

## YEARLY PROGRESS REPORT – PROJECT 74019

**Project Title:** Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance

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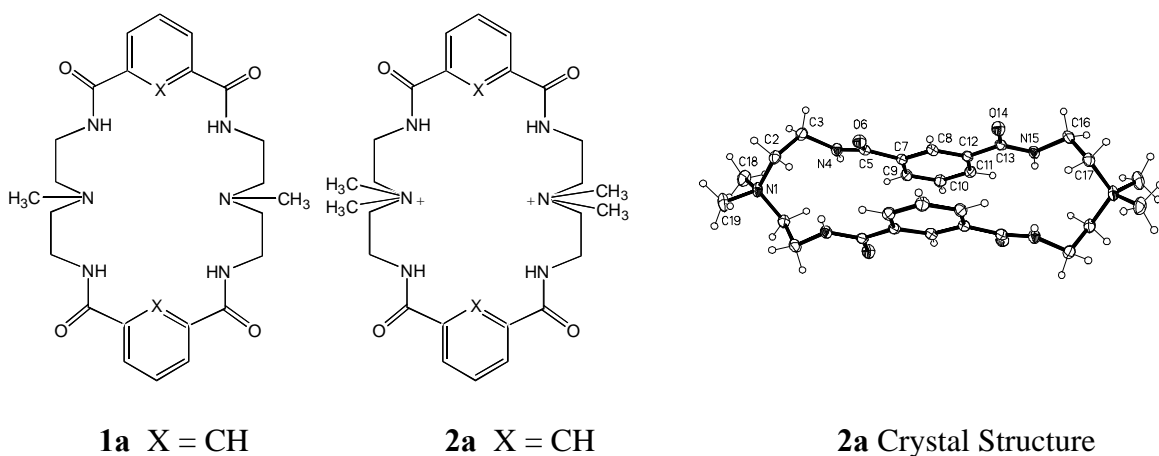
**RESEARCH OBJECTIVE:** This project involves the design and synthesis of receptors for anions of environmental importance, including emphasis on high level and low activity waste. Polyammonium macrocycles as receptors and nitrate as target anion were the focus of the first phase of this project. A second phase involved the synthesis of lipophilic amide-based receptors in order to increase the potential for obtaining workable receptors for both separations and sensing applications on site. In the renewal of this project, anions have been extended especially to include selective recognition and binding of sulfate. A three tier approach was employed: **I.** Design, synthesis, and physical and structural characterization of receptors; **II.** Examination of the technique known as ITIES, Interface Between Two Immiscible Electrolyte Solutions, as an analytical probe for anion analysis; and **III.** Separations studies using lipophilic amide receptors for anion binding done at the Oak Ridge National Laboratory by Bruce Moyer. The result of this program will impact a variety of needs of the Environmental Science Management Program in both sensing and separations areas.

## RESEARCH PROGRESS AND IMPLICATIONS

As of June 15, this report summarizes work 1 year and 2 months of a after the start of the renewal of the Environmental Management Science Program project funded in 1996. The project has been ongoing since that time.

**Halide binding.** While oxo anions are a primary focus of our research, halides are of interest for certain sites, and particularly INEEL, where conditions are very acidic, and there is currently concern about halides such as chloride and fluoride.<sup>1</sup> We have also found that <sup>19</sup>F NMR techniques are very useful as a solution structural probe.<sup>2</sup> In addition to the discovery (reported last year) that a tiny aza cryptand previously known only to complex fluoride selectively, was found to show enhanced binding for chloride low pH (<2.5),<sup>3</sup> we have found that an expanded cavity binds two fluorides bridged by a water molecule.<sup>4</sup> The same macrocycle only binds one chloride or bromide with water in the other side of the cavity. These findings, part of the basic research component of our program, lend considerable new knowledge to anion coordination chemistry, bringing to light amazing correlations between anion and traditional transition metal coordination chemistry.

**New receptor systems.** Explorations for the new class of receptors noted in the previous report are those containing amides and are more suited for applications involving separations. What is unique about these systems is that they consist of mixed amide and amine receptors, and so retain some of the desirable characteristics of both. As noted in the last report, the macrocyclic amide, **1a**, shows selective binding for both phosphate and sulfate in CDCl<sub>3</sub>.<sup>5</sup> Binding is diminished, however, in more polar solvents such as DMSO. A new strategy is also being explored which will lead to receptors functional in an anion exchange method. These systems benefit from an added complementarity effect, i.e., charge, as can be seen in **2a**, the diquaternized salt of **1a**. Compounds **1b** and **2b** have also been synthesized and show promise as anion receptors.



<sup>1</sup> TFA Workshop, March 12-15, 2001, Salt Lake City, Utah

<sup>2</sup> Clifford, T.; Mason, S.; Llinares, J. M.; Bowman-James, K. *J. Am. Chem. Soc.* **2000**, *122*, 1814-1815.

<sup>3</sup> Hossain, M. A.; Llinares, J. M.; Miller, C.; Bowman-James, K. *Chem. Commun.* **2000**, 2269-2270.

<sup>4</sup> Hossain, M. A.; Llinares, J. M.; Mason, S.; Morehouse, P.; Powell, D.; Bowman-James, K. *Angew. Chem.*, **2002**, in press.

<sup>5</sup> Hossain, M. A.; Llinares, J. M.; Powell, D.; Bowman-James, K. *Inorg. Chem.* **2001**, *40*, 4710-4720.

**1b** X = N

**2b** X = N

**Table 1.** Binding constants (log  $K_s$ ) for new receptors determined by NMR spectroscopy.

| Anions                                      | Log $K_s$ (DMSO-d <sub>6</sub> ) |                      |                       |                      |
|---|----------------------------------|----------------------|-----------------------|----------------------|
|   | <b>1a</b><br>(X = CH)            | <b>1b</b><br>(X = N) | <b>2a</b><br>(X = CH) | <b>2b</b><br>(X = N) |
| HSO <sub>4</sub> <sup>-</sup>               | 3.02                             | 2.03                 | --*                   | 3.90                 |
| H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> | 2.92                             | 4.05                 | 3.06                  | ---*                 |
| NO <sub>3</sub> <sup>-</sup>                | <1                               | <1                   | <1                    | 2.32                 |
| ClO <sub>4</sub> <sup>-</sup>               | <1                               | <1                   | <1                    | 2.40                 |
| Cl <sup>-</sup>                             | 1.42                             | 2.69                 | 3.23                  | 4.75                 |
| Br <sup>-</sup>                             | 1.31                             | 2.71                 | 2.14                  | 4.38                 |
| I <sup>-</sup>                              | <1                               | <1                   | 2.00                  | 2.21                 |

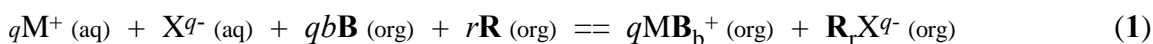
\*Measurements are complicated due to 1:1 and 2:1 L:H<sub>2</sub>SO<sub>4</sub><sup>-</sup> equilibria (**2a**) and to slow exchange and the presence of two amide signals (**2b**). Measurements using other techniques are currently underway.

The synthesis and characterization of **1** and **2** are complete, and binding constants for DMSO-d<sub>6</sub> are shown in **Table 1** for a variety of anions. The initial work with **1a** was done in CHCl<sub>3</sub>, where binding is considerably higher (log  $K_{\text{HSO}_4^-} = 4.50$ , compared to 3.02 in DMSO). The crystal structure of the chloride complex of **2a** indicates charge repulsion between the two ammonium units resulting in an elongated macrocycle with two chlorides outside of the macrocycle. Solution of the crystal structure of the sulfate complex is in progress, but is hampered by severe disorder effects and excess sulfuric acid in the sample. It would appear with the quaternary salt of the pyridine analog (**2b**), binding is generally higher than with the m-xylyl analog, **2a**. Additional information is being accumulated which tends to indicate that the presence of an amine (i.e., the CH<sub>3</sub>N<, in **1a** or the pyridine N, in **1b** and **2b**) aids in binding.

### Separations Studies

Studies done in Bruce Moyer's group at Oak Ridge National Laboratory are currently focusing on extraction experiments with sulfate as the target anion. All of the efforts below have been obtained within the last year with the renewed grant. The findings are summarized.

In general anion binding behavior was surveyed in a dual-host system containing a cesium-selective calixcrown, calix[4]arene-bis(t-octylbenzo)crown-6 (BOBCalixC6), mixed with the anion receptor **1a** in nitrobenzene (NB). In dual-host systems, the expected synergism is ideally ascribable to a new reaction in which the *cation receptor* **B** binds the cation M<sup>+</sup> and the *anion receptor* **R** binds the anion X<sup>q-</sup>, resulting in extraction of the M<sub>q</sub>X salt in excess over that which would be extracted by **B** and **R**, each acting independently. If the diluent is sufficiently polar that no ion-pairing occurs in the solvent phase, the new reaction may be expressed ideally in the following manner:



The polar diluent NB was chosen so as to minimize any effect of ion-pairing interactions. The cation receptor BOBCalixC6 was chosen for convenience as a strong cesium extractant.

An extraction survey was performed with various concentrations of **1a** added to 10 mM BOBCalixC6 in NB. The aqueous phases consisted of single 1:1 or 2:1  $Cs_qX$  ( $q = 1$  or  $2$ ) salts to which was added 1 mM NaOH and  $^{137}Cs$  tracer. The cesium distribution ratio was determined radiometrically. In general, it was found that **1a** enhances  $Cs_qX$  extraction by BOBCalixC6, and the enhancement increases with increasing anion hydration, decreasing anion radius for a given charge, increasing charge, and increasing anion-receptor concentration. Among all the anions the strongest enhancement occurred with sulfate (4.2-fold) and hydroxide (4.7-fold). Almost enough data has been accumulated to write a paper on this system, and the rest is projected to be in hand shortly.

A series of experiments have been conducted with  $^{35}SO_4^{2-}$  tracer for a direct measurement of sulfate distribution. The sulfate distribution ratio  $D_{SO_4}$  was measured directly by beta scintillation counting. Beta counting is more difficult than gamma counting ( $^{137}Cs$ ), owing to quenching effects. With some attention to correcting for quenching, or avoiding it when possible, good measurements have been obtainable. All the rest of the results below were obtained in this manner.

Several experiments were conducted in which sodium sulfate extraction into 1-octanol was measured. 1-Octanol is reasonably good at solvating both cations and anions, as it is both a good electron-pair donor and hydrogen-bond donor. Even so, extraction still tends to be weak, as alcohols solvate ions more weakly than water. Using an aqueous phase consisting of 1 M NaOH, 0.1 mM  $Na_2SO_4$ , and tracer, we obtained a feeble  $D_{SO_4}$  of  $2 \times 10^{-6}$ . It was first shown that addition of hydrogen-bond donors such as monofunctional hydroxy compounds also aided in sulfate extraction, attributed to their ability to donate protons. Addition of the anion receptor **1b** to 1-octanol appears to have a small enhancement effect on sulfate extraction, and a 10 mM addition increased  $D_{SO_4}$  from  $2 \times 10^{-6}$  to  $3 \times 10^{-5}$ .

Synergistic enhancement of anion exchange by mixtures of anion receptors and quaternary ammonium salt Aliquat 336 has also been demonstrated. An experiment measuring sulfate selectivity vs. nitrate, a key parameter for waste applications, was performed. By monitoring  $D_{SO_4}$  as different anion receptors are added, one can assess whether a given receptor exhibits a greater affinity for sulfate vs. nitrate. For 10 mM the Aliquat in 1-octanol, addition of 10 mM MMEAM nearly doubled the value of  $D_{SO_4}$  from  $4.4 \times 10^{-3}$  to  $7.3 \times 10^{-3}$ . Although this appears promising, when the concentration of the quaternary ammonium salt was raised 10-fold to 100 mM in 1-octanol, addition of 10 mM **1a** approximately halved the value of  $D_{SO_4}$  from  $3.6 \times 10^{-1}$  to  $1.9 \times 10^{-1}$ . Interestingly, this was also seen when the hydroxy compounds cited above were also tested with Diquat. This apparent dependence of the enhancement on the exchanger concentration strongly suggests an effect of aggregation. Work will continue using the new quaternary ammonium receptors **2a** and **b**.

### Planned Activities

Now that **2a** and **2b** have been synthesized, characterized, and preliminary binding studies performed, they are being synthesized in bulk quantities for shipment to Oak Ridge in the next several weeks. The studies with these systems will clearly blend with Moyer's

investigation using Diquat. Additional quaternized systems are being synthesized, including pyridine-quaternized systems and the synthesis of a new guanidinium-containing macrocyclic receptor. The latter is based on some preliminary evidence obtained in the Moyer group that guanidinium groups may be promising. The charged receptors now being explored are appealing in that they can impart charge complementarity as part of the selectivity factors. At Oak Ridge effort will be placed on assessing whether an ion pair extraction (the dual receptor concept) or anion exchange strategy (the ammonium salt receptors) is a better strategy to use for applications at the waste sites.

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