NEW PROTON-IONIZABLE, CALIXARENE-BASED LIGANDS
FOR
SELECTIVE METAL ION SEPARATIONS

FINAL SCIENTIFIC REPORT
FOR THE PERIOD OF
JANUARY 1, 1994 – DECEMBER 31, 2011

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MAY 2012

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER GRANT NUMBER DE-FG02-9414416

A. Executive Summary

The project objective was the discovery of new ligands for performing metal ion separations. The research effort entailed the preparation of new metal ion complexing agents and polymers and their evaluation in metal ion separation processes of solvent extraction, synthetic liquid membrane transport, and sorption. Structural variations in acyclic, cyclic, and bicyclic organic ligands were used to probe their influence upon the efficiency and selectivity with which metal ion separations can be performed. A unifying feature of the ligand structures is the presence of one (or more) side arm with a pendent acidic function. When a metal ion is complexed within the central cavity of the ligand, ionization of the side arm(s) produces the requisite anion(s) for formation of an overall electroneutral complex. This markedly enhances extraction/transport efficiency for separations in which movement of aqueous phase anions of chloride, nitrate, or sulfate into an organic medium would be required. Through systematic structural variations, new ligands have been developed for efficient and selective separations of monovalent metal ions (*e.g.*, alkali metal, silver, and thallium cations) and of divalent metal ion species (*e.g.*, alkaline earth metal, lead, and mercury cations). Research results obtained in these fundamental investigations provide important insight for the design and development of ligands suitable for practical metal ion separation applications.

B. Background

DOE-BES funding for the earliest stage of this research effort was initiated in 1980 with studies of “Metal Ion Complexation by Ionic Crown Ethers” in 1980-1983. Financial support was continued to investigate “Metal Ion Complexation by Ionizable Crown Ethers” in 1984-1990, “Metal Ion Complexation by Proton-Ionizable Crown Ethers” in 1991-1992, and “Metal Ion Complexation by Lariat Ethers and Their Polymers” in 1993. At the end of 1993, a ‘final’ scientific report was requested by DOE-BES summarizing results obtained for the period of 1980-1993. That report was prepared and submitted.

During these earlier funding periods, series of proton-ionizable cyclic and acyclic polyether ligands were prepared and their utility in the separation of alkali metal, alkaline earth metal, and some heavy and transition metal cations was assessed. Compared with non-ionizable polyether analogues, these novel complexing agents offer a special advantage that movement of the metal

cation from an aqueous phase into an organic phase in a solvent extraction or liquid membrane transport process does not require concomitant transfer of an aqueous phase anion. This factor is of immense importance for potential practical metal ion separation schemes in which the aqueous phase anions would be the commonly encountered, hard, hydrophilic, anionic species of chloride, nitrate, or sulfate.

Proton-ionizable polyethers possess the additional advantage of being ‘switchable’. Thus in a solvent extraction process, contact of the separated organic phase that contains the ionized polyether-metal ion complex with aqueous mineral acid protonates the ionized group(s) and efficiently strips the metal ions into a new aqueous phase for recovery. When proton-ionizable polyethers are employed as metal ion carriers for transport across organic liquid membranes, movement of the metal ions from the aqueous source phase through the membrane and into the aqueous receiving phase is coupled with back-transport of protons. In this case, proton-coupled transport can be employed to transport metal ions against their concentration gradients from an aqueous source phase through an organic liquid membrane and into an aqueous receiving phase.

For cyclic polyethers with pendant side arms containing acidic functions (*i.e.*, proton-ionizable lariat ethers), the selectivity and efficiency of metal ion complexation was found to be influenced by the: i) polyether ring size; ii) substitution pattern and symmetry of the polyether ring; iii) attachment of alkyl or aryl groups to the polyether ring; iv) presence or absence of benzo group substituents on the polyether ring; v) attachment site(s) for lipophilic group(s); vi) number of carbon atoms in the lipophilic groups(s) and their arrangement (linear or branched); vii) identity of the proton-ionizable group; and viii) length of the side arm that connects the pendant acidic group to the crown ether ring.

In this earlier work, the effects of systematic structural variations in the extractants were conducted with acyclic and cyclic polyether carboxylic acids, phosphonic acids and their monoalkyl esters, phosphinic acids, and sulfonic acids. More recently, the investigations have been expanded to include a new acidic function, the *N*-(X)sulfonyl carboxamide group, $C(O)NHSO_2X$, in which the acidity can be ‘tuned’ by changing the electron-withdrawing ability of X.

For 1994-1998, the title of the funded project continued as “Metal Ion Complexation by Lariat Ethers and Their Polymers”. The synthesis of new proton-ionizable acyclic polyethers

(podands) and cyclic polyethers (lariat ethers) with systematic structural variations and their evaluation in metal ion separations continued.

Then attention was shifted to the use of calix[4]arene as a scaffold for the preparation of new proton-ionizable ligand series and evaluation of their properties in metal ion separations, primarily solvent extraction. Structural features of calix[4]arene make it a more versatile scaffold for the design and preparation of cyclic ligands with multiple pendant proton-ionizable groups (see below).

For the period of 1999-2011, the project was identified as “New Proton-Ionizable, Calixarene-Based Ligands for Selective Metal Ion Separations.” During the period of 1994-2011 covered by this final report, a total of 88 publications appeared. Primarily these were articles in chemistry and separation science journals and reported original findings. Also included were several monograph chapters and short reviews in which results obtained in the research project were summarized.

C. Results and Discussion

1. Perspective and Initial Results

In calix[4]arene (**1**), four phenolic units are connected with four methylene groups to form a macrocyclic structure. In **1**, the four aryl groups of calix[4]arene form the upper rim and the four phenolic hydroxyl groups are situated on the lower rim. The phenolic oxygens provide convenient sites for side arm attachment. By an appropriate combination of alkyl groups and side arms bearing acidic functions, calix[4]arenes with one, two, three, and four pendant proton-ionizable groups may be realized providing potential ligands for complexation of mono-, di-, tri-, and tetravalent metal ions, respectively. (Note that the synthesis of crown ethers with multiple acidic side arms is much more difficult synthetically.)

Since the earlier phases of this research dealt primarily with mono-ionizable lariat ethers and their application in the separation of alkali metal cation species, attention was now focused largely on di-ionizable calix[4]arene ligands for complexation of divalent metal ions.

Our initial investigation of metal ion separations by di-ionizable calix[4]arene ligands involved solvent extraction of divalent metal cations from aqueous solutions into chloroform by compounds **2b-e**.¹ For this series of *N*-(*Z*)sulfonyl carboxamide ligands, the acidity increased

as the electron-withdrawing power of Z was enhanced, **2b**, **2c** < **2d** < **2e**. Very exciting results were obtained.¹ Efficient extraction of Pb²⁺ from nitric acid solutions into chloroform was observed. For **2b-e**, the extraction efficiency was found to increase with enhanced acidity of the extractant compound. *Ligand 2e gave quantitative Pb²⁺ extraction from aqueous solutions of pH 2.5 or higher.* The quantitative extraction of Pb²⁺ by **2e** was unaffected by the presence of equimolar Cd²⁺, Co²⁺, Cu²⁺, Ni²⁺, Zn²⁺ and most of the alkali or alkaline earth metal cations. However, the presence of equimolar Hg²⁺ produced strong interference to Pb²⁺ extraction.

Subsequently, the apparent strong Hg²⁺ complexation of these ligands was exploited.² It was found that *di-ionizable calixarenes 2b-e efficiently extracted Hg²⁺ from acidic aqueous nitrate solutions with excellent selectivity over alkali metal, alkaline earth metal, and many transition and heavy metal cations, including Ag⁺, Pb²⁺, and Pd²⁺.* The Hg²⁺ extraction efficiency was shown to be much higher than that for the corresponding calix[4]arene dicarboxylic acid **2a**. To provide insight into the mode of Hg²⁺ coordination, UV spectra of **2b-e** in chloroform solutions were taken before and after mercuric nitrate extraction. The Hg²⁺ coordination caused absorption changes for the substituted benzene rings of the ligands after Hg²⁺ extraction. Analogous spectral changes were not observed after lead nitrate extraction. These results suggested a significant contribution of the π -electron-rich aromatic units of **2b-e** in the coordination of Hg²⁺.

This work was extended to the design and synthesis of the first calixarene-based fluorogenic Hg²⁺ extractant **2f**.³ In solvent extraction from aqueous nitric acid solutions into chloroform, ligand **2f** exhibited excellent selectivity for Hg²⁺ over a wide range of transition, heavy, alkali metal, and alkaline earth metal cations. Quenching of its fluorescence due to Hg²⁺ coordination was unaffected by the presence of 100-fold excesses of alkali metal cations, alkaline earth metal cations, Ag⁺, Tl⁺, Cd²⁺, Co²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Pd²⁺, Zn²⁺, or Fe³⁺.

In conducting these extraction experiments, it was observed that the *N*-(*Z*)sulfonyl carboxamide-containing ligands **2b-e** were more soluble in the chloroform diluent than was the carboxylic acid-containing analogue **2a**. Thus, incorporation of this new type of pendant acidic function alleviated some of the solubility problems often encountered with calixarene ligands.

These exciting initial results indicated exceptional promise for calix[4]arenes with one or more pendant proton-ionizable groups as a new generation of selective metal agents for use in separation processes.

2. Further Investigations for Proton-ionizable Calix[4]arene-based Ligands

The following subsections summarize results obtained in this project for three classes of proton-ionizable calix[4]arene-based ligands:

- i) di-ionizable calix[4]arenes;
- ii) di-ionizable calix[4]arene-crown ethers; and
- iii) mono-ionizable calix[4]arene-bis(crown ethers).

For each class, one or two, more-detailed case studies is presented.

References are given to publications derived from results obtained in this project. Background and supporting information included in publications by others are given in our papers.

The metal-ion selectivity of calixarene-based ligands is known to depend upon the conformation of the calixarene unit. The three limiting conformations of di-ionizable-di-R-calix[4]arene shown in Figure 1 differ in spatial arrangements of the four aryl groups with respect to one another. In cone conformation **3**, the four phenolic oxygens are oriented on the same side of the calix[4]arene unit. In partial-cone conformation **4**, one of the aryl groups has been flipped to the other side of the calix[4]arene framework. In 1,3-alternate conformation **5**, a second aryl group has been flipped to provide an alternating up-and-down arrangement. (A much less frequently encountered 1,2-alternate conformation is excluded from this discussion.) If the R substituent is small (*e.g.*, methyl), rapid conformational interconversion is expected. However, if R is a propyl group or larger, the conformation of the calix[4]arene unit is locked. When the ring conformation is locked, the spatial arrangement of the two pendant acidic side arms with respect to each other and to the aromatic rings of the calix[4]arene skeleton are fixed.

In the electroneutral complex of the di-ionized ligand with a divalent metal ion, positions of the two anionic centers are fixed.

Figure 1. Limiting conformations of di-R-calix[4]arene ligands.

The effects of systematic structural variations within proton-ionizable calix[4]arene ligands upon the efficiency and selectivity of metal ion complexation were primarily assessed by solvent extraction from aqueous solutions into chloroform. These surveys included competitive solvent extraction of alkali metal cations (Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺), competitive solvent extraction of alkaline earth metal cations (Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺), and single species solvent extractions of Pb²⁺ and Hg²⁺. The selected divalent metal cations included varying degrees of hardness: alkaline earth cations (hard); Pb²⁺ (intermediate); and Hg²⁺ (soft). This allowed effects of varying the hardness of the complexed metal ion on the extraction efficiency and selectivity to be probed.

a. Di-ionizable calix[4]arenes

Several factors of di-ionizable calix[4]arene structural variation upon metal ion extraction efficiency and selectivity were evaluated, including:

- i) conformational rigidity of the calix[4]arene scaffold by variation of the R group from methyl (conformationally mobile) to butyl (conformationally locked);^{4,5}
- ii) relative positioning of the two acidic groups in conformationally locked structures (cone, partial cone, and 1,3-alternate);⁴
- iii) acidity of the pendant proton-ionizable functions and change of the acidic group structure from carboxylic acid to *N*-(Z)sulfonyl carboxamide with Z variation;^{1,2}
- iii) incorporation of four *p*-*tert*-butyl groups on the aryl groups of the calix[4]arene unit;⁵

iv) increasing the length of the spacer between the phenolic oxygen and the acidic function in the side arm by variation of the number of methylene groups.

At this stage, the non-trivial nature of the synthetic efforts needed to prepare these ligands with systematic structural variations is underscored.⁶

Case Study

Conformations adopted in CDCl₃ solution by alkali metal salts of conformationally flexible, di-ionizable calix[4]arene ligands **2b-e** were studied by NMR spectroscopy.⁷ Systematic changes of the preferred conformation for the calix[4]arene moiety from cone to partial cone to 1,3-alternate were observed for all four ligands as the alkali metal cation was varied from Li⁺ to Na⁺ to K⁺ to Rb⁺ to Cs⁺. This was the first demonstration of such conformational control of calix[4]arenes by variation of the size and softness of the complexed metal cations. *Never before had three different preferred conformations been observed for complexes of a conformationally mobile calix[4]arene ligand only by variation of the complexed metal cation.*

Case Study

To determine the influence of conformation on efficiency and selectivity of metal ion complexation, calix[4]arene dicarboxylic acids **6-10** (Figure 2) were prepared.⁴ In **7-10**, replacement of the two O-methyl groups in conformationally mobile **6** by O-butyl groups locked the ligands in cone, partial cone-butyl up, partial cone-acid up, and 1,3-alternate conformations, respectively. Due to low solubility of these ligands in the usual chloroform diluent for the solvent extraction studies, 1,2-dichloroethane was employed. In solvent extraction from aqueous solutions into 1,2-dichloroethane, competitive extractions of alkaline earth metal cations and single species extractions of Pb²⁺ were performed with ligands **6-10**. For the former, high extraction efficiency was noted for **6-8**, with low extraction efficiency for **9** and heavy precipitate formation for **10**. For **7**, the extraction selectivity order was Ba²⁺>Ca²⁺, Sr²⁺>Mg²⁺; whereas for **6** and **8**, the order was Ca²⁺>Ba²⁺>Sr²⁺>Mg²⁺. Close agreement of the extractions selectivities for **6** and **8** suggests that the preferred conformation for conformationally mobile ligand **6** is partial cone-methyl up. For single species extraction of Pb²⁺ by ligands **6-8** and **10**, quantitative loading was observed with much less efficient extraction by **9**. The results obtained

for alkaline earth metal cation and Pb^{2+} extraction revealed that it is important for divalent metal ion complexation to have the two carboxylic acid-containing side arms on the same face of the calix[4]arene scaffold.

Figure 2. Structures of Calix[4]arene Dicarboxylic Acid **6** and Calix[4]arene Dicarboxylic Acid Conformational Isomers **7-10**.

b. Di-ionizable Calix[4]arene-Crown Ethers

When two of the phenolic oxygens of calix[4]arene are connected with a polyether unit, a calixarene-crown ether (also called a calixcrown) is formed. This is a hybrid between a calixarene and a crown ether unit. Most commonly, diametrically opposed oxygens are linked producing a 1,3-calixarene-crown ether. Less frequently encountered are the 1,2-calixarene-crown ether compounds formed when adjacent, geminal, phenolic oxygens are joined.

Several factors of di-ionizable calix[4]arene-crown ether structural variation upon metal ion extraction efficiency and selectivity were evaluated, including:

- comparison of analogous 1,3-calixcrown and 1,2-calixcrown ligands;⁸⁻¹⁷

- ii) variation of the crown ether ring size;⁸⁻¹⁷
- iii) positioning of the two acidic groups relative to the polyether cavity in conformationally locked structures (cone, partial cone, and 1,3-alternate);⁸⁻¹⁷
- iv) acidity of the pendant proton-ionizable functions and change of the acidic group structure from carboxylic acid to *N*-(*Z*)sulfonyl carboxamide with *Z* variation.⁸⁻¹⁷
- v) movement of the two ionizable side arms from the lower rim to the upper rim;¹⁸
- vi) positioning of the two acidic groups relative to the polyether cavity in conformationally locked structures by variation of the side arm length;

Case Study

Figure 3 presents structures for three di-ionizable calix[4]arene-1,3-crown-6 isomers in which the calix[4]arene units are locked in the cone (**11**), partial cone (**12**), and 1,3-alternate (**13**) conformations. The conformation of the calixarene unit controls the positioning of the two proton-ionizable side arms with respect to the cyclic polyether cavity.

Figure 3. Locked Conformations of Di-ionizable Calix[4]arene-1,3-crown-6 Ligands

For competitive solvent extraction of alkaline earth metal cations from aqueous solution into chloroform by ligands **11-13**, the extraction efficiency and selectivity were found to be strongly influenced by the conformation of the calix[4]arene scaffold. For cone ligands **11** with *N*-(*Z*)-sulfonyl carbamoyl acidic side arms, very high selectivity and efficiency for Ba² (appropriately sized of fit a crown-6 cavity) extraction were observed.⁸ The 1,3-alternate analogues **13** were

next best and the partial cone analogues **12** were the poorest extractants. This pronounced effect of the calix[4]arene conformation is rationalized in Figure 4, which depicts the spatial relationship between the polyether-complexed divalent metal cation and the two anions provided by the ionized side arms. With the calixarene unit locked in the cone conformation, one ionized group is above and one below an approximate plane of the crown ether oxygens. Both anions are positioned close to the complexed metal ion. When the calixarene unit is locked in the partial cone conformation, only one anion is near the complexed metal ion. With the calixarene unit locked in the 1,3-alternate conformation, both anions are distant from the complexed metal cation. The extraction results showed that the best complexation of the divalent metal cation is provided when it is encased in a cycle of polyether oxygens and capped with one anion above and one below it.

Figure 4. Representation of the spatial relationship of the polyether-complexed cation to the two anionic centers in the extraction complex.

Thus *this research allowed the preferred spatial arrangement* of the two ionized groups relative to a polyether cavity-complexed divalent metal cation *in the extraction complex in solution to be ascertained*. Since most metal ion separations are performed in solution, this probing of the extraction complex structure offers a more realistic picture than can be obtained from a solid-state structure.

Case Study

Previous research by others has shown that calix[4]arene-1,2-crown ethers without acidic side arms are inefficient and unselective ligands for metal ion separations. However, *we have discovered that di-ionizable calix[4]arene-1,2-crown ethers may provide highly efficient and selective ligands for divalent metal ion extractions.* Competitive solvent extraction of alkaline earth metal cations by *p*-*tert*-butylcalix[4]arene-1,2-crown-4 compounds **14** gave quantitative metal ion loading with very high selectivity for Ba²⁺.^{10,14}

This was very surprising since Ba²⁺ is far too large to fit within the crown ether cavity. It was envisioned that in the extraction complex the Ba²⁺ perches on the crown ether oxygens and is also coordinated by the two ionized side arms, as represented in **15**.

Subsequently it was found that the very high selectivity for Ba^{2+} extraction was lost upon going to crown-6, crown-5, and crown-3 analogues.^{11,13-15} The outstanding complexation abilities of ligands **14** raise the intriguing possibility that these compounds may also possess good $\text{Ra}^{2+}/\text{Ba}^{2+}$ extraction selectivity. Unfortunately, the PI does not have the appropriate radiochemical facilities in his laboratories to evaluate this potential. An attempt to have the studies done elsewhere was unsuccessful.

c. Mono-ionizable Calix[4]arene-Bis(crown Ethers)

Separation of trace amounts of highly radioactive $^{137}\text{Cs}^+$ from solutions with very high levels of NaNO_3 is a critical factor for nuclear waste remediation and nuclear fuel reprocessing. It has been found the calix[4]arene-bis(crown-6) ligands possess extremely high Cs^+/Na^+ selectivity. At the DOE Savannah River Site, the current leading technology for removal of Cs^+ from DOE nuclear wastes in the lipophilic calix[4]arene-bis(crown-6) ligand **16**, known as “BOBCalixC6”. A 1,3-alternate conformation of the calixarene unit is required for two polyether fragments to be attached to distal phenolic oxygens. This arrangement provides a spherical cavity in which the Cs^+ is strongly complexed by interactions with the ether oxygens and with the π -electron clouds for the aryl units. Although ligand **16** has the requisite Cs^+/Na^+ selectivity, it suffers from poor extraction efficiency. For extraction of Cs^+ into the organic diluents, concomitant transfer of hydrophilic NO_3^- is required to maintain electroneutrality in the extraction complex.

By changing to a proton-ionizable calix[4]arene-bis(crown-6) ligand, the need to transfer an aqueous phase anion into the organic phase in solvent extraction would be eliminated. This should markedly affect the extraction efficiency. Ligands **18-21** with a proton-ionizable group positioned directly over the face of one crown-6 ring were prepared and evaluated.¹⁹⁻²¹ For solvent extraction of alkali metal cations into chloroform, it was shown that these proton-ionizable ligands gave high levels of Cs⁺ loading. Under the same conditions, extraction of Cs⁺ by non-ionizable ligand **17** was undetectable. Thus, *incorporation of a proton-ionizable function into the ligand structure markedly increases the extraction efficiency, while maintaining a high selectivity for Cs⁺*

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D. Project Supported Publications by Year for 1994-present

For the period of 1994-2011, a total of 88 publications acknowledging BES-DOE support of the project appeared. This included primarily articles in chemistry and separation science journals with a lesser number of monograph chapters. Two additional papers in scientific journals have been published to date in 2012.

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1. “An Acyclic Polyether Dicarboxylic Acid Ionophore with High Selectivity for pH-driven Uphill Transport of Lead(II) Ion,” K. Hiratani, H. Sugihara, K. Kasuga, K. Fujiwara, T. Hayashita and R. A. Bartsch, *Journal of the Chemical Society, Chemical Communications*, **1994**, 319-320.

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