Environmental Management Science Program

Project ID Number 55087

Design and Synthesis of the Next Generation of Crown Ethers for Waste Separations: An Inter-Laboratory Comprehensive Proposal

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June 1, 1998

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Research Objective

The purpose of this task is to undertake the design, synthesis, and characterization of the next generation of crown ethers for metal-ion separations applicable to USDOE's environmental needs. Target problems include: Li^+ ions leaching from burial sites at the Oak Ridge Y-12 Plant; fission products ^{90}Sr and ^{137}Cs contaminating high-level tank wastes at Hanford, INEEL, and Savannah River; and radium in wastes at the Niagara Falls Storage Site. Unfortunately, the technologies needed to address these problems either do not exist or exhibit substantial deficiencies. Separation techniques such as solvent extraction and ion exchange promise to play a strong role, especially as enhanced with highly selective crown ethers and calixarenes.

Research Progress and Implications

This project is midway through year 2 of a 3-year effort. Below is given a summary of progress in the approximate period September, 1997, to May, 1998, for each of the four co-investigators at Pacific Northwest National Laboratory (PNNL), Argonne National Laboratory (ANL), Oak Ridge National Laboratory (ORNL), and the University of Tennessee (UTK). The overall approach entails utilization of theory and molecular modeling (PNNL), organic synthesis of novel crown compounds (ORNL), solvent extraction studies (ORNL and ANL), and studies of polymer-immobilized crown ethers (UTK).

Molecular Modeling (J. B. Nicholas, D. A. Dixon, and B. P. Hay, PNNL). Towards increasing the selectivity of calixarene-crown sequestering agents for cesium, effort in FY98 has concerned the role that the pi-cation interactions play in the complexation of alkali metal ions by calixarenes. The various modes of cation binding to a calixarene conformation differ with respect to the number of oxygens and arenes that serve as donor groups. To better understand the energetics and geometries of these interactions, we have completed high-level MP2/dzvp+ calculations on complexes of the alkali cations with benzene and anisole. Non-local density functional theory calculations are being used to identify all stable binding modes of tetramethoxy-calix[4]arene with sodium and cesium and to rank these modes in order of stability. Calculations at the B3LYP/dzvp level have been in progress on the EMSL supercomputer since the start of the fiscal year. So far we have determined the relative energies of the cone, partial cone, 1,3 alternate, and 1,2 alternate forms of tetramethoxy-calix[4]arene and have located eight minima for binding sodium by these conformers.

Univalent Metal Ions (R. A. Sachleben, J. C. Bryan, T. J. Haverlock, and B. A. Moyer, ORNL). A notable accomplishment in the past year was the development of improved syntheses of calix[4]arene-biscrown ethers and bis-alkyloxy calix[4]arene-crown ethers. Resulting lower costs for these important extractants directly benefit the development of processes for Cs removal from tank waste under funding by the Efficient Separations and Processing (ESP) Crosscutting Program.

In addition, detailed solvent-extraction studies aided by computer equilibrium modeling have revealed the underlying extraction equilibria by which Cs^+ ion is extracted by calix[4]arene-bis(t-octylbenzo-crown-6) in a model diluent, 1,2-dichloroethane. It has also been shown that the Cs/K separation factor for this extractant depends upon several environmental factors. These insights have been useful in interpreting and improving extraction and stripping behavior in process flowsheet development under ESP.

Guided by molecular-modeling results at PNNL, a series of 15 novel calix[4]arene-crown compounds has been synthesized in the past year toward understanding effects of substituents on the calixarene ring and on the attached crown-6 bridge. We have shown that systematic changes in the bulkiness of particular substituent groups effect changes both in the conformations observed in crystal structures, extraction strength, and Cs/K selectivity. This result has led to a new class of calix[4]arene-crown ethers with Cs/K selectivity an order of magnitude greater than the previously reported calix[4]arene-crown-6 compounds.

Divalent Metal Ions (M. L. Dietz and R. Chiarizia, ANL). In an effort to develop guidelines for the rational design of synergistic extraction systems for alkaline earth cation separations employing crown ethers, we have been examining combinations of dialkylphosphoric acids with pure isomers of dicyclohexano-18-crown-6 ($DCH_{18}C_6$). The extent of interaction between each of the organophosphorus extractants and the various crown ether stereoisomers has been investigated in detail using solvent extraction, infrared spectroscopy, and vapor phase osmometry. The osmometric studies indicate that each of the dialkylphosphoric acids exists as a dimer in toluene, while the $DCH_{18}C_6$ stereoisomers are monomeric. In addition, the VPO results indicate no interaction between $DCH_{18}C_6$ and the organophosphorus acids. Extraction data indicate that the extracted species in each of the systems is of the form $M(DCH_{18}C_6)(HA_2)^2$ (where M = Sr^{2+} or Ba^{2+}). Continuous variation studies employing dialkylphosphoric acid / $DCH_{18}C_6$ mixtures show only small synergistic effects in the extraction of calcium ion. For barium and strontium, however, appreciable synergistic effects are observed upon addition of the cis-syn-cis (A) isomer, while other isomers show less effect. In all cases in which synergism is observed, the ratio of dialkylphosphoric acid to $DCH_{18}C_6$ in the extracted complex has been found to be 4:1 (2 acid dimers to 1 crown ether molecule). The pH, dialkylphosphoric acid, and $DCH_{18}C_6$ dependencies in the synergistic systems exhibit slopes near 2, 2, and 1, respectively.

Polymer-Immobilized Crown Ethers (S.D. Alexandratos, UTK; R.A. Sachleben, T.J. Haverlock, and B.A. Moyer, ORNL). The synthesis effort at the University of Tennessee has focused on immobilizing the crown ether monomers received from ORNL. Early experiments established that the crown with the methylene group off of the ring was incapable of polymerizing directly into a macromolecular structure. It was then decided to attempt the immobilization of the crown compound onto a polymer support already containing a group capable of covalently bonding the crown. Five different approaches were devised, and experiments are continuing within each approach. Results have been obtained on the following two of the approaches: (1) Schiff base formation of polystyrene-containing-CH_2NH_2 groups with keto-crown. (2) Immobilization of the methylene-containing crown with polystyrene containing a relatively acidic C-H bond was attempted with polystyrene containing the beta-ketophosphonate ligand. Unfortunately, extraction tests of the corresponding two resin samples provided to ORNL have revealed that the first does not extract alkali metals detectably and that the second is relatively nonselective.

Planned Activities

At PNNL, calculations are currently in progress for binding of cesium ion by tetramethoxy-calix[4]arene. The results will be used to understand Cs/Na selectivity. Efforts at ANL to model the extraction equilibria for the synergistic systems, to examine possible correlations between ligand strain energy and synergistic effects, and to extend this work to solid-supported systems are now in progress. At ORNL, efforts will be made to attach ionizable groups to calix[4]arene-crown-6 compounds. Polymer synthesis at UTK will focus on three alternative means for attaching 14-crown-4 ethers to suitable immobilized functional groups.

Other Access To Information

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