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# DIAMIDE DERIVATIVES OF DIPICOLINIC ACID AS ACTINIDE AND LANTHANIDE EXTRACTANTS IN A VARIATION OF THE UNEX PROCESS

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*The Universal Extraction (UNEX) process has been developed for simultaneous extraction of cesium, strontium, and actinides from acidic solutions. This process utilizes an extractant consisting of 0.08 M chlorinated cobalt dicarbollide (HCCD), 0.007-0.02 M polyethylene glycol (PEG-400), and 0.02 M diphenyl-N,N-di-n-butylcarbamoylmethylphosphine oxide (Ph<sub>2</sub>CMPO) in the diluent trifluoromethylphenyl sulfone (CF<sub>3</sub>C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>, designated FS-13) and provides simultaneous extraction of Cs, Sr, actinides, and lanthanides from HNO<sub>3</sub> solutions.*

*The UNEX process is of limited utility for processing acidic solutions containing large quantities of lanthanides and/or actinides, such as dissolved spent nuclear fuel solutions. These constraints are primarily attributed to the limited concentrations of CMPO (a maximum of ~0.02 M) in the organic phase and limited solubility of the CMPO-metal complexes. As a result, alternative actinide and lanthanide extractants are being investigated for use with HCCD as an improvement for waste processing and for applications where higher concentrations of the metals are present.*

*Our preliminary results indicate that diamide derivatives of dipicolinic acid may function as efficient actinide and lanthanide extractants. The results to be presented indicate that, of the numerous diamides studied to date, the tetrabutyl diamide of dipicolinic acid, TBDPA, shows the most promise as an alternative actinide/lanthanide extractant in the UNEX process.*

## I. INTRODUCTION

Chlorinated cobalt dicarbollide (CCD) is a well-studied cesium extractant from acidic, aqueous media. The acidic form of chlorinated cobalt dicarbollide (HCCD) is a strong acid in polar, organic diluents and extremely hydrophobic. Many extractants exhibit a strong synergism when used in conjunction with HCCD for the extraction of metal ions from acidic media. The addition of polyethylene glycols (PEG) or crown ethers affords simultaneous extraction of both cesium and alkali earth elements.<sup>1</sup> Incorporating bidentate organophosphorus

compounds in the organic phase results in the simultaneous extraction of the actinide (An) elements and lanthanide (Ln) elements.<sup>2</sup> Mixtures of various carbamoylmethylphosphine oxides (CMPO) with HCCD make it possible to simultaneously obtain very high distribution ratios for cesium, An and Ln elements from acidic media.

Collaborative efforts between the Idaho National Laboratory (INL) and Khlopin Radium Institute (KRI) began in 1994 to evaluate solvent extraction technologies developed in Russia and in the Czech Republic for their applicability to legacy acidic radioactive liquid wastes. The collaboration resulted in the successful demonstration of HCCD (Cs extraction) and HCCD/polyethylene glycol (Cs and Sr extraction) flowsheets on samples of actual INL tank waste.<sup>3,4</sup> Ongoing collaborative efforts focused on development and demonstration of a Universal Extraction (UNEX) process flowsheet to simultaneously and selectively extract all the major radionuclides (137Cs, 90Sr, and TRU elements) from INL wastes.<sup>5-8</sup> In its current state of development, the UNEX process incorporates HCCD, polyethylene glycol with an average molecular weight of 400 g/mol, (PEG-400), and diphenyl-N,N-di-n-butylcarbamoylmethylphosphine oxide (Ph<sub>2</sub>CMPO) dissolved in a suitable diluent to simultaneously extract the major radionuclides. UNEX development efforts culminated with the identification of trifluoromethylphenyl sulfone (CF<sub>3</sub>C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>, designated FS-13) as a suitable, polar diluent for the UNEX process, eliminating the use of nitrobenzene and nitroaromatic-based diluents. The FS-13 diluent exhibits excellent radiolytic and chemical stability, is relatively innocuous, and provides necessary solubility of HCCD, PEG-400, and Ph<sub>2</sub>CMPO and their respective metal complexes.<sup>9</sup> Finally, the density and viscosity of the organic phase are suitable for processing applications.

The UNEX demonstrations on actual acidic waste samples are a significant milestone; it is the only demonstrated concept for the simultaneous removal of the major radionuclides from radioactive waste in a single step. Removing all major radionuclides in a single process represents a significant economic advantage by

providing substantial capital and operating cost savings, compared to using multiple (two or three) unit operations to remove the different radionuclides. Recent studies at the INL confirm that the UNEX process could provide substantial lifecycle cost savings compared to other treatment options for legacy INL radioactive wastes.<sup>10,11</sup>

The UNEX process was initially developed for the treatment of acidic aqueous radioactive wastes, which contain relatively low concentrations of the target radionuclides. The UNEX process is of limited utility for processing acidic solutions containing large quantities of lanthanides and/or actinides, such as dissolved spent nuclear fuel solutions. These constraints are primarily attributed to the limited concentrations of  $\text{Ph}_2\text{CMPO}$  (a maximum of  $\sim 0.02$  M) attainable in the organic phase and the limited solubility of the CMPO-metal complexes. As a result, alternative actinide and lanthanide extractants are being investigated for use with HCCD as an improvement for waste processing and for applications where higher concentrations of metals are present.

Various diamides have been proposed as synergist agents with HCCD for the extraction of actinide and lanthanide ions from acidic media.<sup>2,12</sup> Our preliminary results indicate that diamide derivatives of dipicolinic acid may function as efficient actinide and lanthanide extractants. The general structure of substituted 2,6-pyridinedicarboxamide derivatives ( $(\text{R}'\text{R}''\text{NCO})_2\text{C}_5\text{NH}_3$ ) studied in this work is shown in Figure 1.

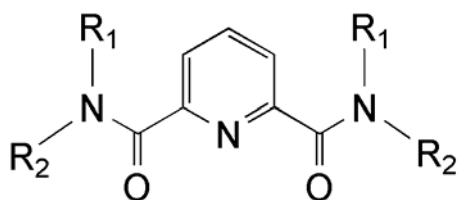


Fig. 1. General structure of 2,6-pyridinedicarboxamide derivatives ( $(\text{R}'\text{R}''\text{NCO})_2\text{C}_5\text{NH}_3$ ) studied in this work.

The results to be presented indicate that, of the numerous diamides studied to date, the tetrabutyl diamide of dipicolinic acid, TBDPA, (see Figure 2) shows the most promise as an alternative actinide/lanthanide extractant in the UNEX process.

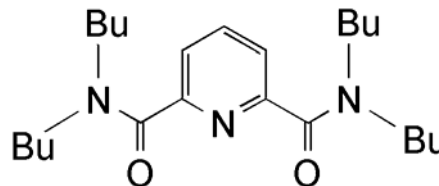


Fig. 2. Structure of tetrabutyl diamide of dipicolinic acid, TBDPA.

## II. EXPERIMENTAL

The dichloroanhydride of picolinic acid was prepared in accordance with literature accounts.<sup>13</sup> Chloroanhydride (5 mM in chloroform) prepared in this manner was added to a solution of chloroform containing 20 mM di-*n*-butylamine, stirred and cooled to  $\leq 40^\circ\text{C}$ . After addition of the entire amount of dichloroanhydride, the mixture was kept overnight. This was followed by washes with 3 M HCl, water, 5% NaOH solution and again with water. Thereafter, the product was dried over anhydrous sodium carbonate and the chloroform was distilled. The tetra-*n*-butyl DPA (TBDPA, 60% yield) was obtained as an oil and purified by column chromatography on silica gel.

NMR and mass-spectroscopy were used to confirm the structure and purity of the resulting compound. The final purity of the TBDPA derivative was not lower than 98%. NMR-spectra were taken on a Bruker, Avance DPX-300 spectrometer. Solutions in  $\text{CDCl}_3$  and chemical shifts were calculated from residual solvent proton signals (7.28 ppm) for  $^1\text{H}$ -spectra and from the average carbon-13 triplet signal of the solvent (77.4 ppm) for  $^{13}\text{C}$ -spectra.

Chlorinated cobalt dicarbollide was obtained from Katchem Co. (Czech Republic) as the Cs salt ( $\text{CsCCD}$ ) and used without additional purification. Stock, concentrated solutions of  $\text{CsCCD}$  were converted to the acid form, HCCD, by repeated contacts with dilute  $\text{HClO}_4$ . The resulting HCCD stock solutions were subsequently washed with dilute  $\text{HNO}_3$  to remove traces of  $\text{HClO}_4$  from the organic phase prior to preparation of the test solution. The concentration of dicarbollide in the organic phase is determined indirectly by potentiometric titration of HCCD with standard base assuming formation of the 1:1  $\text{H}^+:\text{CCD}^-$  entity. Other reagents were of analytical grade and used as received. The  $^{137}\text{Cs}$ ,  $^{85}\text{Sr}$ ,  $^{154}\text{Eu}$ , and  $^{241}\text{Am}$  radiotracers were obtained from Isotope Products (Burbank, CA) and used as received. Polyethylene glycol with an average molecular weight of 400 was obtained from Fisher Scientific and used as received.

Distribution ratios ( $D = [\text{Metal}]_{\text{org}} / [\text{Metal}]_{\text{aq}}$ ) were measured by equilibrium batch contacts between the

organic phase and aqueous phase at an organic-to-aqueous phase ratio of unity ( $O/A = 1$ ). The aqueous phase was of the appropriate  $\text{HNO}_3$  concentration and spiked with the major radionuclides of interest ( $^{137}\text{Cs}$ ,  $^{85}\text{Sr}$ ,  $^{154}\text{Eu}$ , or  $^{241}\text{Am}$ ) in trace quantities (typically, less than  $10^{-7}$  M each). The phases were contacted using a vortex mixer for two minutes, which was determined to be sufficient mixing time to ensure equilibrium conditions were met. Following mixing, the phases were separated by centrifugation. In all cases the organic phase was pre-equilibrated by contacting it three times with fresh  $\text{HNO}_3$  of the appropriate concentration to ensure that the  $\text{HNO}_3$  was present in equilibrium quantities. The pre-equilibrated organic phase was then contacted with an aqueous phase containing trace amounts of all the aforementioned radionuclides and the distribution ratios were calculated from the results of gamma spectroscopy.

### III. RESULTS AND DISCUSSION

#### III.A. Cesium and Strontium Extraction

In order to examine the distribution behavior of cesium and strontium in the presence of TBDPA, solvents containing a fixed concentration of 0.13 M HCCD and 0.027 M PEG-400 and varying concentrations of TBDPA were prepared in the UNEX diluent, FS-13. This solvent composition was chosen based upon the results of previous experiments.<sup>3-8</sup> Distribution ratios for  $^{137}\text{Cs}$  and  $^{85}\text{Sr}$ , as a function of aqueous phase nitric acid concentration and TBDPA concentration are given in Figures 3 and 4, respectively. The cesium and strontium distribution ratios both exhibit a near linear decrease with increasing TBDPA concentration.

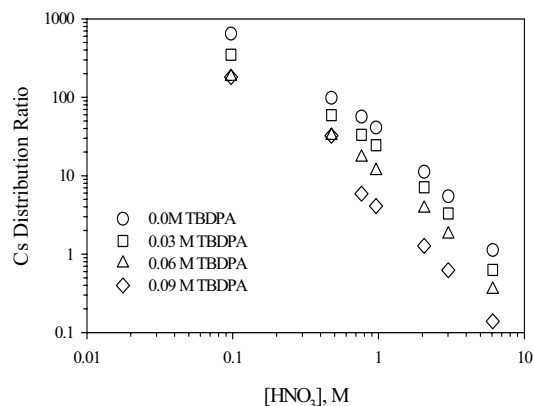


Fig. 3. Distribution ratios for  $^{137}\text{Cs}$  as a function of nitric acid concentration and concentration of TBDPA for solvents containing 0.13 M HCCD and 0.027 M PEG-400 in FS-13.

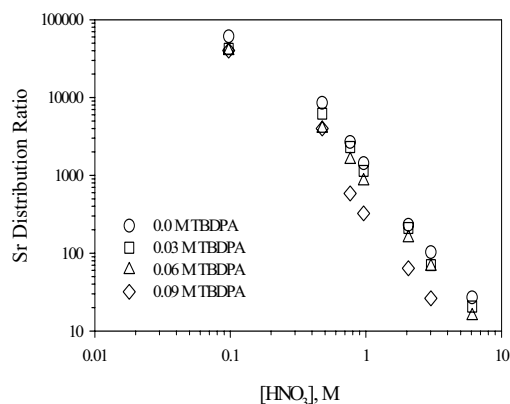


Fig. 4. Distribution ratios for  $^{85}\text{Sr}$  as a function of nitric acid concentration and concentration of TBDPA for solvents containing 0.13 M HCCD and 0.027 M PEG-400 in FS-13.

The observed trends are consistent with those observed with other HCCD-based extraction systems. Metal extraction in solvent systems containing HCCD occurs by a liquid-liquid cation exchange mechanism with complete dissociation of the solvated metal cation in the organic phase. The  $\text{CCD}^-$  anion serves to stabilize the extracted metal cation by formation of an outer-sphere complex with the cation in the organic phase. The observed decreases in Cs and Sr distribution ratios as a function of both nitric acid concentration and TBDPA concentration are the direct result of competition between the metal cation and solvated proton for the  $\text{CCD}^-$  anion in the process solvent.

#### III. B. Actinide and Lanthanide Extraction

Previous work has demonstrated that the diamides of DPA are not capable of extracting metals from acidic solutions in the absence of a synergist.<sup>14,15</sup> In order to examine the synergistic extraction of lanthanides and actinides, mixtures containing HCCD, PEG-400 and TBDPA in FS-13 were prepared. The HCCD and PEG-400 composition was chosen based upon the results of previous experimental observations [5-8]. Distribution ratios for  $^{154}\text{Eu}$  and  $^{241}\text{Am}$ , as a function of aqueous phase nitric acid concentration and TBDPA concentration are given in Figures 5 and 6, respectively.

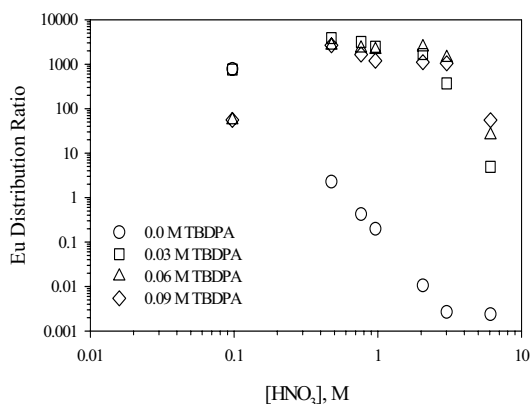


Fig. 5. Distribution ratios for  $^{154}\text{Eu}$  as a function of nitric acid concentration and concentration of TBDDPA for solvents containing 0.13 M HCCD and 0.027 M PEG-400 in FS-13.

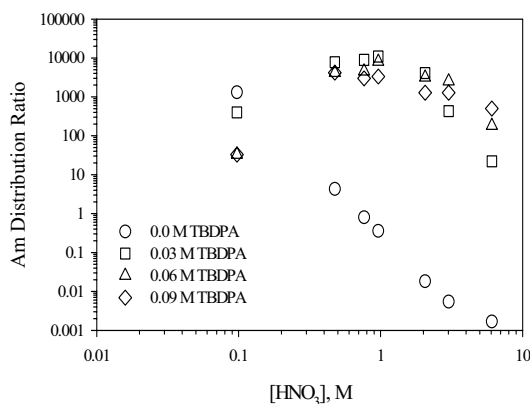


Fig. 6. Distribution ratios for  $^{241}\text{Am}$  as a function of nitric acid concentration and concentration of TBDDPA for solvents containing 0.13 M HCCD and 0.027 M PEG-400 in FS-13.

In the absence of TBDDPA, the measured  $^{154}\text{Eu}$  and  $^{241}\text{Am}$  distributions are greater than 1 for aqueous acid concentrations less than approximately 0.5 M  $\text{HNO}_3$ . As the acid concentration is increased above this value, the observed distributions fall below unity. This trend has been previously observed in the UNEX solvent system [5-8] and indicates that HCCD is capable of extracting lanthanides and actinides from dilute acid solutions. The decrease in the measured Eu and Am distribution ratios at 0.1 M  $\text{HNO}_3$  as the TBDDPA concentration is increased from 0.00 to 0.09 M is attributable to the competition between HCCD and TBDDPA for the metal cation.

The distribution data presented in Figures 5 and 6 demonstrate that TBDDPA in the presence of HCCD and PEG-400 exhibits a synergistic extraction of Eu and Am from  $\text{HNO}_3$  solutions. The maximum distributions for Eu ( $D_{\text{Eu}} > 3000$ ) and Am ( $D_{\text{Am}} > 10000$ ) are observed for  $[\text{TBDDPA}] = 0.03 \text{ M}$ . The Eu and Am distribution ratios exhibit some dependence upon the concentration of acid present in the aqueous phase, however, the distribution ratios are significantly greater than unity even at an acid concentration of 6 M  $\text{HNO}_3$ . While the measured Ln and An distributions for the TBDDPA extractant are lower than those observed when using  $\text{Ph}_2\text{CMPO}$ , the data clearly demonstrate the ability of TBDDPA to serve as An/Ln extractant in a UNEX-type solvent extraction system.

As the  $\text{HNO}_3$  concentration is increased (especially above 1.0 M) the measured Eu and Am distribution ratios decrease for all TBDDPA concentrations examined. This decrease is attributed to the increased concentration of solvated-proton in the organic phase at higher acid concentrations and the resulting decrease in the free TBDDPA concentration in the organic phase due to protonation of TBDDPA.

#### IV. CONCLUSIONS

The Universal Extraction (UNEX) process has been developed previously for the simultaneous extraction of cesium, strontium, and actinides from acidic solutions. Due to the limited solubility of the actinide/lanthanide extractant ( $\text{Ph}_2\text{CMPO}$ ) used in the UNEX process solvent, alternative extractants are of interest. Preliminary results indicate that diamide derivatives of dipicolinic acid may function as efficient actinide and lanthanide extractants. Experiments utilizing a synergistic mixture of HCCD, PEG-400, and the tetrabutyl diamide of dipicolinic acid (TBDDPA) in FS-13 have demonstrated the utility of TBDDPA to serve as an actinide/lanthanide extractant from acidic solutions. Based upon these results, TBDDPA may be a suitable replacement for  $\text{Ph}_2\text{CMPO}$  in the UNEX process. Additional studies are required to fully assess the utility of TBDDPA as a replacement An/Ln extractant for the UNEX process.

#### ACKNOWLEDGMENTS

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