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PROJECT TITLE: "SUPERCRITICAL CARBON DIOXIDE LIGANDS
FOR EXTRACTING ACTINIDE METAL IONS
FROM POROUS SOLIDS"

Final Scientific/Technical Report, with DOE F 241.3, for the Period
September 16, 1998 to September 15, 2002

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This is the Final Scientific/Technical Report, with DOE F 241.3, for the Period September 16, 1998 to September 15, 2002 for the project entitled: "SUPERCRITICAL CARBON DIOXIDE LIGANDS FOR EXTRACTING ACTINIDE METAL IONS FROM POROUS SOLIDS." The report is being submitted from Loyola University of Chicago, 6525 N. Sheridan Road, Chicago, IL 60626 for Instrument No. DE-FG07-98ER14928. The recipient project director, Dr. Albert W. Herlinger, may be reached at (773) 508-3100. The recipient business officer, Dr. William Yost, may be reached at (773) 508-2471. The DOE contract administrator is Ms. Linda A. Hallum.

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Graduate student/postdoctorate involvement:

Three graduate students at Loyola University Chicago (all of whom hold joint appointments with Argonne National Laboratory) have performed research under this program.

Research Objective:

Numerous types of actinide-bearing waste materials are found throughout the DOE complex. Most of these wastes consist of large volumes of non-hazardous materials contaminated with relatively small quantities of actinide elements. Separation of these wastes into their inert and radioactive components would dramatically reduce the costs of stabilization and disposal. For example, the DOE is responsible for decontaminating concrete within 7000 surplus contaminated buildings. The best technology now available for removing surface contamination from concrete involves removing the surface layer by grit blasting, which produces a large volume of blasting residue containing a small amount of radioactive material. Disposal of this residue is expensive because of its large volume and fine particulate nature. Considerable cost savings would result from separation of the radioactive constituents and stabilization of the concrete dust. Similarly, gas diffusion plants for uranium enrichment contain valuable high-purity nickel in the form of diffusion barriers. Decontamination is complicated by the extremely fine pores in these barriers, which are not readily accessible by most cleaning techniques. A cost-effective method for the removal of radioactive contaminants would release this valuable material for salvage.

The objective of this project is to develop novel, substituted diphosphonic acid ligands that can be used for supercritical carbon dioxide extraction (SCDE) of actinide ions from solid wastes. Specifically, selected diphosphonic acids, which are known to form

extremely stable complexes with actinides in aqueous and organic solution, are to be rendered carbon dioxide-soluble by the introduction of appropriate alkyl- or silicon-containing substituents. The metal complexation chemistry of these new ligands in SCCO_2 will then be investigated and techniques for their use in actinide extraction from porous solids developed.

Research Progress and Implications:

This report summarizes the work performed during the last four years of this program. Because our planned studies of metal complexation and the development of techniques for actinide removal from solids are dependent on the availability of suitable ligands, our initial efforts focused primarily on the synthesis of selected alkyl- or silicon-containing diphosphonic acids. Our principal targets have been derivatives in which the silicon-containing groups either serve as the ester function or are attached to the anchor carbon of the diphosphonic acid. Because methylenediphosphonic acid (MDPA) is commercially available and because its esterification with simple alcohols to yield symmetrical di-esters is well established, our studies have focused on the reaction of this ligand and its homologues with silyl alcohols.

Success was achieved in the reaction of MDPA and its ethylene, propylene, butylene, pentylene and hexylene homologues with 3-(trimethylsilyl)-1-propanol. Using a procedure similar to that previously employed for the synthesis of C-8 dialkylmethylenediphosphonic acids, this series of alkylenediphosphonic acids has been esterified in good yield (ca. 60%) to the symmetrically-substituted diesters. Vapor phase osmometric and cryoscopic studies of these compounds in toluene and 1-decanol, respectively, indicate that their aggregation properties closely parallel those of the dialkyl-substituted alkylenediphosphonic acids, specifically, the P,P'-bis(2-ethylhexyl) alkylenediphosphonic acids, $\text{H}_2\text{DEH}[\text{ADP}]$. Infrared spectroscopy and molecular mechanics methods have been employed to obtain information about the structures of the dimers of P,P'-di-[3-(trimethylsilyl)-1-propylene] methylenediphosphonic acid, $\text{H}_2\text{TMS}[\text{MDP}]$, and its propylene and pentylene homologues. Infrared spectroscopy has also been employed to provide qualitative information on the binding of various metal ions by $\text{H}_2\text{TMS}[\text{MDP}]$. The metal complexation properties of this ligand have been found to be similar to those of di-(2-ethylhexyl)methylenediphosphonic acid, examined previously. Studies of the extraction of various cations (*e.g.*, Fe(III), Th (IV), Am(III)) by $\text{H}_2\text{TMS}[\text{MDP}]$ and its homologues in conventional organic diluents (*e.g.*, o-xylene) indicate that the extraction behavior of the silyl-derivatized diphosphonic acids closely mimics that of conventional alkylenediphosphonic acids. Thus, derivatization has no adverse impact on the complexation or extraction properties of the diphosphonic acids.

Using a dynamic flow method, the supercritical carbon dioxide solubilities of two series of symmetrically-substituted alkylenediphosphonic acids, bearing 2-ethylhexyl and 3-trimethylsilyl-1-propyl ester groups, respectively, were determined as a function of the number of methylene groups separating the two phosphorus atoms. An even-odd effect, similar to that observed previously for the aggregation of these compounds in non-polar diluents, was observed, with compounds that form more highly aggregated species in

non-polar diluents exhibiting lower solubility in SCCO₂. Differences in the relative solubilities of analogous members of these series prompted the study of the SCCO₂ solubilities of symmetrically-substituted methylenediphosphonic acids bearing seven- and eight-carbon ester groups of various degrees of branching to determine the relative importance of steric and electronic effects in determining SCCO₂ solubilities. When molecular connectivity indices were used to quantify the extent of branching in the ester groups, a remarkable correlation between these molecular descriptors and SCCO₂ solubility was observed.

It is important to note that H₂DTMSP[MDP] is roughly an order of magnitude more soluble in SCCO₂ than would be expected from its molecular connectivity index alone. Thus, the greater solubilizing effect of the TMSP group vs. the EH group arises not merely from the introduction of greater branching into the extractant, but also from the presence of the silicon atoms. The observed solubility (*ca.* 0.054 M at 60 °C and 200 bar) of H₂DTMSP[MDP], while not as great as that of tri-*n*-butyl phosphate (1.2 M under the same conditions of temperature and pressure), is comparable to that of diisodecylphosphoric acid (0.041 M) and octyl(phenyl)(*N,N*-diisobutylcarbamoyl)-methylphosphine oxide (0.089 M), two organophosphorus extractants regarded as having sufficient SCCO₂ solubility to render them applicable in the supercritical fluid extraction (SFE) of metal ions.

The results obtained, in addition to elucidating the factors governing the solubility of alkylenediphosphonic acids in SCCO₂, represent the first demonstration of the utility of simple branching indices in the design of carbon dioxide-soluble metal ion extractants. In addition, the results provide the first indication that metal ion extractants having SCCO₂ solubility adequate for application in SFE can be prepared by incorporation into the extractant of simple, structurally well-defined, silicon-bearing substituents. The papers and presentations at scientific meetings that have resulted from this program are listed below.

Planned future unsupported activities:

Work addressing the opportunities for improved CO₂-based systems for metal ion separations suggested by these results will continue in this laboratory. We expect that shortly, conditions suitable for the optimal solubilization of diphosphonic acids in SCCO₂ will be identified. Work to examine their metal complexation chemistry in SCCO₂ will then be performed, along with the design and testing of procedures for the removal of actinides from porous solids.

EMSP accomplishments:

Papers

1. "High Yield Synthesis of Tetraethyl Alkylenediphosphonates via the Michaelis-Arbuzov Reaction," J. A. Griffith, D. J. McCauley, R. E. Barrans, Jr., and A. W. Herlinger, Synthetic Commun., **28**, 4317-4323 (1998).
2. "Synthesis and Characterization of P,P'-Di-[3-(trimethylsilyl)-1-propylene] Alkylenediphosphonic Acids", J. A. Griffith-Dzielawa, R. E. Barrans, Jr., D. R. McAlister, M. L. Dietz, and A. W. Herlinger, Synthetic Commun., **30**, 2121-2132 (2000).
3. "Metal Ion Extraction by Silyl-Substituted Diphosphonic Acids. Part I. P,P'-Di-[3-(trimethylsilyl)-1-propylene] Methylene- and Ethylene- Diphosphonic Acids", D. R. McAlister, M. L. Dietz, R. Chiarizia and A. W. Herlinger, Sep. Sci. Technol., **36**, 3541-3562 (2001).
4. "Metal Extraction by Silyl-Substituted Diphosphonic Acids. Part II. Effect of Alkylen Bridge Length on Aggregation and Metal Ion Extraction", D. R. McAlister, M. L. Dietz, R. Chiarizia, P. R. Zalupski and A. W. Herlinger, Sep. Sci. Technol., **37**, 2289-2315 (2002).
5. "Aggregation and Metal Ion Extraction Properties of Novel, Silicon-Substituted Alkylenediphosphonic Acids", D. R. McAlister, M. L. Dietz, R. Chiarizia and A. W. Herlinger, (Proceedings of the International Solvent Extraction Conference (ISEC '02 Cape Town, South Africa, March 18-21, 2002), Vol. 1, K. C. Sole, P. M. Cole, J. S. Preston and D. J. Robinson, eds., Chris van Rensburg Publications, Melville 2109, South Africa, 2002, pp. 390-395).
6. "Synthesis and Characterization of Metal Complexes of P,P'-Di-[3-(trimethylsilyl)-1-propylene] Methylene-diphosphonic Acid", D. R. McAlister, A. W. Herlinger, John R. Ferraro and M. L. Dietz, Synth. React. Inorg. Met-Org. Chem., **32**, 277-290 (2002).
7. "Aggregation, Metal Ion Complexation and Solubility Properties of Silyl-Substituted Diphosphonic Acids", A. W. Herlinger, D. R. McAlister, R. Chiarizia and M. L. Dietz, Separation Sci. Technol., **38**, (2003) accepted for publication.
8. "Application of Molecular Connectivity Indices to the Design of Supercritical Carbon Dioxide-Soluble Metal Ion Extractants: SC-CO₂ Solubilities of

Symmetrically-Substituted Alkylenediphosphonic Acids”, D. R. McAlister, M. L. Dietz, D. C. Stepinski, P. R. Zalupski, J. A. Dzielawa, R. E. Barrans, Jr. and A. W. Herlinger, Separation Sci. Technol., (2003) manuscript submitted.

9. “Carbon Dioxide Solubility Enhancement Through Silicone Functionalization: “CO₂-philic” Oligo(dimethylsiloxane) Substituted *gem*-Diphosphonates”, J. A. Dzielawa, A. V. Rubas, C. Lubers, D. C. Stepinski, M. L. Dietz, R. E. Barrans, Jr., A. W. Herlinger and J. F. Brennecke, Green Chemistry, (2003) manuscript to be submitted.

Presentations and Invited Seminars

In 2002

1. “Solvent Extraction of Novel, Silicon-Substituted Alkylenediphosphonic Acids”, D. R. McAlister, M. L. Dietz, R. Chiarizia and A. W. Herlinger, (for presentation at the International Solvent Extraction Conference (ISEC '02), Cape Town, South Africa, March 18-21, 2002).
2. “Ester Group Substituent Effects on Phosphoryl Oxygen Basicity in Bisphosphonate Extractants”, P. R. Zalupski, D. R. McAlister, D. C. Stepinski and A. W. Herlinger, (poster #46 presented in the Division of Industrial and Engineering Chemistry at the 224th National A.C.S. Meeting, Boston, MA, August 18-22, 2002). Paper #551232.

In 2001

1. “Silyl-Substituted Alkylenebisphosphonic Acids: Synthesis, Characterization and Metal Ion Extraction“, P.R. Zalupski, D. R. McAlister and A. W. Herlinger, (poster presentation #6 at the Sigma Xi 2001 Graduate Forum, Loyola University Chicago, Chicago, IL, May 16, 2001. Presentation awarded first place.
2. “Aggregation, Metal Ion Complexation and Solubility Properties of Silyl-Substituted Diphosphonic Acids”, A. W. Herlinger, D. R. McAlister, R. Chiarizia and M. L. Dietz, (paper presented at the 12th. Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, Oct. 15-18, 2001.

In 2000

1. “Aggregation, Solvent Extraction and Metal Ion Complexation Studies of P,P’ Di-[3-(trimethylsilyl-1-propyl)] Alkylenediphosphonic Acids”, D. R. McAlister, A. W. Herlinger, R. Chiarizia and M. L. Dietz, (poster presented in the Division of Analytical Chemistry at the 35th Midwest Regional A.C.S. Meeting, St. Louis, MO, October 25-27, 2000). Poster #235.

2. "Aggregation, Solvent Extraction and Metal Ion Complexation Studies of P,P' Di-[3-(trimethylsilyl)-1-propyl] Alkylenediphosphonic Acids", A. W. Herlinger, D. R. McAlister, R. Chiarizia and M. L. Dietz, (paper presented at the 24th Actinide Separations Conference, Las Vegas, NV, August 14-17, 2000).
3. "Solvent Extraction and Metal Ion Complexation Studies of P,P' Di-[3-trimethylsilyl)-1-propylene] Alkylenediphosphonic Acids", D. R. McAlister and A. W. Herlinger, (oral presentation #1 at the Sigma Xi 2000 Graduate Forum, Loyola University Chicago, Chicago, IL, May 16, 2000. Presentation was awarded third place.
4. "Design and Synthesis of Functionalized Diphosphonic Acids for Metal Ion Extraction", D. C. Stepinski and A. W. Herlinger, (poster #2 presented at the Sigma Xi 2000 Graduate Forum, Loyola University Chicago, Chicago, IL, May 16, 2000.
5. "Functionalized Diphosphonic Acid Ligands for Metal Ion Coordination in Supercritical Carbon Dioxide", A. W. Herlinger, J. A. Griffith, D. R. McAlister, M. L. Dietz and R. E. Barrans, Jr., (poster presented in the Environmental Management Sciences Program National Workshop sponsored by the U. S. Department of Energy, Atlanta, GA, April 25-27, 2000).
6. "Synthesis of Supercritical Carbon Dioxide-Soluble Methylenediphosphonic Acids for Metal Ion Extraction", J. A. Dzielawa, A. V. Rubas, R. E. Barrans, Jr., A. W. Herlinger and M. L. Dietz, (poster presented in the Division of Organic Chemistry at the 219th National A.C.S. Meeting, San Francisco, CA, March 26-30, 2000). Paper #361875.

In 1999

1. "Aggregation of Dialkyl-Substituted Diphosphonic Acids and Its Effect on Metal Ion Extraction", R. Chiarizia, A. W. Herlinger, D. R. McAlister, R. E. Barrans, Jr., and J. R. Ferraro, (paper presented at the 11th. Symposium on Separation Science and Technology for Energy Applications, Oak Ridge, TN, Oct. 15-17, 1999).
2. "Functionalized Diphosphonic Acid Ligands for Metal Ion Coordination in Supercritical Carbon Dioxide", A. W. Herlinger, J. A. Griffith, D. R. McAlister, and R. E. Barrans, Jr., (poster #33 presented in the symposium "First Accomplishments of the Environmental Management Sciences Program" sponsored by the Division of Nuclear Chemistry and Technology at the 218th National A.C.S. Meeting, New Orleans, LA, August 22-26, 1999).
3. "An Investigation of Di-[3-trimethylsilyl)-1-propylene] Methanediphosphonic Acid and Its Coordination Chemistry", D. R. McAlister and A. W. Herlinger, (poster #2

presented at the Sigma Xi 1999 Graduate Forum, Loyola University Chicago, Chicago, IL, May 19, 1999. Presentation was awarded first place (tie).

4. "Silicone-functionalized Diphosphonic Acid Ligands for Metal Coordination in Supercritical Carbon Dioxide," R. E. Barrans, Jr., J. A. Griffith, and A. W. Herlinger, (poster #45 presented in the Division of Industrial & Engineering Chemistry at the 217th National A.C.S. Meeting, Anaheim, CA, March 21-25, 1999).

In 1998

1. "Synthesis and Reactivity of Tetraethyl Alkylenediphosphonates," J. A. Griffith, A. W. Herlinger, and R. E. Barrans, Jr., (poster presented at the 31st A.C.S. Great Lakes Regional Meeting, Division of Organic Chemistry, Milwaukee, WI, June 1-3, 1998), Abstract No. 210.
2. "Synthesis of Siloxane-Substituted Diphosphonic Acids for Supercritical Fluid Extraction," J. A. Griffith, A. W. Herlinger, and R. E. Barrans, Jr., (paper presented at the Sigma Xi Graduate Student Forum, Loyola University, Chicago, IL, May 19, 1998).