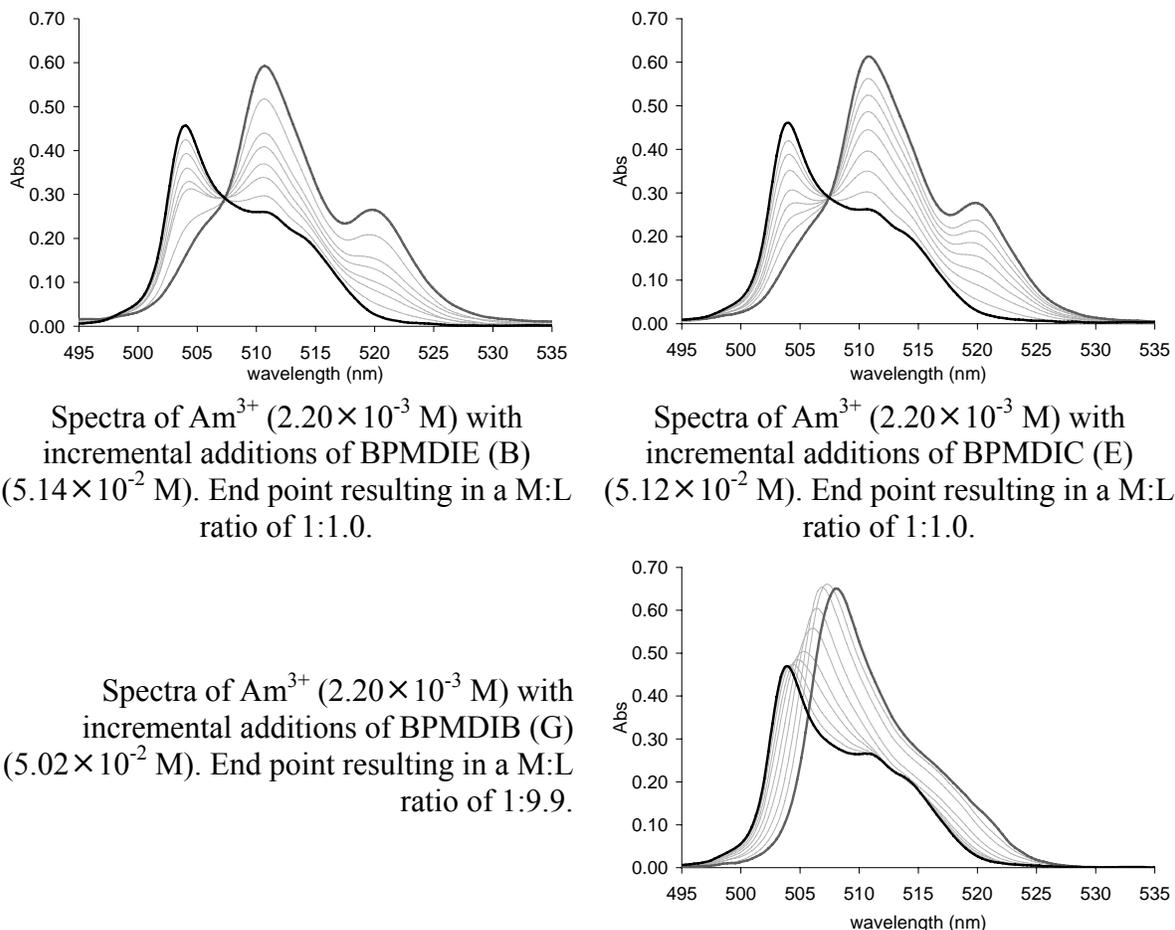


Figure 11. Am(III) spectrophotometric titrations with N_4 -Tetradentate diimine based ligands, using 1 cm cuvette. Black lines represent Am^{3+} in methanolic media, dotted grey lines represent incremental additions and dark grey lines represent end points.

Table 2. Stability constants ($\log K_{101}$) for complexation of M(III) and MO_2^{2+} with N_4 -tetradentate ligands at 21 °C and low ionic strength (0.015-0.03 M). M(III) constant calculated previously.

Ligand	Acronym	Nd(III)	Am(III)	U(VI)	Pu(VI)
A	BPMDAE	2.0 ± 0.3	2.52 ± 0.07	2.0 ± 0.1	1.9 ± 0.1
B	BPMDAP	1.74 ± 0.02	2.43 ± 0.04	2.72 ± 0.08	2.70 ± 0.06
C	BPMPPI	0.72 ± 0.09	1.20 ± 0.08	2.57 ± 0.03	N/A
D	BPMDAC	2.5 ± 0.1	4.1 ± 0.1	2.51 ± 0.08	2.50 ± 0.03

Constraining the two amine groups into a conformation that is more preoriented for binding, for example by introducing the cyclohexane ring, results in an increase in complex stability. On the other hand, incorporation of the two amine donors into the piperazine ring in BPMPPI results in a dramatic decrease in complex stability, suggesting significant conformational rearrangement would be required to force the boat conformation of this ligand. In the case of BPMDAP,

expansion of the chelate ring size by insertion of a methylene group into the ligand backbone also results in decreased binding strength compared to BPMDAE. In the latter case, some aspect of the decrease in binding affinity might also be attributed to an energy penalty caused by additional conformational changes revolving around the added methylene group.

For the ligands with bridging diimine groups, the complexation constants followed the order:



Again, inclusion of the cyclohexane ring in the ligand backbone increases the stability of the BPMDIC complexes compared to BPMDIE. Interestingly, further constraining of the ligand geometry into a plane (as in BPMDIB) results in decrease complex stability. Although from previous work on the BPMDIB it is more likely that we are dealing with the complexation of a bidentate ligand 2-pyridin-2-yl-1*H*-benzimidazole (PBI_m) in solution.^[39]

Theoretical separation factors (comparative values of Nd and Am stability constants) compare favorably with separation factors available from solvent extraction systems available in the literature (Table 4). TPEN and R-BTP molecules still offer the better separation factors. It is clear that ligands possessing preoriented ligand donor atoms are better suited for complexing than those that require rearrangement. It is also clear that the greater number of nitrogen donors engaged in cation binding improve the separation factor as evidenced by TPEN. BPMDAC shows the most promise of all the N₄-tetradentate ligands for application in solvent extraction systems. The ligands BPMDAE, BPMDAP and BPMDAC can be further derivatized at the amine nitrogens to make them more compatible with aliphatic organic diluents. These heterocyclic nitrogen ligands will extract metals by a solvation mechanism. Even though all these compounds have the benefit of conforming to the CHON principle in that they only contain carbon hydrogen and nitrogen^[40], there are caveats to all the systems investigated and compared within this body of work.

1. Extraction methods based on solvation processes usually suffer from low distribution values. By combining acidic extractants with a solvating extractant increased distribution ratios are often observed^[41]. Though no single mechanism describes this “synergistic” extraction system it usually occurs by either expansion of the inner metal coordination sphere of the extracted metal complex or replacement of waters of hydration. Either way the increased hydrophobicity of this metal complex will lead to enhanced extraction. The R-BTP systems that have been investigated require the presence of 2-bromodecanoic acid (BDA) or bis-(2-ethylhexyl)-phosphoric acid (HDEHP) as a synergist to increase extraction^[42].
2. With the complexes formed by nitrogen heterocycles in the extraction system the kinetics are reduced. These reagents also show poor compatibility with aliphatic polar diluents and thus a phase modifier needs to be added (e.g. 2EhOH) or the extraction switched to a more polar diluent such as nitrobenzene^[42]. This is predominantly due to the need to incorporate of 1 to 3 anions required for charge neutralization. In polar diluents with the comparatively weak nitrogen donor ligands, these anions are often not directly coordinated to the metal center.. This is the case with almost all the N-donor based extraction systems represented in this chapter. This effect is particularly true in the R-BTP system, where the 1:3 stoichiometry $[\text{M}(\text{R-BTP})_3]$ ^[43] has been shown by in both

crystal structure and solvent extraction slope analysis^[42]. If these species readily form in solution, and it is the 1:3 M:L complex that is extracted, it would be expected that the extraction will only be compatible with more polar diluents. It is clear that the lanthanide or actinide complexed with three BTP molecules is coordinatively saturated, thus charge neutralization must occur in the outer coordination sphere. If the same were observed in solution, it will affect the extraction, in that the solubility of the anion will determine the phase transfer of the complex. With this in mind it can be predicted that the distribution coefficients would follow the trend $\text{ClO}_4^- > \text{SCN}^- > \text{NO}_3^- > \text{Cl}^-$. For the R-BTBP and N_4 -tetradentate systems theoretically we would expect partial or full charge neutralization to take place in the outer coordination sphere depending on the extraction stoichiometry and thus potentially the same solvent compatibility problems will be demonstrated by this system.

Of future interest with the BPMDAE, BPMDAP and BPMDAC ligands is that the proton on the amine can be substituted not just for aliphatic groups but with carboxylic acids, amides, phosphonic acids, phosphinic acids and phosphine oxides to create a bank of compounds for An(III) and Ln(III) complexation and separation. Further insight into these systems presented could be gained by applying computational tools such as molecular mechanics. Most interestingly is the observable trend that by switching to pure N-donor systems the strength of the binding of Am^{3+} when compared to Nd^{3+} is increased by approximately 30% which is much greater than that observed for polyaminocarboxylates.

In summary, this ambitious program of investigation of selected features of actinide/lanthanide separation includes a broad selection of approaches to enhance the probability of developing a successful hydrometallurgical separation of these groups. The essential incorporation of soft donor atoms into any aqueous process both creates opportunities for conducting unconventional studies and imposes limitations on what performance might be achievable. Because so much effort has been dedicated over the years without the development of a fully acceptable alternative for the accomplishment of this difficult separation, we have proposed a multifaceted approach.

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Selective Separation of Trivalent Actinides from Lanthanides by Aqueous Processing with Introduction of Soft Donor Atoms

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