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PROJECT TITLE: “SUPERCritical CARbon DIOXIDE LIGANDS FOR EXTRACTING ACTINIDE METAL IONS FROM POROUS SOLIDS”


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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, H$_2$DEH[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, H$_2$TMSP[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 H$_2$TMSP[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 H$_2$TMSP[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 SCCO$_2$. Differences in the relative solubilities of analogous members of these series prompted the study of the SCCO$_2$ 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 SCCO$_2$ 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 SCCO$_2$ solubility was observed.

It is important to note that H$_2$DTMSP[MDP] is roughly an order of magnitude more soluble in SCCO$_2$ 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 H$_2$DTMSP[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 disodecylphosphoric acid (0.041 M) and octyl(phenyl)(N,N-diisobutylcarbamoyl)-methylphosphine oxide (0.089 M), two organophosphorus extractants regarded as having sufficient SCCO$_2$ 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 SCCO$_2$, 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 SCCO$_2$ 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 CO$_2$-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 SCCO$_2$ will be identified. Work to examine their metal complexation chemistry in SCCO$_2$ will then be performed, along with the design and testing of procedures for the removal of actinides from porous solids.
EMSP accomplishments:

Papers


8. “Application of Molecular Connectivity Indices to the Design of Supercritical Carbon Dioxide-Soluble Metal Ion Extractants: SC-CO₂ Solubilities of


Presentations and Invited Seminars

In 2002


In 2001


In 2000


**In 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).

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


In 1998
