

DE-FC07-06ID14730 SF269A Final Report

Project Title: Design and Development of Selective Extractants for Ln/An Separations

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Statement on Distribution Limitations

None. This report contains no patentable material or protected data.

Executive Summary:

This study has succeeded in further developing phosphinoylmethyl pyridine compounds as selective recognition and separations agents for trivalent lanthanide and actinide ions present in nuclear materials. The parameters for efficient separations have been further elucidated and factors important to further development have been identified. Further development will lead to optimal extractant design for effective actinide ion partitioning under process practical conditions.

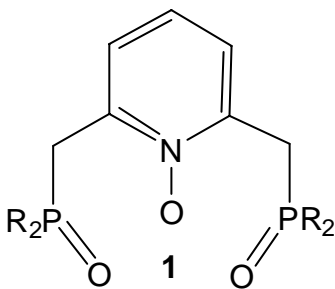
Project Objectives:

The primary objective of the project involved the design, synthesis, and characterization of the extraction performance of 2,6-bis(phosphinomethyl)pyridine N,P,P'-trioxides (NOPOPO) as potential reagents for the separation of Am, Cm, and fission product lanthanides from other transuranics and fission products and for acting as a separations “platform” for the mutual separation of Am/Cm from the lanthanides. The secondary but critical objective of the project focused on the characterization of aqueous acid and radiation stability of NOPOPO ligands. Further, the project served as a interdisciplinary training vehicle for new, young investigators in actinide separations chemistry.

Summary of Research Activities:

NOPOPO Ligand Development

At the initiation of the project, our prior work had indicated that NOPOPO ligands **1** served as promising liquid-liquid extraction platforms for trivalent actinide and lanthanide ions present in highly acidic aqueous solutions.^{1,2} It had been further demonstrated that one derivative with R = 2-ethyl hexyl (EtHx) (**1a**) groups had superior extraction performance features compared to the well known CMPO extractants. Therefore, the initial objective involved development of a general scaled-up synthesis procedure for **1a** and new derivatives.



During Year 1 of the project, this goal was achieved by using a Grignard-based synthesis variation used to prepare the derivative with R = Ph¹. Sample runs that produced in excess of 25 g of **1a** were accomplished and plans were made for further scale-up (not an entirely routine task in an academic research lab setting). Inquiries were also made with two custom synthesis laboratories regarding potential for technology transfer of the synthesis to a commercial manufacturer.

However, during the course of the Year 1 scale-up studies it was also noted that several low-level phosphorus containing impurities were appearing in the latest samples of **1a**. Subsequent extraction analyses performed with new samples of **1a** clearly demonstrated the negative impact of the low level impurities on Ln(III) extractions. A lengthy effort was then devoted to determining the identity of the impurities and their source. It was discovered that the recent commercial source of starting material, (EtO)₂P(O)H carried an impurity that is converted under the synthesis conditions to (EtHx)₂P(O)(OH) that acts as an acidic extractant. Although the impurity could be removed via extensive chromatographic separations, this reduced the attractiveness of the ligand to some degree. It is also possible to obtain a pure starting material by in-house synthesis; however, this too reduces the attractiveness of the material. Part of the difficulty in removing the impurity appears due to the physical characteristic that makes the ligand useful. Namely, the large branched R groups that are responsible for the ligand's high solubility in dodecane also render the ligand to be a heavy, sticky oil that retains its impurities.

The difficulties with the purification of large samples of **1a** led us to consider the development of other derivatives of **1** that might be more easily purified from acidic alkylated phosphonic acid impurities. Four new ligands based upon the same NOPOPO platform were then prepared during the latter part of Year 2 and in Year 3. Two possess straight chain alkyl group substituents R = n-octyl (**1b**) and n-dodecyl, (**1c**) and two contain fluorinated aryl groups R = 2-CF₃C₆H₄ (**1d**)^{3,4} and 3,5-(CF₃)₂C₆H₃ (**1e**).^{3,4} Ligands **1b** and **1c** show very good solubility in arene solvents while **1d** and **1e** show good solubility in sulfone solvents. The especially noteworthy benefit of these ligands is that they are isolated as solids that are much more easily purified than **1a**. The characterization of the new ligands was completed and samples were prepared for stability studies and radiochemical extraction analyses that are still underway at the close of the project.

NOPOPO Acid Stability Studies

Pure samples of **1a** were subjected to chemical stability studies as a function of exposure time to aqueous HNO₃ solutions (1-3 M). Samples showed no evidence for growth of new species by ³¹P NMR analysis of the two-phase system. Likely impurities that would form (phosphonic or phosphinic acids) would be easily detected by ³¹P NMR of the aqueous and organic fractions. The fact that no new species were detected with contact times > 1 year are favorable for the use of these ligands. Long term stability studies for **1b** - **1e** were not accomplished but short term (1-2 mo.) exposure suggest that these ligands are stable to HNO₃.

NOPOPO Radiation Stability Testing

The radiation stability studies were performed by Dr. Leigh Martin at Idaho National Laboratory using facilities at INL and the University of Notre Dame.⁵⁻⁸ All of the work was performed on purified samples of **1a**. The preliminary findings from these studies appear to indicate that **1a** has good radiation stability although heavy gamma dosing causes radiation damage. The details of these studies will be described in a publication presently under preparation.

Extraction Analyses

Extraction analyses of **1a** were performed during Year 1 and 2 at Washington State University. Initial samples appeared to behave in a fashion closely parallel with our prior work that had been accomplished at Argonne National Laboratory. The intent of these studies was to verify the prior performance and then undertake more detailed simulated waste partitioning studies. That effort was interrupted by the difficulties uncovered with ligand **1a** impurities. The development of **1b** led in Year 3 to a shift in attention to the characterization of the extraction performance of that ligand. That work has progressed through the end of the grant period and will continue as other funding sources are found. A manuscript describing the initial results is under preparation at WSU and samples have been made available for the companion solution thermodynamics study that will take place over the next year.

References, Publications and Presentations for NOPOPO Studies

1. X.Gan, E.N. Duesler and R.T. Paine, "Synthesis and Coordination Properties of New Bis(Phosphonomethyl) Pyridine N,P,P' Trioxides," *Inorg. Chem.*, **40**, 4420 (2001).
2. K.L. Nash, C. Lavallette, M. Borkowski, R.T. Paine and X. Gan, "Features of the Thermodynamics of Two-Phase Distribution Reactions of Americium (III) and Europium (III) Nitrates into Solutions of 2,6-bis[(di-2-ethylhexylphosphino)methyl]pyridine-N,P,P-trioxide" *Inorg. Chem.* **41**, 5849 (2002).
3. S. Pailloux, C.E. Shirima, A.D. Ray, E.N. Duesler, R.T. Paine, J.R. Klaehn, M.E. McIlwain and B.P. Hay "Synthesis and Coordination Chemistry of Trifluoromethyl Decorated Derivatives of 2,6-Bis[(diphenylphosphino)methyl]pyridine N-Oxide Ligands with Lanthanide Ions" *Inorg. Chem.*, **48**, 3104 (2009).
4. S. Pailloux, C.E. Shirima, E.N. Duesler, R.T. Paine, J.R. Klaehn, M.E. McIlwain and B.P. Hay "Synthesis and Lanthanide Coordination Chemistry of Trifluoromethyl Derivatives of Phosphinomethyl-pyridine N-oxides" *J. Chem. Soc. Dalton Trans.*, 7486 (2009).
5. K.L. Swancutt, S.P. Mezyk, L.R. Martin, I. Binyamin, S. Pailloux and R.T. Paine "Kinetics and efficiencies of radiolytic degradation in lanthanide/actinide separation ligands" Abstracts of Papers, 238th ACS National Meeting, Washington DC., United States, August 16-20, 2009.
6. L.R. Martin, R.S. Herbst, R.D. Tillotson, M.R. Greenhalgh and R.T. Paine "Gamma radiation effects on the performance of NOPOPO for trivalent actinide/lanthanide separations" Abstracts of Papers, 237th ACS National Meeting, Salt Lake City, UT, United States, March 22-26, 2009.
7. K.L. Swancutt, S.P. Mezyk, L.R. Martin, R.T. Paine, I. Binyamin and S. Pailloux "Radiolytic degradation of lanthanide/actinide separation ligands" Abstracts of Papers, 237th ACS National Meeting, Salt Lake City, UT, United States, March 22-26, 2009.
8. L.R. Martin, R.S. Herbst, R.D. Tillotson, M. Greenhalgh and R.T. Paine "Gamma Radiation Effects on the Performance of NOPOPO for Trivalent Actinide/Lanthanide Separations" 32nd Actinide Separations Conference, Park City, UT, May 12-15, 2008.

Comparison of Goals v.s. Accomplishments

Considerable progress in the development of the NOPOPO platform as a selective Ln/An extractant system was made during the project grant period. A synthetic pitfall was discovered during extractant scale-up that originates from an impurity found in the commercial supplier of the phosphorus starting material. This problem would be dealt with in a large custom synthesis scale-up effort by preparation of this starting material in-house with attention given to elimination of the by-product during formation of $(\text{EtO})_2\text{P}(\text{O})\text{H}$. Although time spent on the effort to overcome this extractant purity issue diverted from the production of large quantities of **1a** for stimulant waste separation studies, the thorough study led to a much improved understanding of the general synthetic scheme and led to the discovery and study of alternatives **1b** - **1d**. These ligands are of interest for their own unique features.

Products Developed under the Award

1. A generalized procedure for synthesis of extractants of the general type **1**.
2. Improved methods for extractant purification.
3. Characterization of long term chemical stability of **1a**.
4. Characterization of radiation stability of **1a**.
5. Confirmation of the general utility of NOPOPO-class ligands for trivalent Ln/An separations.
6. Publications/presentations found in 3 - 8 above and two more publications that are under preparation at this time.