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Selective Extraction of Minor Actinides from Acidic Media Using Symmetric and Asymmetric Dithiophosphinic Acids

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The minor actinides (Am and Cm) and other transplutonium elements represent significant, long-term hazards found in spent nuclear fuel. The selective extraction of the minor actinides from the lanthanides is an important part of advanced reprocessing of spent nuclear fuel. This separation would allow the minor actinides to be fabricated into a target and recycled to a reactor and the lanthanides to be disposed. Due to the similarities in the chemical properties of the trivalent actinides and lanthanides, this separation is difficult to accomplish. The introduction of soft donor groups, such as N or S, into similarly structured ligands increases the differentiation between An(III) and Ln(III) cation coordination. Partly because of limitations imposed by synthetic methodologies, previous studies of dithiophosphinic acid (DPAH) extractants has been restricted to a comparatively small number of symmetrical dialkyl and diaryl derivatives. Research efforts at the Idaho National Laboratory have resulted in the recent development of an innovative synthetic pathway yielding new regiospecific DPAH extractants. The synthesis improves DPAH designs that can address the issues concerning minor actinide separation efficiency and extractant stability. Several new symmetric and asymmetric DPAH extractants have been prepared. The use of these extractants for the separation of minor actinides from lanthanides will be discussed. In addition, the variation in the extent of Am(III) extraction by a related series of DPAH isomers will be presented.

Keywords dithiophosphinic acid; separation; trivalent actinide; trivalent lanthanide

INTRODUCTION

The minor actinides (MA) Am, Cm, and other transplutonium elements represent a significant, long-term hazard found in spent nuclear fuel (SNF). The hazards of the MA elements are mainly related to the heat produced by their radioactive decay and the inherent radiotoxicity of the MA elements. The removal of these elements from SNF will reduce the overall hazards of the remaining material. Unfortunately, Am/Cm and Ln ions are most stable in the trivalent oxidation state and, as a result, have quite similar chemical behavior. Separation of the MA from the lanthanides is recognized as one of the most difficult challenges in separation science.

An important approach to the realization of an effective An(III)/Ln(III) separation is the incorporation of softer donor atoms (e.g., N or S) into ligands of suitable geometries. It has been argued that increased covalency in the interaction of An(III) with the soft donor atom and/or changes in coordination geometries account for these effects (1–6). While there are many examples in the literature reporting the use of ligands incorporating either S (2,7–9) or N (10–13) donor atoms for the separation of An(III) from Ln(III) species, the largest An(III)/Ln(III) selectivities reported used the dialkyldithiophosphinic acid, bis(2,4,4-trimethylpentyl)-dithiophosphinic acid, the active component of the commercial extractant Cyanex 301. Using Cyanex 301, Chen et al. (14), reported a separation factor of Am(III) from Eu(III) ($SF = D_{Am}/D_{Eu}$) of SF ~4700 in nitrate media.

Recently, researchers have examined other sulfur-containing phosphonic and phosphinic acid derivatives. Zalupski et al. (15) studied the extraction of lanthanides and actinides with P,P′-di(2-ethylhexyl)methylenebisthiophosphonic acid. Qichu et al. (16) reported a high Am/Eu separation factor of $SF = 2500$ at $pH \sim 3$ in sodium nitrate media using 0.5 M di(2-ethylhexyl) dithiophosphinic acid dissolved in toluene.

Recent work at our laboratory (17,18) has led to the development of a new synthetic pathway for the preparation of a more diverse series of dithiophosphinic acid (DPAH) extractants. In this work, the extraction behavior of three DPAH derivatives prepared in our laboratory was contrasted. One of the first DPAH extractants developed (ortho-trifluoromethylphenyl dithiophosphinic acid referred to as **1**), exhibits significantly better separation efficiency and extractant stability relative to commercially available examples (18). The remaining DPAH derivatives (*o*-trifluoromethylphenyl)-(*m*-trifluoromethylphenyl)-dithiophosphinic acid (referred to as **2**) and bis(*m*-trifluoromethylphenyl)dithiophosphinic acid (referred to as **3**) were prepared in order to examine what effects, if any, positional isomerization would have on the Am(III)/Eu(III)

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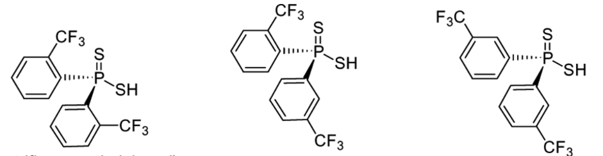


Bis(*o*-trifluoromethylphenyl)-dithiophosphinic acid
(1)

(*o*-Trifluoromethylphenyl)-(*m*-trifluoromethylphenyl)-dithiophosphinic acid
(2)

Bis(*m*-trifluoromethylphenyl)-dithiophosphinic acid
(3)

FIG. 1. Structures of the dithiophosphinic acids utilized in this study.

separation efficiency (relative to **1**). The structures of the ligands utilized in this study are given in Fig. 1.

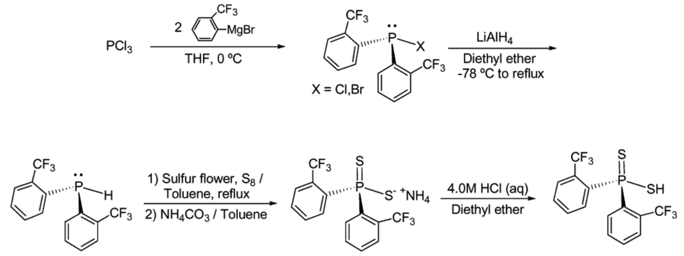
EXPERIMENTAL

All reagents (HNO_3 and $NaNO_3$, etc.) utilized in these experiments are of reagent grade quality and used as received. The trifluoromethylphenyl sulfone (FS-13) is obtained from Marshallton Research Laboratories Inc. (King, NC) and used as received. All aqueous solutions are prepared using filtered, high resistivity water (Barnstead Nanopure). The ^{241}Am radiotracer are obtained from laboratory stocks. The ^{152,154}Eu radiotracer is obtained from Isotope Products Laboratories (Burbank, CA). Aliquots of these nuclides are adjusted to 0.001 M HNO_3 to ensure no acid interference in the subsequent experiments.

The following reagents were obtained from commercial sources and used without further purification: dichloro-(diethylamino)phosphine [$(Et_2NPCl_2]$ (Aldrich), phosphorus trichloride [PCl_3] (Aldrich), magnesium shavings [Mg^0] (Aldrich), *o*-trifluoromethylbromobenzene [*o*-$(CF_3)C_6H_4Br$] (Aldrich), *m*-trifluoromethylbromobenzene [*m*-$(CF_3)C_6H_4Br$] (Aldrich), lithium aluminum hydride [$LiAlH_4$] (Aldrich), ammonium chloride [NH_4Cl] (Aldrich), flowers of sulfur [S_8] (Aldrich), anhydrous sodium sulfate [Na_2SO_4] (Aldrich), concentrated hydrochloric acid [HCl, trace metal grade] (Fisher), and ammonium carbonate [$(NH_4)_2CO_3$] (Fisher). Solvents such as anhydrous diethyl ether, anhydrous tetrahydrofuran [THF], anhydrous toluene, THF, toluene, petroleum (PET) ether, and hexanes were used as received (Aldrich). All reactions were carried out under a nitrogen atmosphere, unless otherwise indicated. The standard setup uses the following: round bottom 3-neck flask, water-jacketed condenser, gas inlet adaptor and magnetic stir bar. Proton, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DMX 300WB spectrometer operating at 7.04 T: 300 MHz (^1H), 282 MHz (^{19}F), 121 MHz (^{31}P), and 75 MHz (^{13}C).

Synthesis of Bis(*o*-trifluoromethylphenyl)dithiophosphinic Acid (1) and (*o*-Trifluoromethylphenyl)(*m*-Trifluoromethylphenyl)dithiophosphinic Acid (2)

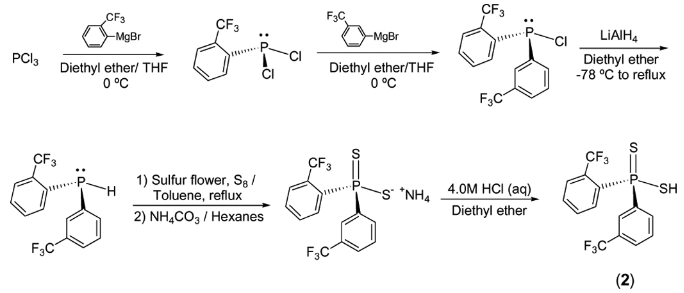
The synthesis of **1** is shown in Scheme 1 and described in detail in an earlier publication (17). The synthesis of **2** uses similar phosphorus(III) chemistry while using two different ligands. The synthetic details for **2** are given here and shown in Scheme 2.



(1)

SCH. 1. Synthesis for bis(*o*-trifluoromethylphenyl)-dithiophosphinic acid (**1**).

The starting phenyl Grignard reagents were synthesized as ~1.0 M solutions of *o*-$(CF_3)C_6H_4MgBr$ and *m*-$(CF_3)C_6H_4MgBr$. PCl_3 (5 mL, 7.6 g; 0.055 mol; via syringe), and anhydrous tetrahydrofuran (THF; 300 mL; via cannula) were added to a 500 mL three-neck round bottom flask. The first Grignard reagent [*o*-$(CF_3)C_6H_4MgBr$] (~1.0 M in diethyl ether, 55 mL, 0.055 mol) was added to an addition funnel via a syringe and then slowly added to the PCl_3 solution at 0°C. Once the addition was finished, the reaction solution was warmed to room temperature for 2 hours. The reaction vessel was then cooled to 0°C and the next Grignard reagent [*m*-$(CF_3)C_6H_4MgBr$] (~1.0 M in diethyl ether, 55 mL, 0.055 mol) was slowly added to the solution via the addition funnel at 0°C. After the addition was complete, the addition funnel was removed and replaced with a stopper. The mixture warmed to room temperature while stirring overnight. After this time, about 50% of the ether/THF solution was removed under reduced pressure, leaving behind a slurry. Using airless techniques, the slurry was carefully washed three times with 200 mL of hexanes to precipitate the side product salts. The supernatant [containing (*o*-$(CF_3)C_6H_4$)(*m*-$(CF_3)C_6H_4$)P-X; X=Cl,Br] was transferred by cannula through an airless filter and into a nitrogen purged,



(2)

SCH. 2. Synthesis of (*o*-trifluoromethylphenyl)(*m*-trifluoromethylphenyl)dithiophosphinic acid (**2**).

1000 mL round bottom flask. The hexanes were removed at reduced pressure, leaving an oil. The concentrated solution was purified by vacuum distillation to give (*o*-$(CF_3)C_6H_4$)(*m*-$(CF_3)C_6H_4$)P-X, as a colorless liquid. Isolated yields were about 75% with good purity as assayed by ^{31}P NMR. Due to the ability of phosphorus to exchange halogens readily, both bromo- and chloro-products were isolated, as confirmed by the observation of duplicate sets of resonances in the ^{31}P NMR spectra of the oil.

Conversion to the Phosphine Hydride

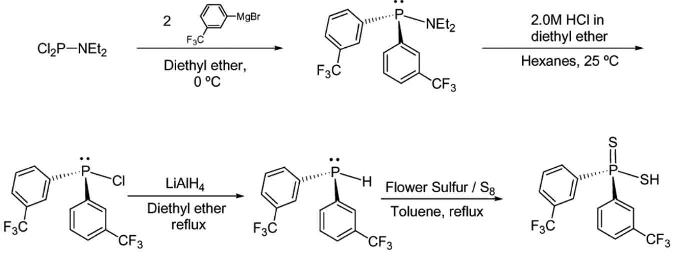
Next, anhydrous diethyl ether (100 mL; via cannula) was transferred into a 250 mL flask via syringe. The reaction vessel was cooled to −78°C in a dry ice/acetone bath and lithium aluminum hydride, $LiAlH_4$, (0.76 g, 0.02 mol) was introduced into the flask. A solution of (*o*-$(CF_3)C_6H_4$)(*m*-$(CF_3)C_6H_4$)P-X, (5.0 g, 0.014 mol) in anhydrous diethyl ether (25 mL) was slowly added to the cooled flask by syringe. After the addition was complete, the dry ice bath was removed and the reaction vessel allowed to slowly warm to room temperature. The gray slurry was subsequently refluxed for 2 hrs, re-cooled to 0°C, and slowly hydrolyzed with 10 wt% aqueous NH_4Cl. The organic layer was separated, and the remaining white precipitate was washed three times with 25 mL of diethyl ether. The combined ether phases were dried with anhydrous Na_2SO_4, filtered, and evaporated to give (*o*-$(CF_3)C_6H_4$)(*m*-$(CF_3)C_6H_4$)P-H as a clear air-sensitive liquid. The concentrated solution was purified by vacuum distillation to give (*o*-$(CF_3)C_6H_4$)(*m*-$(CF_3)C_6H_4$)P-H, as a colorless liquid. Isolated yields were about 75% with good purity as evidenced by ^{31}P NMR analysis, and the purified product is a liquid at room temperature. This product was immediately used for the last reaction step.

Sulfurization Reaction

Using a 100 mL flask, a three-fold excess of sulfur flower (S_8; 0.576 g, 0.018 mol) was added directly to the flask and anhydrous toluene (50 mL) was transferred to the flask, via syringe. (*o*-$(CF_3)C_6H_4$)(*m*-$(CF_3)C_6H_4$)P-H, (2.0 g, 0.006 mol) was dissolved in an additional 10 mL of anhydrous toluene and slowly added to the flask by syringe. The reaction was then refluxed to yield (*o*-$(CF_3)C_6H_4$)(*m*-$(CF_3)C_6H_4$)PS_2H in about 24 hrs as confirmed by ^{31}P NMR analysis. During this time, the solution became a dark-green viscous liquid, and no solid sulfur was observed in the reaction flask while hot. After reflux, the solution was cooled to room temperature and any resulting sulfur precipitates were filtered before proceeding. The solution was transferred to a 100 mL round bottom flask, and the toluene is removed by high vacuum. Hexanes were used to dissolve the dark-green final reaction mixture. Additional sulfur precipitated from the solution at this point so the solution was filtered and transferred to a 250 mL Erlenmeyer flask (open to air). Additional hexanes were used to rinse the reaction flask, and the rinsate was added to the Erlenmeyer flask. A hot plate/stirrer was used to boil the hexanes with vigorous stirring. A slight excess of ammonium carbonate ($(NH_4)_2CO_3$), (0.75 g, 0.008 mol) was added slowly into the reaction mixture (some foaming does occur). This solution was heated and stirred for 1–2 hours, during which time the final product slowly precipitated out as a white solid. While the solution was still hot, it was filtered through a fluted filter paper. Additional cold hexanes were used to wash the filtrate, which was allowed to air dry overnight. A 125 mL separatory funnel was filled with 50 mL of diethyl ether and 25 mL of 4.0 M hydrochloric acid. The white precipitate was introduced into the funnel and shaken vigorously to methathesize the ammonium salt to the free acid which then migrates into the ether layer. After all the product was dissolved, the ether layer was isolated and the water layer was washed two more times with 25 mL of fresh diethyl ether. All of the ether extracts were combined and dried with anhydrous Na_2SO_4. The solution was filtered and the ether subsequently removed at reduced pressure. The pure product, (*o*-$(CF_3)C_6H_4$)(*m*-$(CF_3)C_6H_4$)PS_2H, is a light-green solid and was isolated in good yields of nearly 65%. Recrystallization from hexanes affords light-green prismatic crystals with a melting point at 45°C.

Synthesis of Bis(*m*-trifluoromethylphenyl)dithiophosphinic Acid (3)

The synthesis of **3** uses similar phosphorus (III) chemistry as employed to synthesize **1** and **2**. Instead of using PCl_3, Et_2NPCl_2 was used as the starting phosphorus(III) chloride. Et_2NPCl_2 (10 g, 0.058 mol), and anhydrous diethyl ether (300 mL) was added into a 500 mL three-neck, flask. The solution was cooled to 0°C in a water ice bath and the Grignard reagent [(*m*-$(CF_3)C_6H_4$)MgBr] (~1.0 M in diethyl ether, 116 mL, 0.116 mol) was added into an addition funnel via a syringe. After the addition was complete, the addition funnel was replaced with a stopper.



(3)

SCH. 3. Synthesis of bis(*m*-trifluoromethylphenyl)dithiophosphinic acid (**3**).

The ice bath was removed and the mixture was allowed to warm to room temperature while stirring overnight. After this time, about 75% of the ether was removed under reduced pressure, leaving behind a slurry. The slurry was washed three times with 200 mL of hexanes to completely precipitate the side product salts. The supernatant was decanted (airless filtration) into a nitrogen purged, 1000 mL round bottom flask. Using the previous flask, six equivalents of 2.0 M hydrogen chloride in diethyl ether (150 mL; 0.20 mol) were added to the solution of phosphine in hexanes via syringe. The solution was stirred at room temperature, and the amine salt formed over a 2–4 hour time span. This salt was separated by airless filtration and the solution was concentrated by the removal of excess hexanes under nitrogen. The concentrated solution was purified by vacuum distillation to give $(m\text{-}(CF_3)C_6H_4)_2P\text{-}Cl$ as a colorless liquid. The isolated yields were roughly 70% with good purity as assayed by ^{31}P NMR. The conversion to the phosphine hydride followed the same procedures as for **1** and **2**. (shown above) Finally, the final sulfurization reaction also followed the same procedures as for **2**. The final product, **3** $[(m\text{-}(CF_3)C_6H_4)_2PS_2H]$, was recrystallized in hexanes to give clear, transparent, hexagonal crystals. The yields for this reaction were found to be about 65%.

Radioanalytical Methods

Distribution ratios for ^{241}Am and ^{154}Eu ($D_M = [M]_{org} / [M]_{aq}$) are measured by equilibrium batch contacts between the organic and aqueous phases at an organic-to-aqueous phase ratio of unity (O/A = 1). In all experiments, the organic phase is pre-equilibrated by contacting three times with fresh aqueous phase containing the appropriate concentration of HNO_3 and $NaNO_3$, thus insuring that all matrix components are present at equilibrium concentrations in the organic phase. In all radioactive experiments, the aqueous phase is of the appropriate HNO_3, $NaNO_3$ and stable $Eu(NO_3)_3$ concentrations spiked with the radionuclides of interest (^{241}Am, ^{152,154}Eu) in trace quantities (typically, less than 10^{-7} M each). The phases are mixed by vortex for two minutes which is sufficient time to ensure equilibrium is attained and separated by centrifugation. Each separated phase is sampled and the ^{241}Am and ^{152,154}Eu activity determined using gamma spectroscopy. The pcH of the aqueous phases are determined after the phases are separated using a pH meter and Ross combination electrode (ThermoOrion). The electrode is calibrated at I = 1.0 M $NaNO_3$ by titration of solution of known $[H^+]$ with standard base.

Triplicate experiments indicate that the reproducibility of the measurements is generally within 5% in the range of $10^{-2} < D < 10^{-2}$. For values of $D < 10^{-3}$ the reproducibility is assumed to be within 5–10%.

RESULTS AND DISCUSSION

Classic radioanalytical method of slope analysis is well known and well suited to the study of solvent extraction processes (19–21). The DPAH extractants used in this study behave as acidic liquid-liquid cation exchangers and the following chemical equilibrium applies:

$$M_{aq}^{n^+} + nHL_{org} \leftrightarrow ML_{n,org} + nH_{aq}^+ \qquad (1)$$

where the subscripts 'aq' and 'org' refer to species in the aqueous or organic phases, respectively. This chemical reaction is described by the thermodynamic equilibrium constant, K, which is given by:

$$K = \frac{\left[ML_{n,org}\right]\left[H_{aq}^+\right]^n}{\left[M_{aq}^{n+}\right]\left[HL_{org}\right]^n} = \frac{D\left[H_{aq}^+\right]^n}{[HL]^n} \qquad (2)$$

where the activity coefficients are assumed constant.

By introducing the distribution ratio, $D = [M]_{org}/[M]_{aq}$ and further simplifying Eq. (2) we arrive at the following equation which is the basis of classical slope analysis.

$$\log D = n\log[HL] - n\log[H+] + \log K \qquad (3)$$

Using this expression, a set of experimentally determined distribution coefficients, which are measured under specified conditions, can be used to determine the equilibrium stoichiometry operative in the chemical reaction.

The acid dependence of the extraction of Am (open markers) and Eu (solid markers) from nitric acid solutions by **1**, **2**, and **3** dissolved in FS-13 are shown in Fig. 2. Where no error bar ($\pm\sigma$) is shown, the error bar is smaller than the data marker. The results of linear regression of the

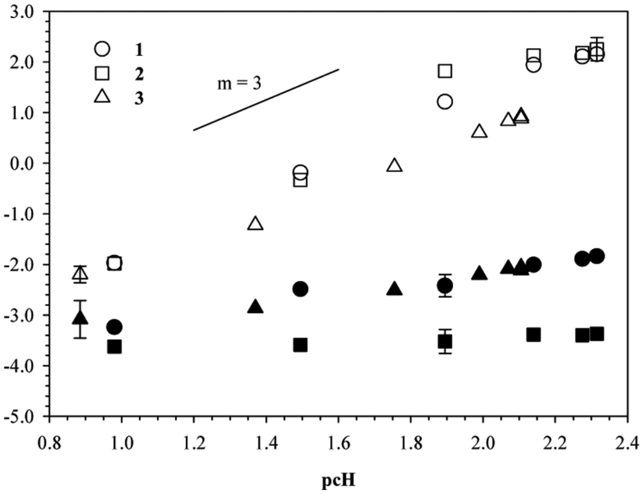


FIG. 2. Acid dependence of the extraction of Am (open markers) and Eu (solid markers) by DPAH ligands. Organic phase: 0.1 M ligand in FS-13. Aqueous phase: 0.001 M $Eu(NO_3)_3$, varying $[HNO_3]$, M total 1.0 M $NaNO_3$.

TABLE 1
Results of linear regression analysis of the ligand dependence of the extraction of Am and Eu by DPAH ligands

		Linear regression	
Ligand	Cation	Slope	Correlation, r^2
1	Am	3.11 ± 0.08	0.998
1	Eu	0.26 ± 0.15	0.510
2	Am	2.90 ± 0.11	0.997
2	Eu	0.40 ± 0.26	0.533
3	Am	3.25 ± 0.21	0.988
3	Eu	0.98 ± 0.43	0.514

TABLE 2
Results of linear regression analysis of the ligand dependence of the extraction of Am and Eu by DPAH ligands

		Linear regression	
Ligand	Cation	Slope	Correlation, r^2
1	Am	3.11 ± 0.08	0.998
1	Eu	0.26 ± 0.15	0.510
2	Am	2.90 ± 0.11	0.997
2	Eu	0.40 ± 0.26	0.533
3	Am	3.25 ± 0.21	0.988
3	Eu	0.98 ± 0.43	0.514

Am and Eu acid dependencies are presented in Table 1. The slopes ($m \sim 3$) of the acid dependence of the extraction of Am by the DPAH ligands are consistent with an acidic, cation-exchange extraction mechanism in which three protons are exchanged to the aqueous phase for each metal cation complex formed in the organic phase. The significantly different slope observed for the Eu acid dependencies indicates the Eu-DPAH complex has a dramatically different stoichiometry or a fundamentally different interaction mode with these extractants. In fact, the D_{Eu} values are likely an "optimistic" estimate of very low Eu partitioning in this system.

Solutions of varying concentrations of the DPAH extractants **1**, **2**, and **3** in FS-13 diluent were used to investigate the stoichiometry of Am-DPAH and Eu-DPAH, complexes formed in the organic phase. These experiments were performed using an aqueous phase containing 0.010 M HNO_3. This acid concentration was chosen so that easily measurable distribution ratios were obtained. The measured distribution ratios are presented in Figure 3. Where no error bar ($\pm\sigma$) is shown, the error bar is smaller than the data marker. The results of linear regression of the Am and Eu ligand dependencies are presented in Table 2. The slope ($m \sim 3.0$) of the D_{Am} (open markers) ligand concentration dependency is consistent with the proposed formation of an ML_3 complex in the organic phase for the **1**, **2**, and **3** DPAH extractants. The significantly different slope ($m < 1.0$) of the D_{Eu} ligand concentration dependency indicates the Eu complex has a dramatically different stoichiometry.

III. C. NITRATE DEPENDENCE OF EXTRACTION

The extraction of both Am and Eu were found to be independent of the concentration of added $NaNO_3$, as indicated in Fig. 4. This result indicates that nitrate

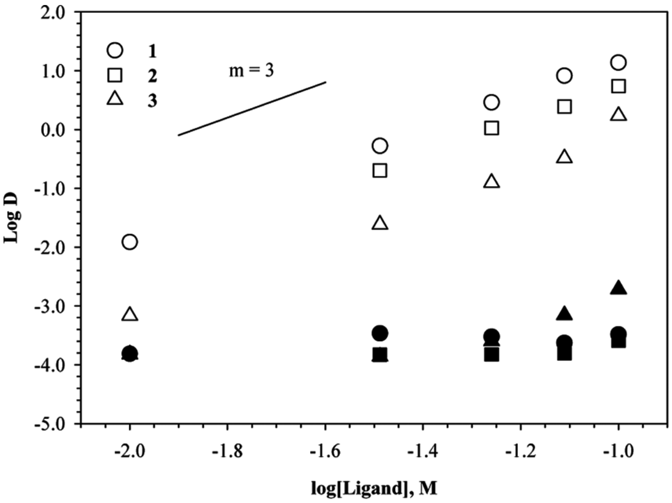


FIG. 3. Ligand concentration dependence of extraction of Am (open markers) and Eu (solid markers) DPAH ligands. Organic phase: varying [ligand] in FS-13. Aqueous phase: 0.001 M $Eu(NO_3)_3$, 0.010 M $[HNO_3]$, total 1.0 M $NaNO_3$.

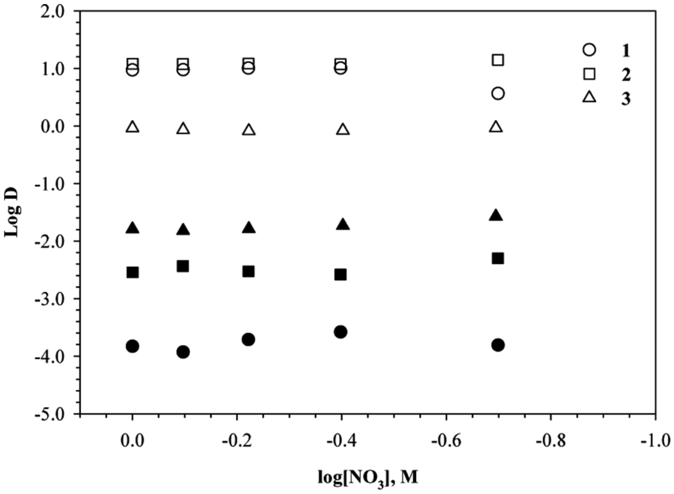


FIG. 4. Nitrate concentration dependence of extraction of Am (open markers) and Eu (solid markers) by DPAH ligands. Organic phase: 0.01 M ligand in FS-13. Aqueous phase: 0.001 M $Eu(NO_3)_3$, 0.010 M $[HNO_3]$, varying $[NaNO_3]$.

ions do not accompany the metal cation into the organic phase, thus confirming that cation exchange is the most important pathway to cation phase transfer. The measured Am and Eu distribution ratios have not been corrected for variation in the solution activity. The lack of a dependence on solution ionic strength indicates that cation/complex/organic solvent hydration effects are complex in this system and play an integral role in the apparent separation efficiency.

The separation factors ($S_{Eu}^{Am} = D_{Am}/D_{Eu}$) calculated for ligands **1**, **2**, and **3** are plotted in Fig. 5. The observed values of S_{Eu}^{Am} far exceed those previously reported for ligands of this type (13) including similarly structured reagents. The differences in the values of S_{Eu}^{Am} for the **1** and **2** ligand systems at high pcH are attributed to the variations in the measured D_{Eu} values. Distribution ratios on the order of 10^{-3} or less are very difficult to measure accurately leading to very high uncertainty. Therefore, the calculated separation factors for 1 and 2 are considered to be approximately the same in this discussion. The separation factors calculated for **3**, is approximately one order of magnitude less than for **1** or **2** at high pcH. Clearly, minor structural variations have a significant impact on the separations performance of this class of DPAH extractants.

Aromatic dithiophosphinic acids are better extractants than their alkyl counterparts due to the high An(III)/Ln(III) separation factors and markedly increased stability (7) that serve to address difficulties associated with radiolytic and hydrolytic degradation. The three ligands presented in this study are the ortho-ortho, ortho-meta, and meta-meta positional isomers of the DPAH parent structure. These isomers were chosen in order to determine the necessity of the o-CF_3 moiety for the efficient separation of Am from Eu in acidic media. The data presented in Figs. 2, 3, and 5 indicate that ortho-ortho DPAH isomer provides for the most efficient Am/Eu separation, but even the meta-meta isomer is capable of effectively separating Am from Eu in acidic media. However, the details of the coordination chemistry responsible for this remarkable separation are lacking.

The pK_a values would provide insight into the relative An(III)/Ln(III) extraction efficiencies of this series of ligands. Due to the inductive electron withdrawing effect of the trifluoromethyl (-CF_3) group, the DPAH with the -CF_3 group closest to the thiol proton would be expected to exhibit the lowest pK_a. Unfortunately, the aromatic dithiophosphinic acids studied in this work exhibit limited solubility in water. This low solubility in aqueous solution makes the determination of accurate pK_a values of the DPAH ligands by classical potentiometric techniques difficult. Benson et al. (22) used the density functional theory with a continuum solvation model to calculate values of several dithiophosphinic acid derivatives. They report pK_a values of 1.72, 1.52, and 0.20 for **1**, **2**, and **3**, respectively. The calculated pK_a values exhibit a trend opposite to that expected. The authors propose that the fluorine atoms of the -CF_3 interact with the sulfur centers of the DPAH ligands. This interaction causes an energetic destabilization of the deprotonated ligand. The extent of destabilization decreases as the -CF_3 moves further away from the thiol proton, resulting in the observed trend in the calculated pK_a values. Experiments are underway in our laboratories to determine the pK_a values of the INL DPAH ligands in mixed solvent systems. The results of those experimental pK_a determinations will be detailed in a future publication.

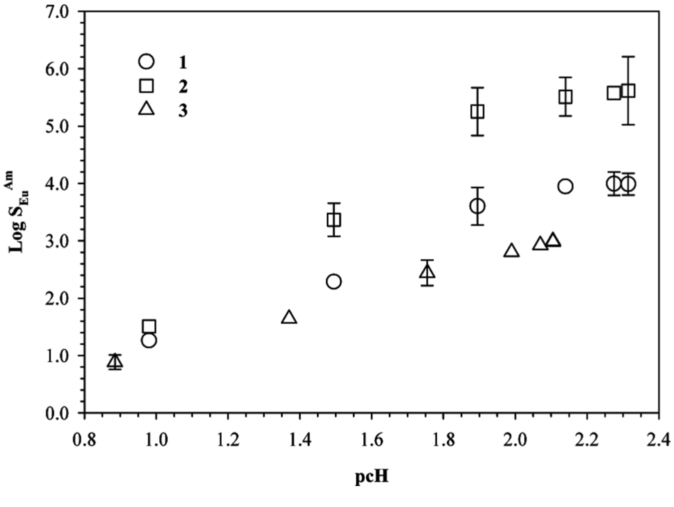


FIG. 5. Separation factors for the separation of Am from Eu by DPAH ligands (O: 1, □: 2, Δ: 3). Organic phase: 0.10 M ligand in FS-13. Aqueous phase: 0.001 M $Eu(NO_3)_3$, 0.010 M [HNO_3], 1.0 M [$NaNO_3$].

CONCLUSIONS

A novel synthetic pathway to an array of dithiophosphinic acid extractants has produced three derivatives which were used to study the selective extraction of Am from Eu. These data show that a cation exchange mechanism is operating in these complexes and that there are no nitrate ions accompanying the complexes into the organic phase. In the course of this work, two striking features of the behavior of these extractants were noted. First, (for **1** and **2**) the separation factors for the Am/Eu extraction are in excess of 10^4, much higher than the separation factors for any previously known DPAH. Second, a very minor structural change, moving a -CF_3 group only one carbon more remote from the metal coordination site, completely alters the efficiency of the An/Ln separation. Work continues in our labs to better understand the behavior of these DPAH extractants and the role of the polar diluent in the extraction process.

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