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DESIGN AND SYNTHESIS OF THE NEXT GENERATION OF CROWN ETHERS FOR WASTE SEPARATIONS: AN INTER-LABORATORY COMPREHENSIVE PROPOSAL

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Executive Summary

This multidisciplinary project united the efforts of four research groups at three National Laboratories and the University of Tennessee to develop design principles, methods, and materials needed to solve the demanding separations problems in environmental and waste management facing the DOE in the 21st century. Included within the broad scope of this project were the development and utilization of computational chemistry and molecular modeling for the rational design of new extractants and extraction systems, detailed thermodynamic and structural studies to elucidate fundamental chemical principles underlying chemical separations and solvent extraction, and the synthesis of new extractants and ion-exchange materials with improved performance. Calixarenes and crown ethers were chosen as the subject of these investigations because of their potential utility in separations of metals that represent particular problems to the USDOE environmental clean-up effort. Significant progress was achieved in all of these areas with direct impacts on specific DOE EM programs, as described below.

In the area of computational chemistry, high-level quantum-mechanical calculations on metal complexes of calix[4]arenes were performed, allowing for the first time a complete evaluation of metal-ion binding modes for these systems. Significantly, it was shown that a rational approach to calixarene-based ligand design must account not only for the ways in which a calixarene molecule can organize itself, but also for the different ways that it can bind different metal cations. The contrasting binding modes of calix[4]arene with sodium and cesium have suggested new approaches to the design of cesium-selective ionophores. Quantum-mechanical calculations also provided the basis for developing Molecular Mechanics (MM3+) force field parameters for organophosphate, -phosphonate, and -phosphinate extractants, as well as improved methods for including π-arene interactions in MM calculations. The enhanced MM

force fields proved instrumental in developing new cesium-selective calix-crown extractants and strontium-selective synergistic crown ether/dialkyl phosphoric acid extraction systems.

Detailed thermodynamic studies on a calix[4]arene crown-6 ether-based cesium solvent-extraction system proved critical in the development of a process, called the Alkaline-Side CSEX process, for removal of cesium from alkaline high-level waste. The speciation modeling performed under this EMSP project revealed the source of inefficient decomplexation of cesium from the organic-phase calixarene-cesium complex and suggested a potential solution. The proposed solution worked exactly as predicted and allowed development of a practical, robust process that is currently the subject of a large, multi-site, multi-million dollar program led by ORNL for the USDOE Savannah River Site (SRS). The contribution of this work was recognized by a 1998 Lockheed Martin Technical Achievement Award for the development of the Alkaline Side CSEX process. The publication reporting the speciation modeling was featured on the cover of the *Journal of Inclusion Phenomena and Macrocyclic Chemistry*.

Utilizing the insight gained from X-ray crystallographic structural studies and molecular mechanics (*vide supra*), a new class of calix[4]arene crown ethers was designed. Altogether, over two dozen new calix[4]arene crown ethers were synthesized and their cesium extraction properties tested. The best of these new compounds exhibits more than an order-of-magnitude improvement in selectivity for cesium over potassium, as well as enhanced selectivity for cesium over sodium and rubidium. The results of this work were shared with another EMSP project at ORNL (project OR17SP23-3THN), resulting in the development of an optical cesium sensor that exhibits both enhanced cesium sensitivity and better cesium/potassium selectivity.

Important advances were made in the stereospecific synthesis of individual isomers of dicyclohexano-18-crown-6 (DC18C6) and in the detailed understanding of extraction of calcium,

strontium, and barium by the different DC18C6 isomers with three dialkyl phosphoric acids. Significantly, these studies demonstrated a linear correlation between the ligand strain energies of the crown ethers as determined by molecular mechanics (*vide supra*) and the synergistic extraction of strontium and barium. Small Angle Neutron Scattering revealed that, consistent with extraction data, the strontium salts of dialkylphosphoric acids aggregate and that the presence of the crown ether inhibits the formation of large aggregates and enhances the formation of discrete, well-defined species. Of particular significance is the conclusion that the synergistic crown ether/phosphoric acid extraction system is well-behaved over a wide range of concentration and loading, which is critical to process-scale applications which invariably operate at high levels of metal loading. The development of optimized synergistic systems has the potential to greatly enhance the applicability of strontium-selective crown ether based systems to contaminated low-ionic-strength media.

The development of an efficient lithium-selective ion-exchange resin was motivated by the presence of lithium as an enviromentally significant groundwater contaminant at the Y-12 plant in Oak Ridge. A method was developed for immobilizing a lithium-selective crown ether (MOM14C4, previously developed at ORNL) on a polymer support. This resin was shown to rapidly and quantitatively complex lithium from solutions containing large amounts of competing sodium ions. The results form the basis of a Ph.D. thesis to be completed in the coming year. A new cation-exchange extractant was synthesized and shown to exhibit remarkably selective synergism for lithium when combined with our lithium selective crown ether. No synergistic enhancement for sodium or potassium was observed. Together these two results demonstrate the feasibility of an ion-exchange resin for the selective removal of lithium from dilute solutions.

Research Objectives

The objectives of this project were to develop the techniques, materials, and fundamental understanding necessary to solve difficult separations problems of the USDOE in the 21st century. The specific goals included developing new, powerful molecular modeling tools for ligand design, performing computational and structural studies to reveal fundamental properties of ligand-metal ion interactions, studying solvent extraction behavior to provide basic understanding of solution speciation and equilibria, and preparing new ion-exchange resins for the separation of metal ions of environmental significance to the USDOE. Contaminants of special interest included alkali and alkaline-earth metal ions, especially, lithium, cesium, and strontium. For example, Li^+ ions contaminate the groundwater at the Oak Ridge Y-12 Plant; Cs^+ and Sr^{2+} represent fission products in groundwater (e.g., INEEL, Hanford), stored waste (e.g., Savannah River Site, Hanford tanks), and process-water streams (e.g., ORNL).

Methods and Results

Due to the broad multidisciplinary nature of this project, a wide variety of experimental methods were used, including quantum mechanical calculations, molecular mechanics, single-crystal X-ray diffraction, Small Angle Neutron Scattering (SANS), high-resolution NMR spectroscopy, liquid-liquid partitioning, potentiometry, and radiotracer techniques, computational modeling of thermodynamic and equilibrium data, organic synthesis, and polymer synthesis. The experimental details are quite voluminous and are described in detail in the manuscripts listed in the publications section of this report. A summary highlighting the most important results of this work follows, with reference to the pertinent papers included. Some 18 publications and 35 presentations have resulted from this work so far, while several additional publications are in preparation.

<u>Molecular modeling and high performance computational studies</u>
(Hay, Dixon, Nicholas, Yang)

Initial modeling studies on calixarenes revealed that the MM and MD force fields (MM3, AMBER, and CHARMM) available in 1997 could not accurately reproduce the experimentally determined (NMR) conformational preferences of tetramethoxycalix[4]arene. Consequently, detailed, high-level quantum mechanical calculations were performed on tetramethoxy calix[4]arene and its complexes with sodium and cesium using the EMSL supercomputer facility. Because tetramethoxycalix[4]arene can be viewed as a cyclic tetramer of anisole bridged by methylene groups, a preliminary study on benzene and anisole (methoxybenzene) and their interactions with alkali metal cations was performed in order to obtain starting values for the parameterization of the MM3 force field for pi-cation interactions (Nicholas, Dixon, Hay, 1999; Nicholas and Hay, in press).

The results of these *ab initio* calculations included development of an MM3 parameter set (MM3+) to treat pi-cation interactions between alkali metal cations and uncharged arenes which was shown to reproduce observed M^+-C_{arene} distances to within ±0.2Å. Accurate reproduction of the preferred geometries of tetramethoxycalix[4]arene was achieved using non-local density functional theory (BLYP/6-31+G*), as shown in Table 1 (Nicholas, Bernholdt, Hay, submitted). These results were used, in turn, to optimize the MM3 parameters. The BLYP/6-31+G* results for the sodium and cesium complexes of tetramethoxycalix[4]arene reveal that the coordination

chemistry of the calix[4]arene scaffold is remarkably complex, providing valuable design criteria for structural modifications to enhance calixarene binding affinity for cesium. Comparison of the cesium calixarene structures with those of an isolated cesium anisole complex reveals that, irrespective of the binding mode, the calix[4]arene architecture does not provide optimal oxygen orientation with respect to the metal ion. These results suggest that altering the structure so that optimal orientation can be achieved may lead to significant increases in cesium binding affinity (binding energy increases of 4 – 8 kcal/mol) (Hay and Nicholas, submitted).

Table 1. Relative "Gas-Phase" Energies (Kcal/Mol) And Boltzmann Populations (%) Of Tetramethoxy-Calix[4]Arene Conformers At Various Levels Of Theory

Method[a]	Partial Cone	Cone	1,3 Alternate	1,2 Alternate
NMR ($CDCl_3$, 248 K)[b]	(70.4)	(29.6)	(0)	(0)
B3LYP/DZVP2	0.20 (72.5)	0.00 (27.5)	3.44 (0.04)	5.85 (0.00001)
BLYP/DZVP2	0.10 (76.4)	000 (23.5)	3.04 (0.04)	5.23 (0.0001)
MM3(96), O type 41[c]	0.00 (79.6)	0.24 (14.3)	1.10 (6.1)	4.05 (0.00001)
MM3(96), O type 6[d]	0.00 (84.9)	0.16 (12.9)	0.57 (2.2)	5.25 (0.001)
SYBYL[e]	0.00 (95.6)	0.82 (4.4)	2.91 (0.06)	3.33 0.001()
CHARMm[f]	0.00 (89.3)	1.81 (0.5)	0.38 (10.2)	5.51 (0.00001)
MINDO/d	0.69 (48.8)	2.67 (0.2)	0.00 (51)	3.36 (0.0001)
AMBER[g]	2.99 (0.8)	7.34 (0.0002)	0.00 (99.2)	4.29 (0.003)

a) Populations are calculated after correcting the energies for entropic terms arising from conformational and rotational degeneracies, i.e., $G = E + RT \ln(\sigma/n)$. Symmetry and σ/n values were as follows: partial cone, C_s, 1/8; cone, C_{2v}, 2/4; 1,3 alternate, D_{2d}, 4/2; 1,2 alternate, C_{2h}, 1/2. b) From K. Iwamoto, et. al., Tetrahedron, 1993, ***49***, 9937. c) Oxygen type 41 is recommended for conjugated ethers as described in Hay, B.P.; Yang, L.; Allinger, N.L.; Lii, J.-H. *J. Mol. Struct. (THEOCHEM)* **1998**, 428, 203. d) Relative energies are similar to those reported with MM3(92): cone, 0.27; partial cone, 0.00; 1,3 alternate, 1.50; 1,2 alternate, 4.10 kcal/mol (Harada, T.; Rudzinski, J. M.; Shinkai, S. *J. Chem. Soc. Perkin Trans. 2* **1992**, 2109). e) **SYBYL** as implemented in the MacSpartan Program. f) **CHARMm** Using parameters and partial charges from a prior calixarene study (van Hoorn, W.P.; Briels, W.J.; van Duynhoven, J.P.M.; van Veggel, F.C.J.M.; Reinhoudt, D.N. *J. Org. Chem.* **1998**, *63*, 1299). Relative energies are comparable to those reported for the para t-butyl analogue: cone, 3.3; partial cone, 0.6; 1,3 alternate, 0.0; 1,2 alternate, 6.3 kcal/mol. g) **AMBER** Using the default parameter set of AMBER4.1 with missing parameters and 6-31G* electrostatic potential charges from a prior calixarene study (Grootenhuis, P. D. J.; Kollman, P.A.; Groenen, L.C.; Reinhoudt, D.N.; van Hummel, G.J.; Ugozzoli, F.; Andretti, G.D. *J. Am. Chem. Soc.* **1990**, *112*, 4165-4176). Relative energies are comparable to those reported for the para t-butyl analogue**:** cone, 9.3; partial cone, 4.2; 1,3 alternate, 0.0; 1,2 alternate, 4.2 kcal/mol.

Molecular modeling (MM3+) studies on calix[4]arene crown-6 ethers provided important design criteria that was used to develop a new class of calix[4]arene crown-6 ethers which exhibit enhanced selectivity for cesium extraction (*vide infra*) (Sachleben, et. al., 1999). Modeling results suggested that replacement of two ether groups of a calix[4]arene crown-6 ether with hydrogens would increase the complementarity of the crown ether binding cavity for potassium and cesium cations. Synthetic and structural studies demonstrated the predictive accuracy of the MM calculations. The crystal structure of the cesium nitrate complex of calix[4]arene benzocrown-6 ether matches the conformation of the lowest energy structure predicted by MM for the calix[4]arene cesium complex nearly perfectly, despite the absence of any counter-ion (nitrate) in the computed structure, Figure 1 (Sachleben, et. al., manuscript in preparation).

a. b.

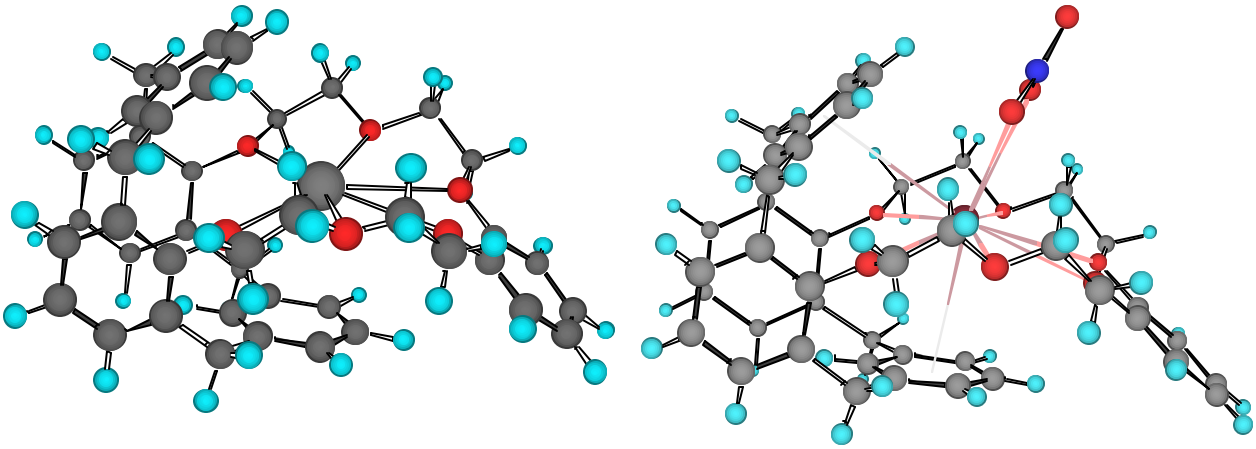


Figure 1. Comparison of a) the MM3+ predicted structure of dihydrocalix[4]arene benzocrown-6 complex with cesium and b) the experimentally determined (X-ray) structure of dihydrocalix[4] arene benzocrown-6 complex with $CsNO_3$.

Further MM Studies of dimethoxy calix[4]arenes suggested that substituents para to the methoxy groups would influence the distance between, and the orientation of, the ether oxygens, with larger groups preorganizing the ethers for cation binding. Subsequent synthetic and extraction studies indeed revealed an increase in cation extraction by calix[4]arene crown ethers as the size of the *p*-substituent increased fom H to *n*-butyl to *t*-butyl, consistent with a increasing predisposition for cation binding by the crown ether oxygens.

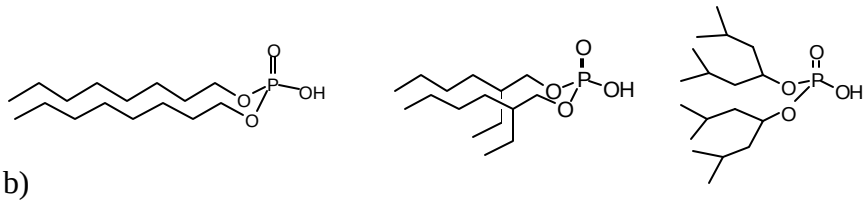
In an effort to bring MM methods to bear on predicting the role of extractant structure in synergistic extractions using crown ethers and lipophilic ion-exchangers, such as dialkyl phosphoric acids, density-functional theory calculations were performed on the dimethyl derivatives of phosphinate, phosphonate, and phosphate and their complexes with Li^+, K^+, Mg^{+2}, and Ca^{+2}. A set of MM3 parameters for these functional groups was developed for use in modeling the interactions of crown ether complexes of metal cations with coordinated $R_2PO_2^-$ anions. Molecular modeling of crown ether complexes with alkaline-earth cations demonstrated a linear relationship between ligand strain and synergistic extraction efficiency (Figure 2) (Hay, 1999; Dietz, et. al., 1999).

<u>Cesium extraction by calix[4]arene crown ethers</u>
(Moyer, Bryan, Engle, Haverlock, Urvoas, Sachleben)

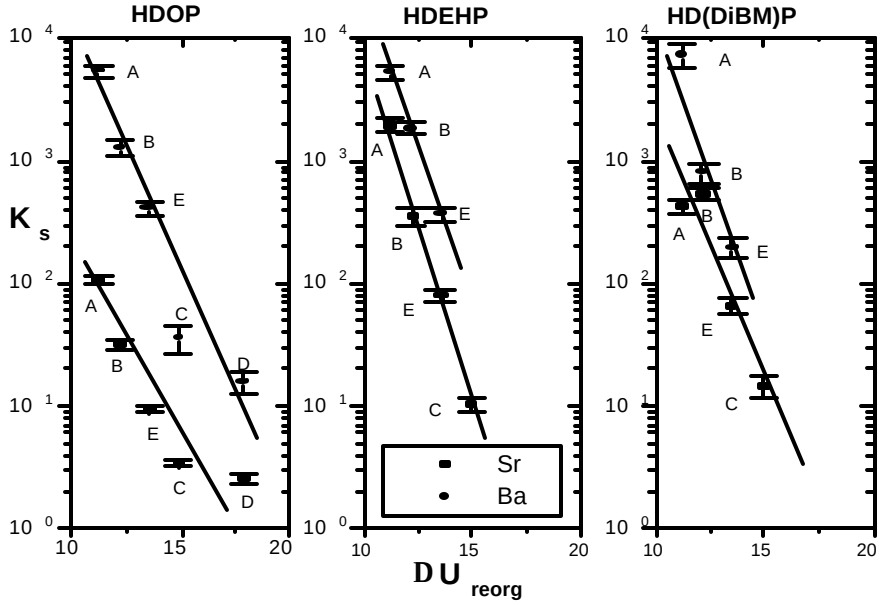
The remarkable cesium extraction properties of calix[4]arene crown ethers provided the impetus to investigate the structural and thermodynamic properties of these compounds and their cation complexes. Detailed studies on the extraction of alkali metal cations by a lipophilic calix[4]arene biscrown ether (BOBCalixC6, Figure 3) in 1,2-dichloroethane (DCE) allowed the determination of precise speciation equilibria for this system (Figure 4a) (Haverlock, et. al., 2000). Of particular significance was the determination that dissociation of nitrate from the cesium-calixcrown complex in the organic phase had a profound impact on the distribution of cesium between the organic and aqueous phases. Specifically, at low cesium nitrate concentrations, dissociation of the nitrate from the cesium-calixcrown complex resulted in an increase of the distribution coefficient for cesium and decreased stripping efficiency. This result proved directly applicable to solving the stripping problem encountered in the calixarene-based

cesium extraction process (Alkaline-Side CSEX) being developed under the EM50 Efficient Separations and Crosscutting program for application at the Savannah River Site (as an alternative to in-tank precipitation with tetraphenylborate). Utilizing the fundamental chemical understanding of the extraction process provided by this EMSP program, a solution to the stripping problem of the CSEX process was developed which resulted in a more practical and robust flowsheet. The solution entailed suppressing the putative ion-pair dissociation in the organic phase by ensuring that the organic-phase ionic strength cannot fall below a certain threshold (nominally 2 x 10^{-6} M). This was at first accomplished by stripping with an aqueous solution containing a preset $CsNO_3$ concentration (1 x 10^{-4} M). A preferred method involves addition of trioctylamine to the process solvent containing calixarene (BOBCalixC6), process modifier, and kerosene. The formation of the trioctylammonium nitrate salt in the organic phase on contact with the acidic stripping solutions suppresses dissociation of the nitrate from the calixarene-cesium complex, increasing the efficiency of stripping.

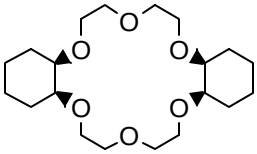
a) Dialkyl Phosphoric Acids



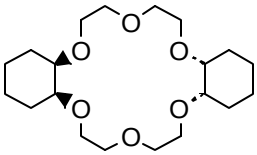
b)



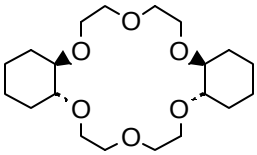
c) DCH18C6 Isomers



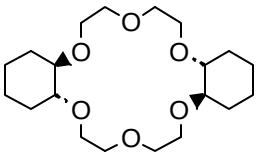
A: *cis,syn,cis*



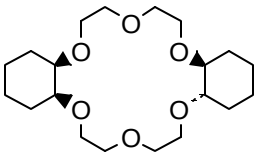
B: *cis,anti,cis*



C: *trans,syn,trans*



D: *trans,anti,trans*



E: *cis,trans*

Figure 2. a) Structures of dialkyl phosphoric acids used in this study. b) Correlation of synergistic equilibrium constant, K_s, with ligand reorganization energy, ΔU_{reorg}, for DCH18C6 isomers. c) Structures of DCH18C6 isomers used in this study.

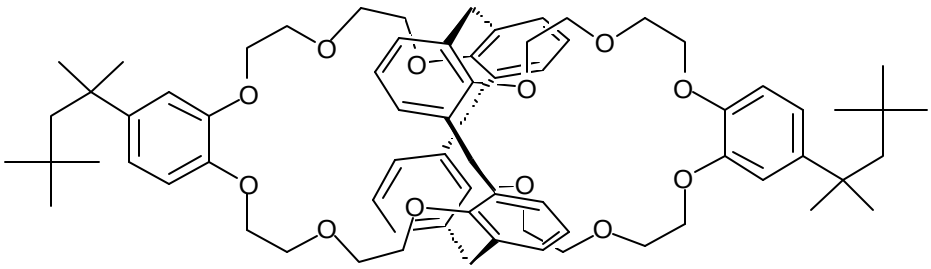


Figure 3. Calix[4]Arene Bis-*t*-OctylBenzocrown-6, **BOBCalixC6**.

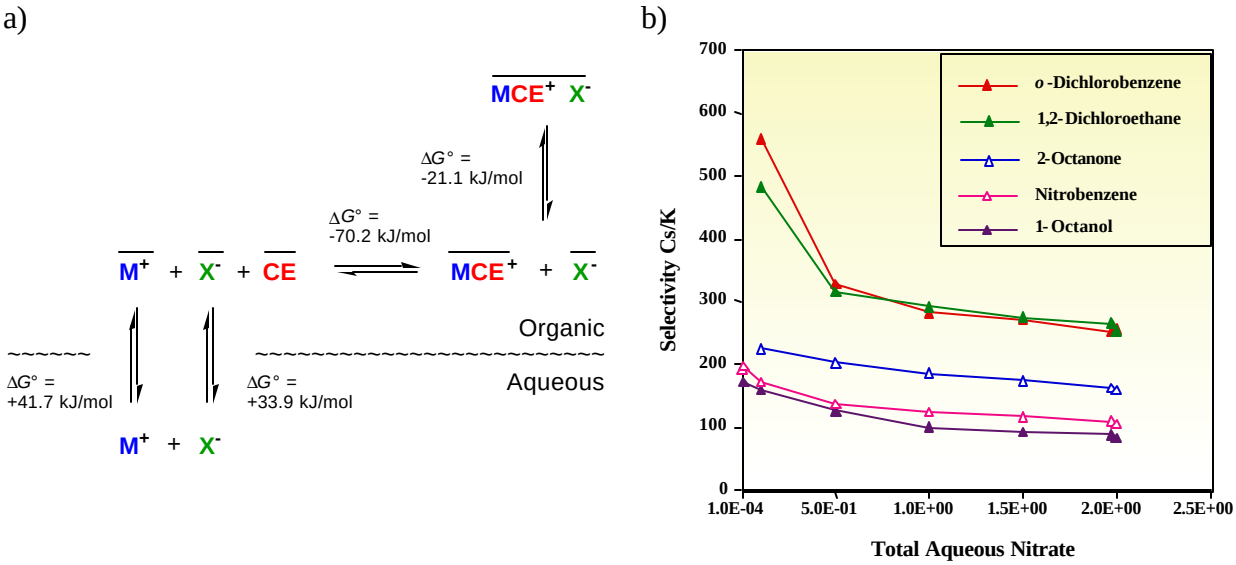


Figure 4. a) Equilibria for cesium nitrate and potassium nitrate extraction and ionization in the 1,2-dichloroethane; only 1:1 complexation is shown. Thermodynamic data are for cesium nitrate extraction by BOBCalixC6 in DCE at 25 °C. b) Effect of increasing potassium nitrate on cesium/potassium selectivity in different solvents.

A second consequence of these detailed equilibrium studies was the demonstration that cesium extraction efficiency and selectivity were strongly influenced by competitive extraction of potassium at low cesium/potassium ratios (Figure 4b). Again, dissociation of ion-pair extraction complexes in the organic phase played a key role; in this case, the co-extraction of potassium nitrate suppressed dissociation of the cesium nitrate complex, reducing both the distribution coefficient for cesium and the cesium/potassium selectivity. Detailed synthetic and structural investigations were undertaken to develop calix[4]arene crown ethers with enhanced cesium/potassium extraction selectivity. Utilizing single crystal X-ray diffraction structural studies and molecular modeling (*vida supra*), a new class of calix[4]arene crown ethers derived from dihydrocalix[4]arene was developed (Figure 5). Over two dozen new calix crowns were synthesized and structurally characterized. Enhanced cesium/potassium and cesium/rubidium selectivities were obtained; the best compound in this series exhibits a cesium/potassium selectivity exceeding 4000, a ten-fold improvement over previously studied calixcrowns, and a cesium/sodium selectivity exceeding 1 million!

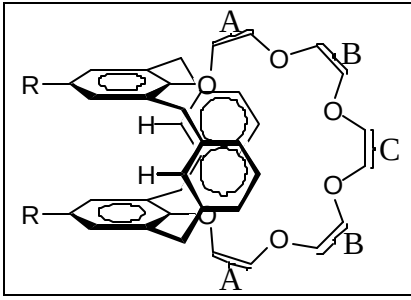
	R = H, *n*-Butyl, *i*-Butyl, *t*-Butyl, *t*-Heptyl A = ethylene, benzo, 4-nitrobenzo B = ethylene, benzo C = ethylene, benzo

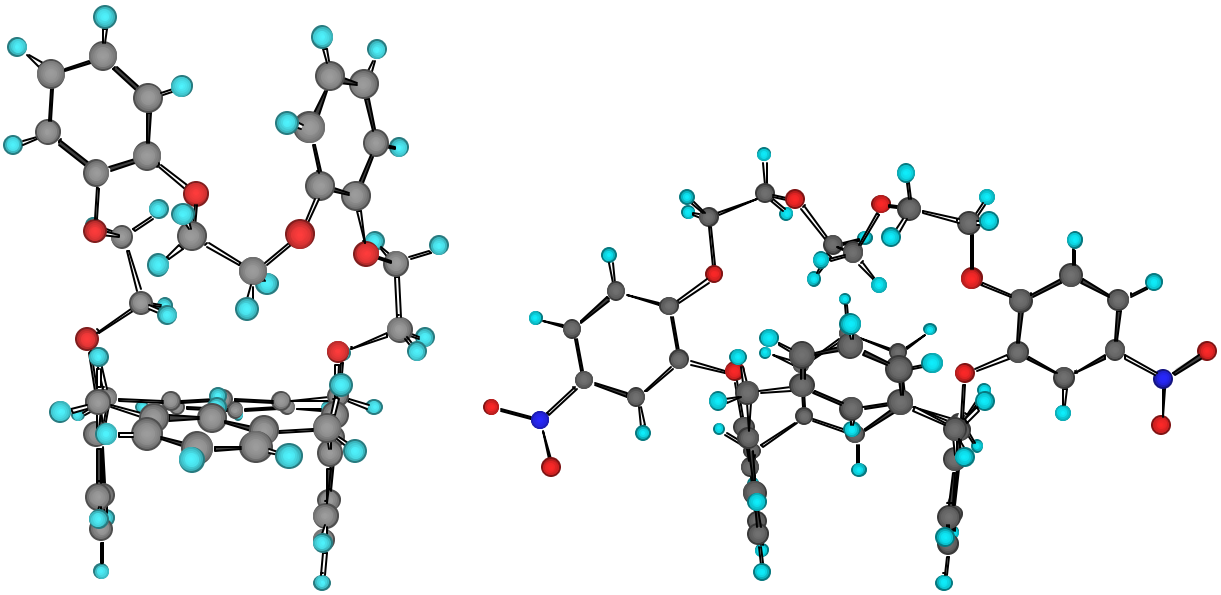
Figure 5. New crown-6 ethers derived from dihydrocalix[4]arene.

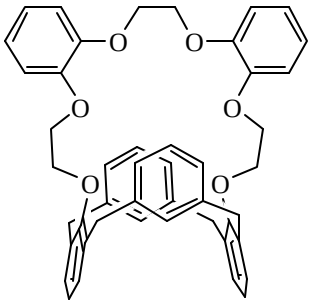
Key to the development of an efficient and more cesium-selective calixarene crown ether, the single-crystal X-ray diffraction studies revealed a potential source for the marked effect that the calixarene substituent has on the complexing ability of crown ethers. Whereas previously the interaction of the complexed cesium ion with the benzene rings of the calixarene (π-cation interactions) had been proposed as contributing to the unique properties of calix-crowns, these studies suggest that preorganization and orientation of the crown ether oxygens play a significant role in determining the complexing strength of calix[4]arene crown-6 ethers. Utilizing the insight gained from the X-ray crystal structure studies and molecular modeling (*vide supra*), the first example of a calix[4]arene crown ether bearing benzo substituents directly attached to the calixarene oxygens was synthesized. The crystal structure revealed that the calixarene ether oxygens were indeed preorganized for cation complexation, and solvent-extraction studies showed that this compound exhibited stronger and more selective cesium extraction than its isomer with the benzo groups located more distant from the calixarene (Figure 6).

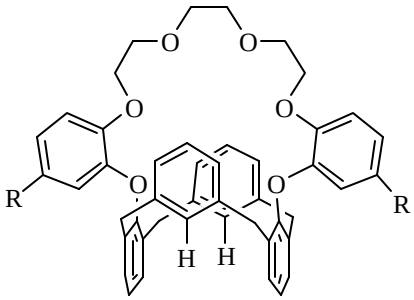
The development of calix[4]arene crown ethers with enhanced cesium selectivity had a significant impact on the development of cesium selective fluorescent sensors (G. M. Brown and R. Dabestani, EMSP project OR17SP23-3THN). It had previously been shown that a calix[4]arene benzo crown ether bearing a fluorescent pendant group exhibited 8-fold enhanced fluorescence in the presence of cesium nitrate. While little or no response was observed for lithium or sodium, the moderate response to potassium indicated that competition to large amounts of potassium relative to cesium might prove problematic for sensor applications. A new calix-crown chemosensor (Figure 7) was developed through a collaboration between these two EMSP projects. The sensor exhibited not only enhanced cesium selectivity, but more significantly, enhanced cesium sensitivity. The fluorescence response in the presence of cesium exceeded 50-fold. Utilizing the insights revealed by our single crystal X-ray diffraction studies, this sensitivity enhancement could be rationalized in terms of a displacement of the cesium ion away from the calixarene moiety and towards the oxygens of the benzo substituent.. Stronger interaction with these oxygens decreased fluorescence quenching resulting in enhanced fluorescence. Further investigations (under OR17SP23-3THN) are underway to incorporate this new chemosensor into a cesium detector.

<u>Synergistic extraction of group II cations by crown ethers and organophosphorus acids</u>
(Dietz, Bond, Chiarizia, Herlinger, Huber, Thiyagaran, Urban)

The potential for enhanced separations utilizing synergistic combinations of crown ethers and organophilic acids will benefit significantly from a thorough evaluation of the structural







D_{Cs} : 2.15 R = H D_{Cs} : 30.9

$S_{Cs/K}$: 2090 $S_{Cs/K}$: 4220

Figure 6. Crystal structures of dihydrocalix[4]arene dibenzocrown-6 ethers with their associated cesium perchlorate distribution coefficients (D_{Cs} = $[Cs]_{organic}/[Cs]_{aqueous}$) and cesium/potassium selectivites ($S_{Cs/K} = D_{Cs}/D_K$).

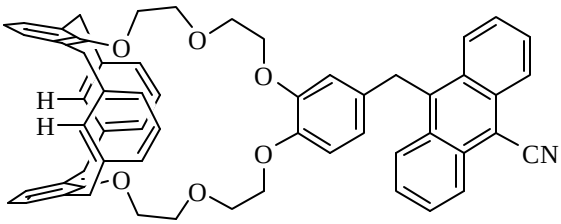


Figure 7. Cesium-sensitive dihydrocalix[4]arene benzocrown-6 chemosensor.

principles underlying these systems. Specifically, understanding the relationships between the structure of the crown ether and the dialkyl phosphoric acid as they effect speciation and extraction equilibria is critically important for establishing rational design criteria for these systems. Detailed investigations on the extraction of calcium, strontium, and barium by five

different isomers of dicyclohexano-18-crown-6 (DCH18C6) and three different dialkylphosphoric acids demonstrated that strontium and barium extraction are strongly enhanced (synergized) by addition of the crown ether, while the synergistic effect is negligible for calcium extraction (Fig. 8). Molecular modeling results demonstrate that the synergistic extraction enhancement correlates with the ligand reorganization energy of the crown ethers (*vide supra*, Fig. 2), while the steric factors related to the branching of the alkyl chains of the dialkylphosphoric acid play a more limited role. Critical to the success of these studies was the availability of the different DCH18C6 isomers (Fig. 2c). Viable methods for the synthesis of isomers C and D, in particular, were developed.

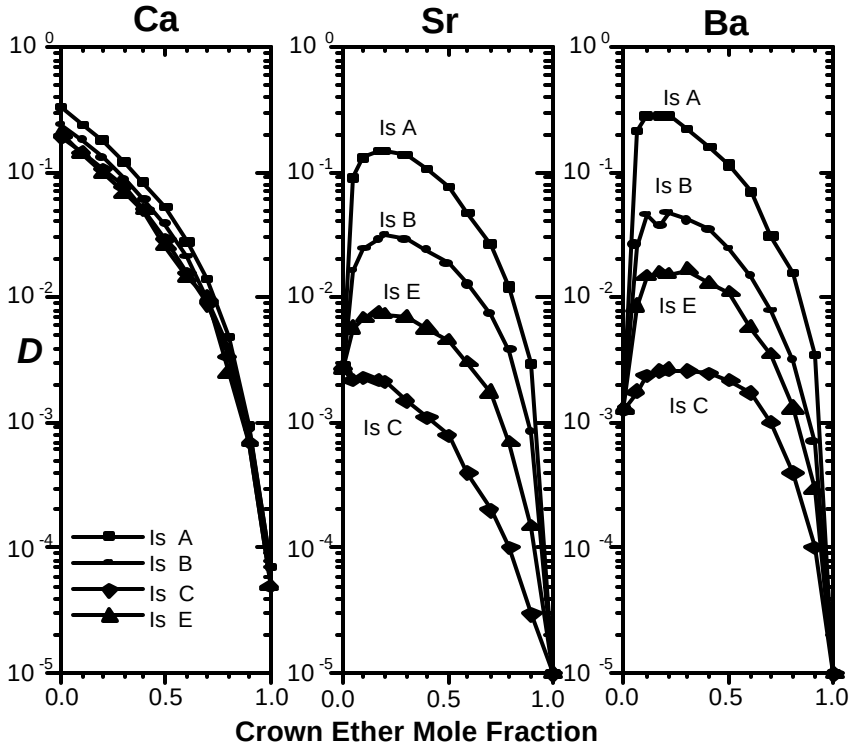


Figure 8. Continuous variation plots for the HDOP-CE system. [HDOP]+[CE] = 0.1 M in toluene; $[HNO_3]$ = 0.01 M; $[M(NO_3)_2]$ = 0.001 M

Equilibrium modeling of cation extraction as a function of varying pH and crown ether mole fraction revealed that speciation is similar for these systems with the predominant extracted species being of the form $M(DCH18C6)(HA_2)_2$, where two dialkylphosphoric acid dimers are associated with one metal cation complexed by one crown ether. Small angle neutron scattering (SANS) experiments support the speciation model obtained from the extraction data. The dialkylphosphoric acids were shown to form dimers in nonpolar diluents (toluene), consistent with previous studies. Addition of DCH18C6 did not alter the dimerization of HDOP in toluene. SANS studies of solutions produced by extracting strontium by HDOP in toluene suggests that the predominant species are of the form $Sr(H(DOP)_2)(HDOP)_2$, consistent with the conclusions made at low (tracer) strontium loading. However, larger aggregates are also present at high

strontium loading. Addition of DCH18C6 suppresses the formation of the larger aggregates, while forming predominantly $Sr(DCH18C6)(H(DOP)_2)_2$. Interestingly, the *cis-anti-cis* isomer, which is the weaker synergist for strontium extraction, appears to be more effective in suppressing aggregation than the *cis-syn-cis* isomer. Although the origin of this effect has not been definitively established, steric differences between the two crown ether isomers may reasonably be considered to play a role in the relative stability of the discrete $Sr(DCH18C6)(H(DOP)_2)_2$ complexes, a proposition consistent with currently available solution and structural data.

Synergistic crown ether extraction and ion-exchange systems for lithium
(Moyer, Alexandratos, Haverlock, Salo, Sachleben)

The effort to develop a lithium-selective ion-exchange resin for application to the groundwater-contamination problem at the Oak Ridge Y-12 site has made progress on two fronts. Strong, synergistic lithium extraction was demonstrated using a new lipophilic sulfonic acid in combination with the lithium-selective crown ether NM14C4 developed previously at ORNL. Lithium was extracted quantitatively from a solution of alkali metal nitrates with high selectivity over Na and K. This synergistic approach to lithium separation was utilized to prepare a solvent-impregnated resin (SIR). Impregnation of strong acid cation-exchange resin with NM14C4 provided a material that removed lithium effectively from an aqueous solution with negligible uptake of competing sodium or potassium. These results demonstrate the feasibility of using a crown ether modified IX resin for selective lithium sorption from dilute sources.

Moving towards direct incorporation into a bifunctional, lithium-selective ion-exchange resin, the lithium-selective crown ether was covalently bonded to a poly(glycidyl methacrylate) resin. This resin exhibited rapid and quantitative uptake of lithium, even in the presence of a large excess of sodium. This development demonstrates that the lithium selectivity of the crown ether remains viable when immobilized on a resin and that the inherent hydrophilicity of the support permits rapid uptake, despite the inherent hydrophobicity of the parent crown ether. Further elaboration of these developments into a practical, lithium-selective ion-exchange resin may provide important technologies for monitoring and remediation of lithium contamination at the DOE Y-12 site.

Relevance, Impact, and Technology Transfer

Major success achieved in addressing problem at the Savannah River Site

This work has assisted in the development of a technology that is currently being tested at the Savannah River Site toward implementation in a billion-dollar plant to remove cesium from high-level waste. Events leading to the current testing program are described below in the Transitions section, and the science is described above in the Methods and Results section. Here we provide more background on the problem itself and how the fundamental results from this EMSP task contributed to the development of a new technology.

Removal of cesium from high-level tank waste, such as that stored at the U.S. Department of Energy (DOE) Savannah River Site (SRS) and Hanford site, continues to be a challenging problem. Difficulties with benzene emissions owing to premature decomposition of cesium tetraphenylborate precipitate in the In-Tank Precipitation process [1] have led to an intensive search for alternative technologies to accomplish the cesium separation [2]. Three

technologies were selected out of approximately 140 considered in 1998 [2]. One of these alternatives was the alkaline-side cesium solvent-extraction (CSEX) process developed recently at the Oak Ridge National Laboratory (ORNL) [3]. This process makes use of an advanced type of extractant that is a hybrid of a crown ether and calixarene. First reported by European groups [4-6], such compounds are generally called calixcrowns. As a result of the EMSP research described above, our knowledge of the organic synthesis of calixcrowns has been improved and expanded. The extraordinary selectivity and strength of calixcrowns makes it possible to remove cesium from concentrated nitrate media, the most exciting potential application being nuclear waste, as recognized immediately by the Europeans in membrane experiments [4-6]. Our first experiments conducted under funding from the EM-50 Efficient Separations and Processing (ESP) Crosscutting Program (TTP = OR16C341) in 1998 confirmed the high selectivity but revealed that much work would be needed to develop a practical solvent-extraction (SX) technology [7]. With the understanding of extraction equilibria provided under this EMSP research [8], a first-generation cesium solvent extraction technology (alkaline-side CSEX) was successfully developed and tested, again under ESP funding [9-12]. It was concluded that the alkaline-side CSEX process meets the requirements for the removal of cesium from SRS high-level waste and is economically competitive with the alternative nonelutable ion-exchange and precipitation technologies [2,13,14]. However, owing to the relative immaturity of the alkaline-side CSEX process coupled with the demanding schedule for implementation, the process was not selected in 1998 to proceed with higher-scale development and testing. Under funding by the ESP Crosscutting Program, however, the major chemical issues of stability and susceptibility to impurity effects were successfully dealt with in 1999 [12,15,16]. Again, insight on extraction equilibria gained in this EMSP research proved critical in designing the second-generation solvent system [12,16]. Based on the performance data for this second-generation solvent system, a conceptual flowsheet was calculated, meeting the SRS requirements in 22 stages [12,16]. A vigorous testing program at the SRS, ORNL, and ANL is now under way.

General Relevance

This task relates to the USDOE's environmental needs through building an understanding of basic factors governing the design, synthesis, and characterization of the next generation of crown ethers for metal-ion separations. 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 the Hanford Site, Idaho National Engineering and Environmental Laboratory, and the Savannah River Site; and radium in wastes at the Niagara Falls Storage Site. At the outset of this work, the technologies needed to address these problems either did not exist or exhibited substantial deficiencies. Based partly on the progress described above, 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.

Nuclear waste and environmental contamination pose special generic challenges to separation science and technology. Whether the objective entails removing contaminant ions from complex salt or acid wastes or from groundwater, for cleanup or analysis, the dissolved contaminants are often found at trace concentrations. Other salts, especially sodium salts, may easily be a factor of 10^6 or higher in concentration. Thus, a major generic issue arising is: How can one attain the required extreme selectivity for target ions? Such a question poses a difficult test of the principles of molecular recognition and host-guest chemistry as well as of the principles of solvent extraction. As described in the Methods and Results section, this EMSP

research contributed in a general way toward a theoretical understanding of the binding of alkali and alkaline-earth metal cations by crown ethers and calixarenes. Synthesis and testing of candidate compounds at ORNL led to a series of new compounds having significantly higher selectivity for cesium. Selective synergism was demonstrated for strontium and barium in combining crown ethers with organophosphorous acids.

One of the major generic problems in the application of selective crown ethers and calixarenes has been the fact that these neutral extractants require co-transfer of an anion; that is, an ion pair is transferred from the aqueous to the organic phase [17-19]. Although the crown compounds accommodate the cation, the anion remains largely solvated by the organic diluent or polymer matrix. The resulting unfavorable thermodynamics associated with anion transfer causes weak extraction, and the polar nature of the complex requires the use of polar diluents. Under this EMSP research, the thermodynamic steps for extraction of cesium nitrate by a calixcrown were determined, illustrating the key role that anion solvation plays in the overall driving force of extraction [8]. It was also shown how a synergistic approach avoids altogether the anion-solvation issue.

Although many of the same contaminants are found in other types of wastes and environmental streams, the applicability of crown ethers has been targeted mostly at treatment of high-level waste. In view of the desirable selectivity of crown compounds, alternate means of employing them, such as attachment to polymeric materials, could pave the way to expanded application such as groundwater remediation. As mentioned above, strides made in this EMSP research have been made in attaching a lithium-selective crown ether to a polymer support. Selective lithium uptake was observed.

Project Productivity

Significant accomplishments were made in every area of this project as described above. Specific goals achieved include:

- Parameterization of Molecular Mechanics force fields for use in modeling calixarenes, crown ethers, and alkylphosphorus acids.
- Application of High Level Quantum Mechanical calculations to ligand design.
- Solution modeling of calixarene and crown ether extraction systems to elucidate fundamental chemical principle underlying solvent extraction in general and specific solvent extraction systems of interest to DOE.
- Solid state and solution structural studies to determine the structural parameters that influence extraction strength and selectivity.
- Demonstration that strontium and barium extraction are strongly enhanced (synergized) by addition of a crown ether to organophosphorous acids.
- Design and synthesis of the next generation of calix[4]arene crown ethers for cesium separation.
- Development of new synthetic methods for the preparation of calixarenes, crown ethers, and ion-exchange reagents for use in the next generation of enhanced separations systems.
- Immobilization of calixarenes and crown ethers on polymeric supports and demonstration that such systems exhibit selective and effective uptake of target cations.

The project proceeded on schedule, and project objectives were achieved in a timely manner. A six-month no-cost extension was obtained to accommodate subcontracting to the

University of Tennessee and to allow project management to close out the project and prepare reports. In general, the work plan proceeded as proposed. Modifications of specific targets were made in response to the knowledge gained from the experimental results in accordance with the natural flow of basic research.

Personnel Supported

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Publications

Peer-Reviewed Journal Article Featured on Journal Cover

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Interactions

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J. B. Nicholas and B.P. Hay, "A Theoretical Study of Alkali Cation Complexes with Tetramethoxycalix[4]arene", Northwest Regional American Chemical Society Meeting, Richland, Washington, June 17, 1998.

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Consulting and advising

Customer #1: USDOE Independent Project Evaluation Committee for cesium-removal technology selection for high-level tank waste at the Savannah River Site.

Objective: Ensure that the committee has the current information on the alkaline-side CSEX process and that visibility remains high for possible testing at the Savannah River Site.

Activity description: Provided members of this team with information concerning the process and its performance. This activity was primarily conducted under the auspices of the EM-50 Efficient Separations and Crosscutting Program, but this EMSP project had direct input into the development of CSEX.

Result: The committee recommended that the process be demonstrated at the Savannah River Site.

Timeframe of activity: 1999.

Customer #2: National Academy of Sciences, National Research Council Committee on Salt Disposition at the Savannah River Site.

Objective: Supply the committee with data needed for its report to the USDOE Under Secretary Knotek.

Activity description: Provided members of this team with information concerning the Alkaline-Side CSEX process and its performance. B. A. Moyer participated in the NRC review meeting held in Sept., 1999, and P. V. Bonnesen gave a presentation in Nov., 1999. In Jan. and Mar., 2000, detailed written answers were provided to questions asked by the committee. Again, the Efficient Separations and Processing Crosscutting Program led this activity.

Result: The information was incorporated into a WSRC report: B. A. Moyer, P. V. Bonnesen, and R. A. Leonard, "SRS High-Level Waste Salt Disposition Responses to NRC Questions of 1-11-00," Report HLW-SDT-2000-00024, R1, Westinghouse Savannah River Company, Aiken, SC, Jan. 27, 2000; pp. 23-30. The NRC committee has not yet issued its final report based in part on this information.

Timeframe of activity: 9/99 to 3/00.

Collaborations

The EMSP project described in this report was, in fact, a large collaboration and has been amply discussed above. The development of calix[4]arene crown ethers with enhanced cesium selectivity had a significant impact on the development of cesium selective fluorescent sensors (G. M. Brown and R. Dabestani, EMSP project OR17SP23-3THN). As described above, a new calix-crown chemosensor (Figure 7) was developed through a collaboration between these two

EMSP projects. A collaboration between the ANL group under the leadership of M. L. Dietz and Loyola University, Chicago was highly productive in revealing the nature of aggregation behavior in synergistic extraction systems containing crown ethers and organophosphorous acids.

Transitions

Fundamental extraction experiments conducted in this EMSP project helped researchers design a process flowsheet for cesium removal from the high-level tank waste stored at the Savannah River Site. Under funding by the EM-50 Efficient Separations and Processing (ESP) Crosscutting Program (TTP = OR16C341), fundamental information obtained in the above-named EMSP project was used by B. A. Moyer and co-workers at ORNL and ANL in the design of a process flowsheet for cesium removal from alkaline tank waste. The information concerned the fundamental thermodynamics of extraction of cesium nitrate by a novel calixarene extractant under very ideal conditions (see above). More specifically, the extraction information dealt with the mechanism of extraction, its dependence on aqueous conditions, and the selectivity for cesium vs. potassium, a key competing ion. In the experiments, the calixarene exhibited strong and extremely selective extraction of cesium nitrate. Actual process development was performed under ESP funding toward adapting the process flowsheet to the high-level waste (HLW) at the Savannah River Site (SRS). The proposed flowsheet was presented to SRS engineers in June, 1998, and it was chosen as one of 4 technologies (out of an original list of 140 technologies) to undergo further testing in the latter third of FY 1998. Additional funding for this testing was provided by the SRS. In the testing, partly conducted at ANL and the SRS, it was shown that this first-generation flowsheet was capable of meeting the challenging needs for decontaminating the SRS HLW. However, in view of the very tight schedule at the SRS, it was subsequently judged that the new calixarene-based extraction technology was insufficiently developed to warrant further investment by the SRS. In the meantime, a second-generation flowsheet with much improved performance was drafted based on further input from this EMSP project. Owing to schedule modifications, the SRS has in FY 2000 concluded that the solvent-extraction process should be examined again, and approximately $4M in EM-40 funds have been allocated in FY 2000 to test and demonstrate the process. To be conducted at ONRL, ANL, and the SRS, the tests will involve a 32-stage centrifugal-contactor demonstration, batch tests with real waste, radiation-stability experiments, and other studies. In FY 2001, the project is expected to be directed under the auspices of the Tanks Focus Area through a final down-selection among the three alternative technologies in the spring of FY 2001.

Patents

No inventions are directly attributable to this research. One patent application and an invention disclosure that will be converted to another patent application in the near future are associated with the Alkaline-Side CSEX process. However, these inventions are more properly identified with the EM-50 Efficient Separations and Crosscutting Program that funded the collection of the corresponding development data. As summarized above, the present EMSP project provided fundamental data that enabled the successful reduction of the inventions to practice.

Future Work

Major questions remain to be addressed in molecular modeling, synthesis, extraction equilibria, and polymer synthesis. Through follow-on proposals, many of these questions will likely be pursued further, and the progress made herein represents a valuable foundation of fundamental information. For example, further model building is expected to lead to greater ability to understand and predict how calixarene derivatives such as calixcrowns bind to metal cations. It is envisioned that with improved models, ligands could be "built" by connecting suitable donor groups for a given metal cation with suitable organic connecting groups. Synergistic extraction offers many possibilities in employing neutral crown ethers and calixarenes for metal ion extraction by imposing a cation-exchange mechanism. However, the combination of two extractants leads to additional complexity that must be understood. Likewise, the equilibria in the extraction of cesium by calixcrowns as applied to high-level waste involve complexity when solvating alcohols and amines are added for process purposes. Additional work is needed to understand such equilibria in order to bring new processes to maturity. As for attachment of crown ethers to polymer backbones, the knowledge gained herein presents many possibilities for synthesis of myriad new ion-exchange resins.

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