Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation

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ANNUAL PROGRESS REPORT

U.S. Department of Energy

Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation

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Number of graduate students: 1 (VPI)
Number of postdocs: 2 (one each at ORNL and TTU)

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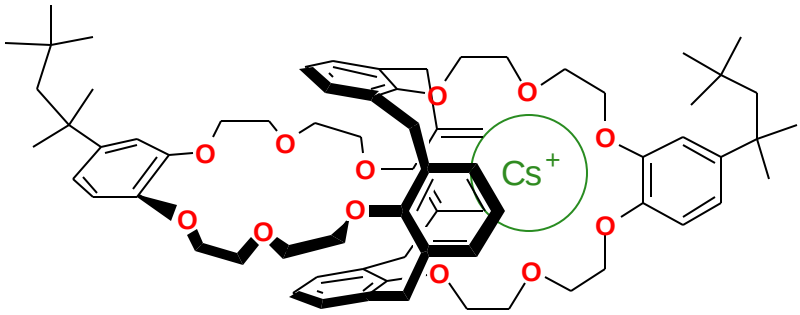
Research Objective

This project seeks a fundamental understanding and major improvement in cesium separation from high-level waste by cesium-selective calixcrown extractants. Systems of particular interest involve novel solvent-extraction systems containing specific members of the calix[4]arene-crown-6 family, alcohol solvating agents, and alkylamines. Questions being addressed pertain to cesium binding strength, extraction selectivity, cesium stripping, and extractant solubility. Enhanced properties in this regard will specifically benefit cleanup projects funded by the USDOE Office of Environmental Management to treat and dispose of high-level radioactive wastes currently stored in underground tanks at the Savannah River Site (SRS), the Hanford site, and the Idaho National Environmental and Engineering Laboratory. The most direct beneficiary will be the SRS Salt Processing Project, which has recently identified the Caustic-Side Solvent Extraction (CSSX) process employing a calixcrown as its preferred technology for cesium removal from SRS high-level tank waste. This technology owes its development in part to fundamental results obtained in this program.

Disposal of high-level waste is horrendously expensive, in large part because the actual radioactive matter in underground waste tanks at various USDOE sites has been diluted over 1000-fold by ordinary inorganic chemicals. Vitrification of the waste to produce a borosilicate glass waste form is currently the preferred treatment of the high-level waste prior to geologic disposal. However, to vitrify the entire mass of the high-level waste would be prohibitively expensive. Accordingly, technologies are needed to remove radionuclides such as ^{137}Cs from the waste so that the bulk of it may be diverted to cheaper low-level waste forms and cheaper storage. After a decade of technology development and demonstration beginning in the early 1990s, some technologies like CSSX are already on their way to implementation. Nevertheless, it is recognized that fundamental results will continue to add value toward improvements in existing technologies and advancement of alternative technologies.

To address such needs, chemical research at Oak Ridge National Laboratory (ORNL) has focused on calixcrown extractants, molecules that possess crown ether functionalities supported on a calixarene framework. This hybrid possesses a cavity that is highly complementary for the Cs^+ ion vs. the Na^+ ion, making it possible to cleanly separate cesium from wastes that contain 10,000- to 1,000,000-fold higher concentrations of sodium. X-ray structural investigations, both at ORNL and elsewhere, have shown that this unique binding site is bounded on two sides by opposing aromatic groups on the calixarene framework. This cleft closely complements the size and "soft" electronic characteristics of the guest Cs^+ ion and is thought to provide for the high selectivity observed. The polyether loop provides additional coordination for cesium, again with size and conformational properties that complement the Cs^+ ion. The overall coordination ability of the calixcrown is strongly



Calix[4]arene-bis(*t*-octylbenzo-crown-6)
"BOBCalixC6"
(As complexed with Cs^+ ion)

influenced by substituents both on the polyether loop and on the aromatic groups of the calixarene framework.

Previous EMSP results elucidated the underlying extraction equilibria in cesium nitrate extraction by the calixcrown used in the CSSX process, calix[4]arene-bis(*t*-octylbenzo-crown-6), designated here as BOBCalixC6 (see structure). This understanding led to key improvements in the development of the CSSX process under the EM Efficient Separations and Crosscutting Program, entailing a method to back-extract or "strip" cesium from the calixcrown subsequent to cesium extraction from waste. Having this stripping method allowed the cesium to be concentrated in a relatively pure aqueous stream and the extractant to be regenerated for recycle. Closing the cycle then made possible the design of a process flowsheet and successful demonstration through collaboration with Argonne National Laboratory and Savannah River Technology Center under funding from the Office of Project Completion and the Tanks Focus Area of the USDOE Office of Environmental Management.

Despite these successes, the CSSX process represents young technology that can benefit substantially from further fundamental inquiry. First, reversibility of the process (stripping efficiency) still presents the greatest potential for improvement. Second, although the calixcrown extractants for cesium are two orders of magnitude stronger than the next best simple crown ether, a minor fraction of the extractant capacity is utilized. Third, potassium competes significantly with cesium for the calixcrown binding site, an important issue in dealing with Hanford wastes having potassium concentrations as high as 1 M. Fourth, the calixcrown solubility needs to be improved. And finally, the mechanism of extraction must be understood in detail to provide the base of knowledge from which further development of the technology can be rationally made.

Toward addressing these needs, synthesis and characterization of new solvent components are being performed at ORNL and through collaboration with Texas Tech University (TTU, Prof. R. A. Bartsch). Extraction behavior is being surveyed to assess the effectiveness of candidate solvent systems, and systematic distribution measurements are being modeled toward a thermodynamic understanding of controlling equilibria. Complexation phenomena are the focus of studies at Virginia Polytechnic Institute & State University (VPISU, Prof. H. W. Gibson). Structure-function relationships will be deduced through X-ray crystallography of candidate extractants at ORNL and collaboration with PNNL on molecular modeling (B. P. Hay). The overall objective is a significant advance in the predictability and efficiency of cesium extraction from high-level waste in support of potential implementation at USDOE sites.

Research Progress and Implications

Reporting Period. This report summarizes work performed during the second year of a three-year project. Significant progress in this time has been obtained at ORNL on synthesis of new alkylated calixcrowns that have enhanced solubility in modified alkane diluents. Structural studies coupled with molecular mechanics at PNNL continue to elucidate underlying bonding and conformational requirements. New ionizable calixcrowns from TTU were shown to possess improved extraction and stripping efficiency, and an equilibrium model explaining their extraction behavior has been developed at ORNL. At VPISU a greater understanding of complexation equilibria is being developed.

Synthesis of Alkylated Calix[4]arene-crown-6 ethers. New calix[4]arene mono- and bis-

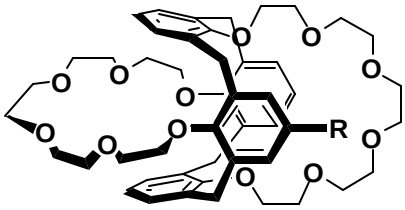
alkylbenzocrown-6 ethers having improved solubility have been synthesized. The *tert*-octyl groups in BOBCalixC6 provide for increased solubility relative to their absence, but the solubility limit of BOBCalixC6 in the solvent is still low, limiting the applicability of the CSSX process. Toward enhanced solubility, the effect of the alkyl chain on overall solubility of the molecule has been investigated. A series of alkylated catechols were prepared, from which the calixarene-crown ethers are synthesized. The synthetic strategies used to prepare the alkyl catechol starting materials can be grouped into two major areas: Friedel-Crafts (FC) alkylation reactions using olefins and FC acylation reactions. Both strategies were examined.

Although FC alkylation had in fact been highly advantageous in the preparation of BOBCalixC6 via acid-catalyzed alkylation of catechol using 2,4,4-trimethylpentene, this strategy has not proven fruitful. First, it was found that the advantages in the particular case of BOBCalixC6 (regiospecificity, few isomers, and ease of separation and purification of the mono-substituted catechol) could not be readily obtained with alternative olefins. For example, use of simple alpha-olefins such as 1-octene under FC conditions leads to a mixture of alkyl chain isomers, and 2-methylpentene leads to difficult-to-separate mixtures of mono- and bis-alkylated catechols. These synthesis problems were successfully circumvented by finding a convenient route to mono-alkylation using catechols already possessing a methyl group at either the 3- or 4-position. Alkylation with 2-methylpentene gave respectively 3-methyl-5-(2,2-dimethylbutyl)catechol and 4-methyl-6-(2,2-dimethylbutyl)catechol. From these two bis-alkylated catechols, the corresponding calixarene-crown ethers were prepared, and their solubility properties in a modified alkane solvent matrix were compared against the known compounds BOBCalixC6, calix[4]arene-bis-(*tert*-butylbenzo-crown-6), and bis-*n*-octyloxycalix[4]arene-*tert*-octylbenzo-crown-6. The results show that the 2,2-dimethylbutyl group slightly enhances solubility vs. BOBCalixC6 when connected at the 5-position but dramatically decreases solubility if connected at the 6-position. However, it was found that placement of alkyl groups, even methyl, adjacent to the catechol oxygens causes sufficient distortion of the corresponding crown ether ring to severely impede good cesium binding.

Unlike FC alkylation, FC acylation has the advantage that once a single acyl group is on the aromatic ring, the ring is deactivated toward further substitution. However, a disadvantage is that it takes two or three steps to obtain the alkyl catechol, which may be obtained in a single step with FC acid catalyzed alkylation. The 2-ethylhexyl (2EH) sidechain is one of the classic "greasy" substituents used to enhance the solubility of extractants and was selected as a first choice to replace the *tert*-octyl sidechain. A synthetic scheme was successfully developed for the 4-substituted 2-ethylhexylcatechol, and the corresponding cesium extractant calix[4]arene-bis(2-ethylhexylbenzo-crown-6) was prepared. At this writing, these two compounds appear to have superior solubility properties relative to analogs with other alkylation, and cesium extraction is comparable to BOBCalixC6. Solubility experiments were initiated to obtain a quantitative comparison of the solubilities of various compounds made to date.

Extraction Properties of Ionizable Calix[4]arene-crown-6 ethers. Ionizable calix[4]arene crown ethers may offer advantages over neutral analogs by allowing more efficient stripping. Our extraction results have shown that neutral calixcrowns like BOBCalixC6 function by a nitrate concentration "swing." That is, extraction occurs by an ion-pair extraction in which the high nitrate concentration in the waste drives the extraction of cesium nitrate. It follows that the extraction may be reversed by then contacting the solvent with water or, say, dilute nitric acid. Since the efficiency of an extraction/stripping cycle controlled by nitrate swing is limited, a strategy for an improved cycle might involve changing the extraction mechanism to ion

exchange. In this case, stripping is effected with acid, which reprotonates the extractant, releasing the cesium ion. Since one can in principle increase the efficiency of stripping by raising the aqueous acidity, a significant improvement in overall performance may be possible. Recent publications describing the new ionizable calix[4]arene-biscrown-6 compounds developed at TTU by R. A. Bartsch and co-workers afford an opportunity to test this concept. Under funding by the USDOE Office of Basic Energy Sciences, Prof. Bartsch graciously provided two samples of their reported compounds for extraction tests (see figure at right). These compounds were expected to exhibit markedly different acidities, owing to the different electronic inductive effects of the $-CF_3$ and $-CH_3$ groups. Extraction experiments showed that these compounds have comparable strength vs. BOBCalixC6 under extraction conditions much like that of the CSSX process. Unlike BOBCalixC6, however, stripping becomes more efficient with increasing nitric acid concentration. As expected, stripping was more efficient with the less acidic compound (i.e., the compound having a terminal $-CH_3$ group on the sidearm), though not quite as efficient as BOBCalixC6. The clear relationship of stripping efficiency with the inductive effect of the sidearm terminal group indicates that compounds with even better stripping efficiency will likely be identified. Equilibrium modeling of the data with the computer program SXLSQI suggests the following tentative conclusions concerning the extraction mechanism by the two compounds: a) Cs^+ is extracted by cation exchange from dilute nitric acid; b) under highly acidic conditions, the mechanism reverts to ion-pair extraction in which the neutral compounds extract cesium nitrate; and c) under alkaline conditions, Cs^+ is extracted by cation exchange, except the two compounds are in their sodium salt forms.



R = $C(O)NHSO_2CF_3$
$C(O)NHSO_2CH_3$

Structural and Theoretical Studies. X-ray structures have proved useful in understanding the effect of preorganization of calixcrown ethers through strategic placement of benzo substituents. Three published papers describe the structures of various precursor molecules in the preparation of dihydroxycalix[4]arene-crown-6 and *paco*-calix[4]arene-crown-6 ether molecules. A paper in preparation describes the use of molecular-mechanics calculations to predict that the 1,3-dihydrocalix-crown-6 derivatives could exhibit greater selectivity for Cs^+ over K^+ ions than the parent 1,3-dialkoxy calixcrowns. X-ray crystal structures of some of the molecules prepared as well as the cesium nitrate complex of dihydrocalix[4]arene-benzocrown-6 ether are also reported. The cesium complex structure corresponds closely to the structure predicted by molecular mechanics, validating this approach to host design. The structural studies reveal that these new calix[4]arene crown ether host molecules have greater conformational flexibility and undergo greater conformational changes upon cesium complexation than previously studied calixarene crown ethers, indicating that there is less preorganization of the binding cavity. Extraction studies show that the dihydrocalix[4]arene-crown-6 ethers do indeed exhibit the anticipated enhanced cesium selectivity. From the computational and structural work, it is clear that the enhanced selectivity is due to the dehydroxylation of the calixarene, which relieves ligand strain upon metal binding. Since this decrease in strain is greater for Cs^+ than it is for K^+, binding of Cs^+ is favored relative to K^+. However, the increase in selectivity comes at the cost of decreased extraction strength, which is also anticipated because of the observed decrease in preorganization of the binding cavity.

In hopes of gaining back some of the lost extraction strength, an idea to increase

preorganization of the calixarene (and thereby the crown ring) was tested by manipulating the steric substituents of the calixarene on the side opposite to the binding site. As described in a draft manuscript, five new calix[4]arene-25,27-diols were prepared with alkyl substituents on the calixarene either *meta* or *para* to the phenolic hydroxy groups, along with ten novel crown-6 ether derivatives. Molecular modeling predicts the *paco* conformation to be of lower energy than the 1,3-*alt* conformation for those with *para* substituents. X-ray crystal structures of three crown-6 ethers derived from calix[4]arene-25,27-diol exhibit either the 1,3-*alt* conformation or a conformation intermediate between 1,3-*alt* and *paco*. It is clear that the rotational barriers for the unsubstituted calix[4]arene rings are quite low, despite various levels of steric bulk placed on the phenolic calix rings. Competitive extractions of alkali metal cations reveal the effect of substitution on the calixarene on cation binding by these ionophores. Generally speaking, alkyl substitution on the phenolic calixarene rings has little or no effect on the binding strength.

A final paper in preparation takes the next logical step: steric manipulation of the crown ring to achieve greater preorganization of the binding cavity. Dihydrocalix[4]arene-crown-6 ether molecules synthesized with benzo substituents on the calixarene phenolic ethers show enhanced cesium extraction strength and selectivity. The X-ray crystal structures of dihydrocalix[4]arene-bis(5-nitrobenzo)crown-6, dihydrocalix[4]arene-tribenzocrown-6, and dihydrocalix[4]arene-dibenzocrown-6 ethers were determined, demonstrating that greater preorganization of the binding cavity is most strikingly achieved by placing benzo substituents on the crown ring proximal to the calixarene.

Homogeneous Complexation Chemistry of Crown Ethers. The impetus for the effort at VPISU has been possible utilization of organic ligand inclusion in the BOBCalixC6 macrocyclic framework, in order to enhance stripping via displacement of Cs^+. Various ammonium salts have been examined for their ability to interact with BOBCalixC6 by ^1H NMR in $CDCl_3$ as a model solvent system. It was found that neither bulky nor straight chain secondary ammonium salts interact with the calixcrown, while small, relatively unhindered salts such as ammonium and guanidinium do bind with the host molecule. The influence of counteranions and other electrolyte species on binding strengths in the organic phase is being addressed using well-known pseudorotaxane motifs. Pseudorotaxane complexes of dibenzo-24-crown-8 with dibenzylammonium hexafluorophosphate were shown in ^1H NMR titration experiments to exhibit 1:1 binding constants that *decrease* with increasing overall ionic strength. This was readily treated as a nonideality effect using the Debye-Hückel limiting law, suggesting the need for similar corrections in many published works. In the present case, the large PF_6^- anion is dissociated, and its effect is thus relegated to that of a spectator ion. Evidence has been found that this role can be deliberately changed by incorporating alcohol functionalities into the crown ether, whereupon the counteranion is drawn by hydrogen bonding into a supramolecular motif that enhances cation binding by the crown ether. In a series of NMR experiments, bis-*m*-phenylene-32-crown-10 containing two pendant methanol groups was shown to bind viologen dications with *increasing* ionic strength upon addition of quaternary ammonium salts of hydrogen-bonding sulfonate and carboxylate anions.

Planned Activities

New alkylated analogs to BOBCalixC6 will be further characterized with regard to solubility and extraction behavior. Definitive solubility values in alcohol-modified alkane

diluents will be measured. Improvements in the synthesis and purification of the 2-ethylhexyl analog of BOBCalixC6 will be sought, and a greater quantity will be synthesized for experiments. Contacts at the Hanford and Savannah River sites will be kept informed of progress in connection with improving and extending the applicability of the CSSX process. Future efforts will also seek enhanced stripping by means of proton switches, that is, to use the large pH change from alkaline extraction conditions to weakly acidic stripping conditions to bring about dramatic decomplexation. Toward this end, new calixcrowns will be synthesized at ORNL. Promising results on ionizable calixcrowns will also be further pursued through collaboration with Prof. Bartsch at TTU. Studies of binding interactions between crown ethers and organic guest species will continue under the direction of Prof. H. W. Gibson at VPISU. These studies are expected to provide insight into the role of the amine in CSSX, perhaps leading to more effective stripping methods. In general, equilibrium extraction and modeling studies will aim to elucidate thermodynamic processes of ion partitioning and complexation in systems containing selected calixcrowns, alcohol synergists, and alkylamines. Basic questions to resolve include the role of ion-pairing and dissociation, the solvation of the anion by the alcohol, the possible proton-ionizable nature of the alcohols, and the role of amine solvent components. Theoretical results from the studies of B. P. Hay at PNNL will be assessed to identify synthetically attractive calixcrown extractants having predicted enhanced selectivity and extraction strength for Cs^+ vs. K^+. Finally, it will be the goal to transfer this basic knowledge to collaborators, site users, private industry, and applied researchers associated with high-level waste remediation.

Information Access

A publication list is provided. See also the www home page of the ORNL Chemical Separations Group: http://www.ornl.gov/csg.

Acknowledgments

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P. V. Bonnesen, L. H. Delmau, T. J. Haverlock, T. G. Levitskaia, R. A. Sachleben, F. V. Sloop, Jr., and B. A. Moyer, "Science to Applications: Development of the Caustic-Side Solvent Extraction Process for Cesium Removal from Savannah River Waste", Proc. 9th Biennial Internat. Conf. Nuclear and Hazardous Waste Management (Spectrum 2002), Aug. 4-8, 2002, Reno, Nevada.

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B. A. Moyer, P. V. Bonnesen, J. C. Bryan, N. L. Engle, T. J. Haverlock, T. G. Levitskaia, R. A. Sachleben, R. A. Bartsch, V. S. Talanov, H. W. Gibson, J. W. Jones, and B. P. Hay, "Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation," FY 2002 Annual Report, Environmental Management Science Program, Aug., 2002; posted on the EMSP web site http://emsp.em.doe.gov/ .

Presentations

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, L. H. Delmau, T. J. Haverlock, T. G. Levitskaia, and F. V. Sloop, Jr., "Fundamental Principles and Applications of Host-Guest Chemistry in Liquid-Liquid Separation Systems," DECHEMA Workshop on Supramolecular Strategies for Selective Solvent Extraction Processes, Nov. 8, 2002, Frankfurt, Germany (Invited).

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