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SEPARATION OF MINOR ACTINIDES FROM LANTHANIDES BY DITHIOPHOSPHINIC ACID EXTRACTANTS

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ABSTRACT

The selective extraction of the minor actinides (Am(III) and Cm(III)) from the lanthanides is an important part of advanced reprocessing of spent nuclear fuel. This separation would allow the Am/Cm to be fabricated into targets and recycled to a reactor and the lanthanides to be dispositioned. This separation is difficult to accomplish due to the similarities in the chemical properties of the trivalent actinides and lanthanides. Research efforts at the Idaho National Laboratory have identified an innovative synthetic pathway yielding new regiospecific dithiophosphinic acid (DPAH) extractants. The synthesis provides DPAH derivatives that can address the issues concerning minor actinide separation and extractant stability. For this work, two new symmetric DPAH extractants have been prepared. The use of these extractants for the separation of minor actinides from lanthanides will be discussed.

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, 8] or N[9-12] 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-dimethylpentyl)-dithiophosphinic acid, the active component of the commercial extractant Cyanex 301. Using Cyanex 301, Chen et al.[13], reported a separation factor of Am(III) from Eu(III) of ~4700 in nitrate media.

Recent work at our laboratory 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 two DPAH derivatives prepared in our laboratory will be 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.[14] The second DPAH derivative (bis(3,5-bis(trifluoromethyl)phenyl) dithio-phosphinic acid, referred to as **2**), exhibits markedly less separation efficiency (relative to **1**). This serves to illustrate how a seemingly minor structural variation can have significant impacts on the observed extraction behavior.

EXPERIMENTAL

Materials

The DPAH extractants (see Figure 1 for structures) are prepared according to published procedures. [15] The DPAH derivatives are isolated as the ammonium salt and converted to the corresponding acid prior to use. Extractant purity is verified by multinuclear (^{31}P, ^{19}F, ^{13}C, ^{1}H) NMR spectroscopy. 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, and ^{244}Cm radiotracers 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 0.001M HNO_3 to ensure no acid interference in the subsequent experiments.
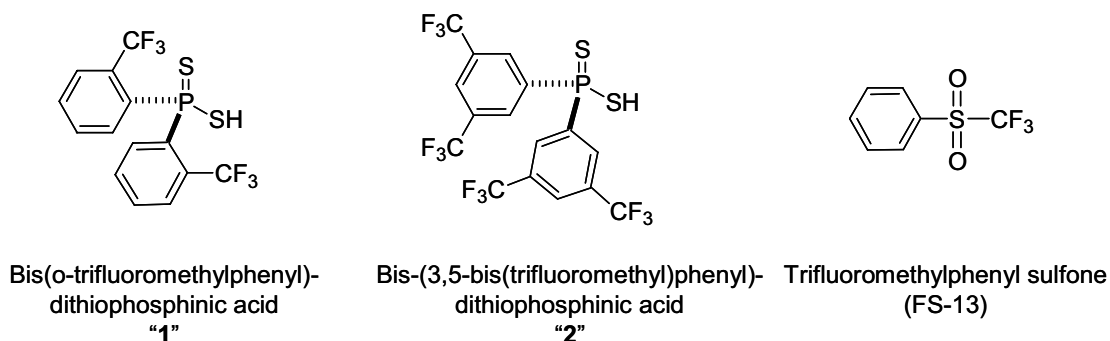

Bis(o-trifluoromethylphenyl)-
dithiophosphinic acid
"**1**"

Bis-(3,5-bis(trifluoromethyl)phenyl)-
dithiophosphinic acid
"**2**"

Trifluoromethylphenyl sulfone
(FS-13)

Figure 1. Structures of DPAH studied in this work and the diluent.

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 containing the appropriate

concentration of HNO_3 and $NaNO_3$, thus insuring 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, ^{244}Cm, $^{152,154}Eu$) 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 activity of ^{244}Cm in each phase is determined by subtracting the activity due to ^{241}Am (determined by gamma spectroscopy) from the total alpha emitter activity in the sample (determined by liquid scintillation).

Prior to the experimental determination of ^{244}Cm distribution ratios, the liquid scintillation counting techniques were developed and validated. A quench curve was determined for the organic phase to correct for any quenching effects caused by FS-13. The aqueous phase did not indicate any negative effects from quenching in the liquid scintillation counting techniques.

RESULTS AND DISCUSSION

Acid Dependence of Extraction

The distribution ratios for the partitioning of Am, Cm, and Eu between a 0.1 M solutions of **1** and **2** in FS-13 solvent as a function of varying $[HNO_3]$ are shown in Figure 2. The aqueous phases contained 0.001 M $Eu(NO_3)_3$ and 1.0 M $NaNO_3$.
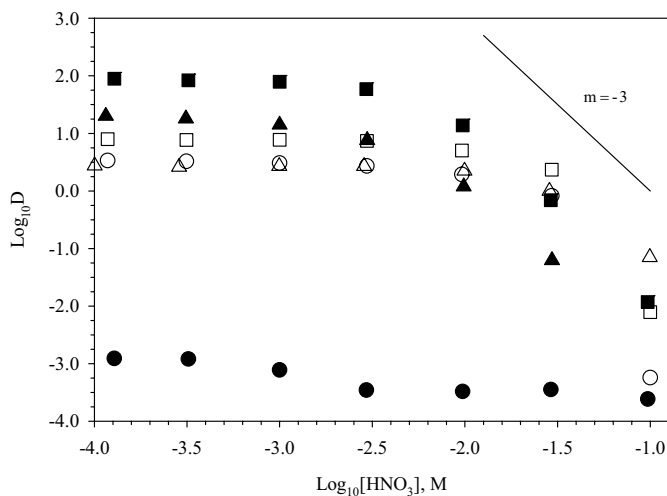

Figure 2. Nitric acid dependence of the extraction of Am (squares), Cm (triangles), and Eu (circles) by 0.1 M **1** (solid markers) and 0.1 M **2** (open markers) in FS-13 solvent. Aqueous phases contain 0.001 M $Eu(NO_3)_3$ and 1.0 M $NaNO_3$. The solid line depicts a slope of m = -3.

The negative slope (m ~ -3.0) of the Am acid dependence (at acid concentration higher than ~0.003 M HNO_3) is 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 slope of the Cm acid dependence (triangles in Figure 1) is similar to that for the Am. The apparent plateau that is seen in D_{Am} at the lower limit of acidity is not explained at present, but could indicate limits in the solubility of **1** in the diluent under high pH conditions or possibly aggregation of the extractant under these conditions. The latter effect is known to reduce selectivity. The significantly different slope in the case of the Eu acid dependence indicates the Eu complex has a dramatically different stoichiometry or a fundamentally different interaction mode with this extractant. In fact, the D_{Eu} values are likely an "optimistic" estimate of very low Eu partitioning in this system.

The separation factors (S_{Eu}^{Am}) observed for **1** are greater than 10^5 at a nitric acid concentration of $[HNO_3] = 0.005$. The observed values of S_{Eu}^{Am} far exceed those previously reported for ligands of this type,[13] including similarly structured reagents. The implicit difference in free energy of the phase transfer reaction for Am^{3+} vs. Eu^{3+} of approximately 28 kJ/mol ($\Delta(\Delta G) = -RT \ln D_{Am}/D_{Eu}$) is not readily explained based on present understanding of lanthanide-actinide coordination chemistry. In the case of extraction by **2**, the acid dependency is strikingly different in that little to no selectivity for Am or Cm over Eu is observed.

Solutions of varying concentrations of the DPAH extractants **1** and **2** in FS-13 diluent were used to investigate the partitioning of Am, Cm and Eu between the organic phase and an aqueous phase containing 0.010 M HNO_3. This acid concentration was chosen to minimize the possible impact of the partitioning of the extractant molecule to the aqueous phase, which may occur at lower acid concentrations as mentioned above. The measured distribution ratios are presented in Figure 3. The slope (m = 3.0) of the D_{Am} and D_{Cm} dependence is consistent with the proposed formation of an ML_3 complex in the organic phase for both **1** and **2** extractants. The significantly different slope (m = 1.0) of the best-fit line in the case of the Eu distribution ratios indicates the Eu complex has a dramatically different stoichiometry.
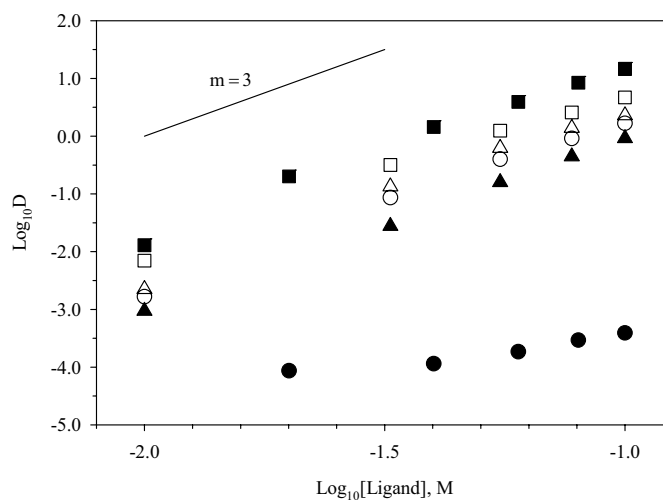

Figure 3. The ligand concentration dependence of the extraction of Am (squares), Cm (triangles), and Eu (circles) by **1** (solid markers) and **2** (open markers) in FS-13 solvent. Aqueous phases contain 0.001 M $Eu(NO_3)_3$ and 1.0 M $NaNO_3$. The solid line depicts a slope of m = 3.

The extraction of Am, Cm, and Eu by **1** was found to be independent of the concentration of added NaNO₃, as indicated in Figure 4. This result indicates that nitrate ions do not accompany the metal cation into the organic phase, thus confirming that cation exchange is the most important mechanism of cation phase transfer. The lack of a salting-out effect indicates that cation/complex/organic solvent hydration effects are complex in this system and play an integral role in the apparent separation efficiency. The slight dependence of the extraction of Am, Cm, and Eu by **2** is likely due to varying extents of Eu(III) complexation by nitrate anion.
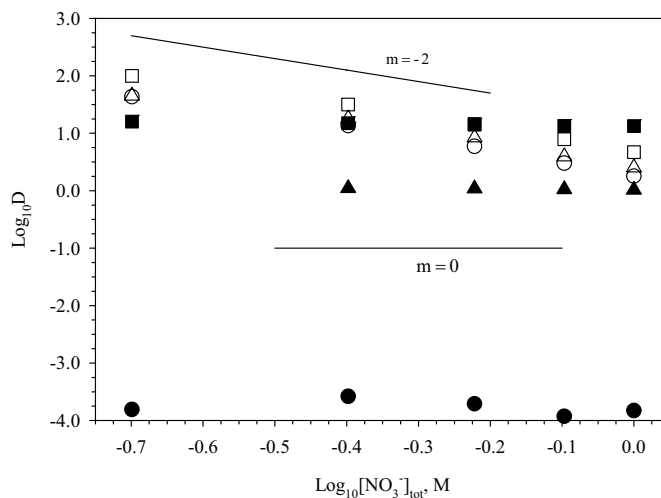

Figure 4. The total nitrate concentration dependence of the extraction of Am (squares), Cm (triangles), and Eu (circles) by 0.1 M **1** (solid markers) and 0.1 M **2** (open markers) in FS-13 solvent. Aqueous phases contain 0.001 M Eu(NO₃)₃ and 0.010 M HNO₃. The solid lines depict slopes of m = 0 and m = -2, respectively.

CONCLUSIONS

A novel synthetic pathway to an array of dithiophosphinic acid extractants has produced two derivatives which are used to study the selective extraction of Am and Cm 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**) the separation factors for the Am/Eu extraction are in excess of 10^5, much higher than the separation factors for any previously known DPAH. Second, a very minor structural change, moving a –CF₃ group over by only one carbon 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 and other structurally similar DPAH extractants.

ACKNOWLEDGMENTS

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