PROGRESS REPORT

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

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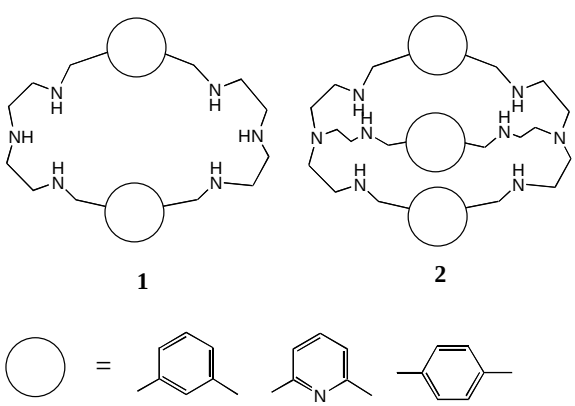
Executive Summary: Certain anions, especially oxoanions, have been prominent as contaminants (e.g., pertechnetate), troublesome species (e.g., sulfate, chromate, and phosphate), or ubiquitous matrix components that can pollute (e.g., nitrate) in

environmental or waste treatment processes in the USDOE complex. In the first phase of this project, we approached the topic of anion recognition and separation broadly targeting such oxoanions, but also including other anions, such as halides, to learn more about the binding aspects of anions with synthetic receptors. In the past several years, however, the presence of sulfate in tank waste has risen to be a critical concern in meeting the objectives of Mission Acceleration at Hanford as it is a key determinant of the volume of expensive low-activity-waste (LAW) glass that will be produced from the waste. It is known that sulfate has a low solubility (typically <1%) in borosilicate glasses and at elevated levels will migrate to the top of the melt as a separate phase. Sulfate phase-separation problems compromise both the vitrification process and the integrity of the final waste form. Specific processing problems include inhibition of melting rate, short-circuiting of the electrodes, corrosion of the melter, electrodes, and off-gas equipment. In addition, the final glass product containing high sulfate levels can exhibit increased leach rates, a waste-form performance issue. Hence, a more recent focus have been directed at synthesizing receptors that selectively bind sulfate, and that will be successful in an extraction approach. The latter efforts have been in collaboration with Dr. Bruce Moyer at Oak Ridge National Laboratory.

In terms of target receptors, emphasis was shifted from polyammonium receptors to lipophilic amide-based receptors more amenable for both separations and sensing applications in the last renewal. The last three years have been focused on the basic chemical aspects of anion receptor design with the ultimate goal of targeting the selective binding of sulfate, as well as design of separations strategies for selective and efficient removal of targeted anions. Key findings during these years include: (1) the first synthetic sulfate-selective anion-binding agents; (2) simple, structure-based methods for modifying the intrinsic anion selectivity of a given class of anion receptors; and (3) the first system capable of extracting sulfate anion from acidic, nitrate-containing aqueous media. Areas probed during the last funding period include: 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. Investigation of anion and dual ion pair extraction using lipophilic amide receptors for anion binding.

I. Design, synthesis, and physical and structural characterization of receptors.



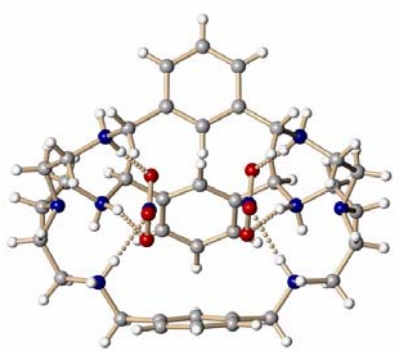
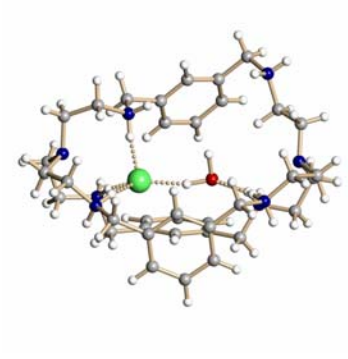


Figure 1. Polyammonium macrocycles **I**

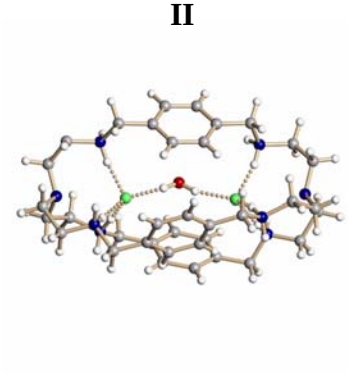
Polyammonium Receptors. The first target hosts investigated included monocyclic, **1**, and bicyclic, **2**, polyammonium systems. Many of these hosts are readily synthesized from Schiff base condensations followed by borohydride reductions, and available with various spacer aromatic or heterocyclic units (**Figure 1**).

The first major result in our project was the isolation and characterization of a ditopic nitrate complex with a polyammonium-based aza cryptand, **I**, with m-xylyl spacers.[*58] Subsequent studies indicated that dimensionality plays a major role on binding affinities in anion complexes [#1-5, 12, 13]. While monocyclic systems may bind multiply valent anions with significant affinity, they do not have even measurable affinities in some cases for monoanions. A number of crystal structures for both cryptand and monocyclic systems also indicated inclusion complex formation for the former, but more generally a layered cation receptor/anion structure for the latter.

A mixed fluoride/water encapsulated complex was also crystallographically characterized, **II** [#5, 12]**.** In addition to the solid state structure, ^{19}F NMR studies (**Figure 2**) allowed an examination of the solution structure with fluoride ion. The ^{19}F NMR clearly showed only one sharp signal at ~ –120 ppm at pH 10.5 (**A**) assigned as solvated fluoride. However, a new signal at –89 ppm arises as protonation of the macrocycle begins, eventually replacing the free fluoride signal (**E**, pH = 6.5). We attribute this signal to encapsulated fluoride.



II



III

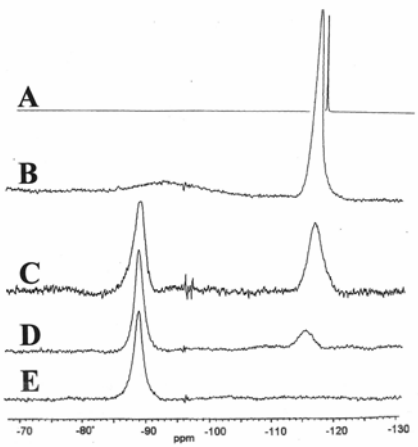


Figure 2. pH: **A**, 10.5; **B**, 9.0; **C**, 8.0; **D**, 7.0; **E**, 6.5.

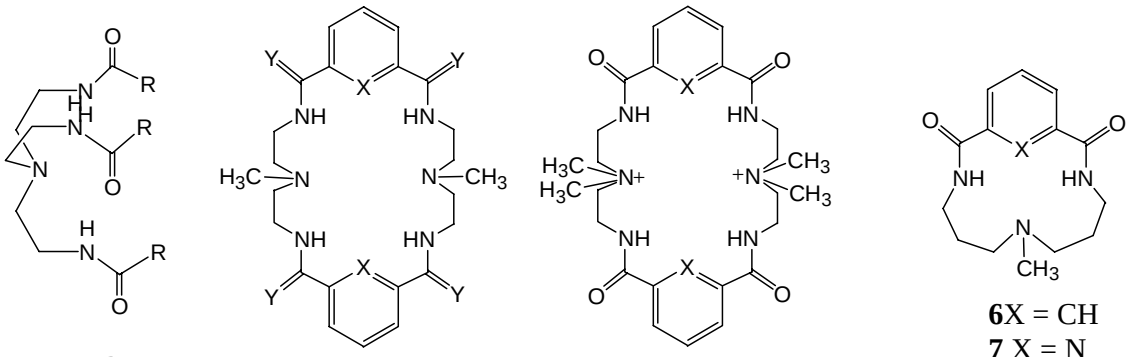
[*] In views of crystal structures, only the central "complex" is shown, and additional anions which may be required to satisfy the charge requirements are omitted.

By expanding the aza cryptand cavity using a *p*-xylyl spacer, we isolated a ditopic fluoride complex that resembles transition metal cascade complexes. In this structure, the two fluorides play the role of the metal ion and are bridged by a "cascading" water molecule (**III**) [#14, 23]. It was revealing that just a minor adjustment in cavity size resulted in a significant structural difference. Furthermore, crystal structures of the chloride and bromide salts with the *p*-xylyl-spaced cryptand show structures similar to that of the fluoride with the *m*-xylyl spacer, i.e., a single halide and water inside the cavity

The structural characterization of an encapsulated chloride in a tiny octaazacryptand, previously assumed to be capable of incorporating only fluoride inside the cavity, was also surprisingly revealing [#7,16]. NMR studies as a function of pH indicated chloride binding to be pH controlled, occurring only at pD 2.5 and lower. This is approximately when the sixth proton is added to the small cryptand. *This finding emphasizes the importance of careful examination of all contributing aspects of anion coordination including pH.*

These early studies using polyammonium macrocycles as receptors for inorganic ions, led to expanded explorations of receptors more readily amenable to applications during this funding period.

Amide/Thioamide-based Receptors. Drawbacks to ammonium-based receptors are water solubility (hampering their use as ion selective electrodes or in separations) and pH sensitivity. Thus neutral receptors fashioned after the polyammonium systems were targeted. Initial studies involved acyclic tripodal amide-based receptors, **3** (**Figure 3**) [#6]. These systems were found to show some unusual structures, including one with R = $(CH_2)_6CH_3$, which showed a lipid bilayer structure. The tripods were used in both the ITIES [#9] and separations[8] studies (*vide infra*).



3

4 X = CH, Y = O
5 X = N, Y = O
4S X = CH, Y = S
5S X = N, Y = S

4Q X = CH, Y = O
5Q X = N, Y = O

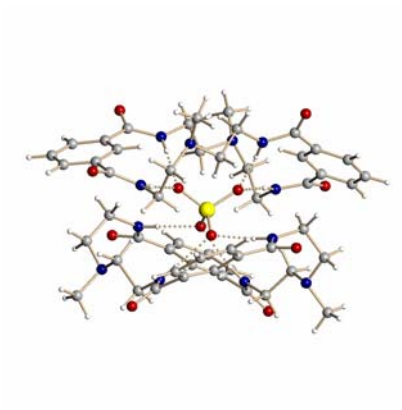
6X = CH
7 X = N

Figure 3. Tripodal and monocyclic amide- and thioamide-based anion receptors.

New mixed amine/amide macrocyclic-based receptors were also synthesized: **4** [#10, 11] and **5**; their quaternized versions, **4Q** and **5Q** [#15]; and thioamide analogs, **4S** and **5S** (**Figure 3**) [#16]. Smaller macrocycles, **6** and **7**, have been isolated from 1:1

condensation reactions. The inclusion of amines in these systems lends chemical versatility. To illustrate, **4** and **5** show high affinity for protonated anions such as HSO_4^- and $H_2PO_4^-$, over others. We attribute this finding to a complex interplay of the acid/base properties of both the anion and the macrocyclic amines. For example, crystals isolated from reacting HSO_4^- with **4** indicated SO_4^{2-} (not HSO_4^-) sandwiched between two molecules of **4**. We also observe even greater binding for almost all anions by changing the *m*-xylyl spacer to pyridine, **5**, **5S**, and **5Q**.

In the sulfate sandwich structure with **4** each of the sulfate oxygen atoms is held by two hydrogen bonds from the amide hydrogens (**IV**). This multiple hydrogen bond network is probably responsible for the high affinity seen for this complex with sulfate (log K = 4.50 in $CDCl_3$) [#10, 11]. The two macrocycles are rotated by 90° in order to accommodate the S_4 symmetry of the sulfate.



IV

Table 1. Association constants of **4** and **4S** with anions in DMSO-d_6 at 25 ºC.

Anions	log K (M^{-1})	
	4	**4S**
$H_2PO_4^-$	831	> 10^4
HSO_4^-	794	1,412
CN^-	---	800
Cl^-	25	107
Br^-	20	100
NO_3^-	<10	10

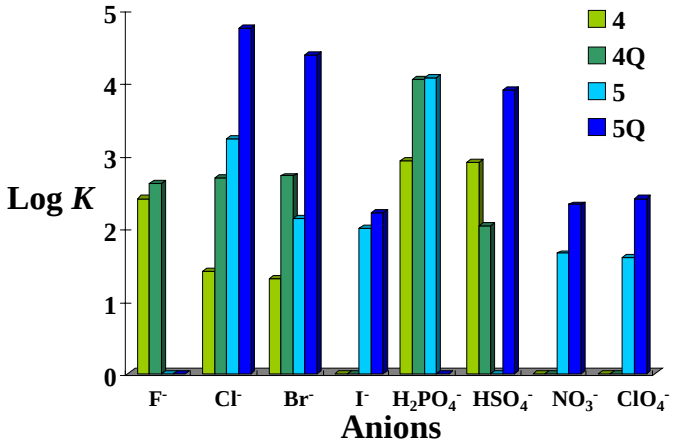
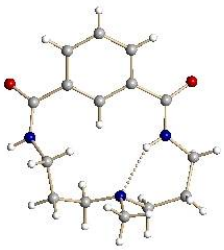


Figure 4. Bar graph illustrating binding (log K) differences between neutral and quaternized receptors.

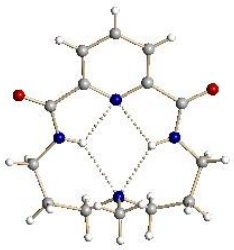
Thioamide macroycles **4S** and **5S** [#16] have been recently synthesized and characterized in our group. *To our knowledge thioamide macrocycles have not been previously reported, and thus represent totally new additions to the macrocyclic arena.* Preliminary binding studies (**Table 1**) have been obtained. The receptor **4S** is exceedingly selective for $H_2PO_4^-$ and studies are currently underway to probe this finding.

Another degree of complementarity, quaternization, gave **4Q** and **5Q** (**Figure 3**) [#15]. The new positively charged receptors showed significantly enhanced binding for anions (in most cases one or more orders of magnitude greater) (**Figure 4**). (Some anions are not shown because of complications in determination of binding, or because binding has not been determined.) In both neutral and quaternized systems, we found that the pyridine analogs showed higher affinity than their *m*-xylyl corollaries in most cases (HSO_4^- the exception). We now attribute this effect to a preorganization influence provided by the pyridine nitrogen.

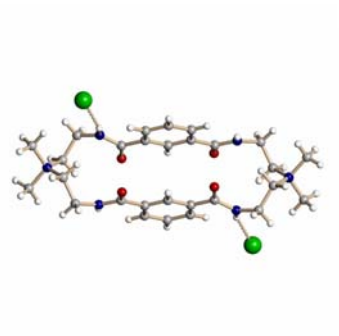
Crystal structures of the small macrocycles, **6** (**V**), **7** (**VI**) and **7S** (not shown) along with the structures of the quaternized receptors **4Q** (**VII**) and **5Q** (**VIII**) [#15] support a preorganization concept for pyridine, compared with the "non-preorganized" *m*-xylyl spacers. The outcome of th is preorganization, which could account for the increased affinities of the pyridine analogs, is the anion equivalent of the chelate effect.



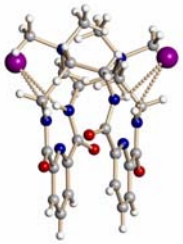
V



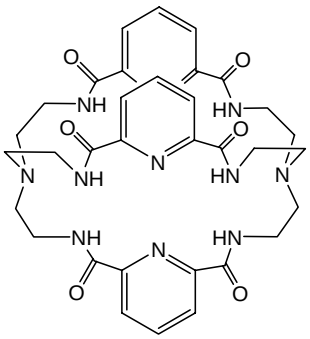
VI



VII



VIII

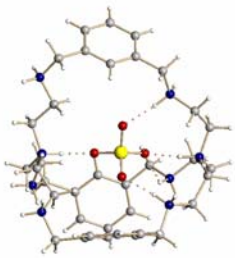


8

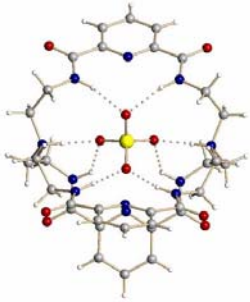
The preorganization influence of the pyridine spacer was used to facilitate synthesis of the amide-based cryptand, **8** [#17].

Very recent studies with **8** in conjunction with the polyammonium cryptand **2**, with *m*-xylyl spacers, as well as the tetraamido macrocycle **4** revealed some important aspects of the binding of sulfate with synthetic receptors [#10, 11, 22] as well as shedding light on

the important contribution of preorganization in anion binding. As seen in **IV** (shown earlier), the sulfate is eight-coordinate with two hydrogen bonds to each sulfate oxygen [#10, 11]. In the sulfate structure of the polyammonium cryptand, **2**, there is no pyridine spacer to affect the preorganization of the ammonium protons. In this sulfate structure, while the sulfate is encapsulated, it only maintains five hydrogen bonds with the cryptand, **IX** [#23]. However, in the structure with the hexaamido cryptand, **8**, as in the structure with **2**, eight hydrogen bonds serve to hold the sulfate in the cavity, **X**. This preference for multiple hydrogen bonds, and particularly for two hydrogen bonds to each of the sulfate oxygen atoms will aid in future design strategies.



IX



X

II. Analytical Applications. Interface Between Two Immiscible Electrolyte Solutions (ITIES). These studies were successful, including the exploration of the dual host concept, and further investigations are not in the scope of this proposal. A summary of the salient results are provided below [#9]. Using laser ablation, 56 small holes (13 μm each in diameter) were drilled in a thin polymer film. The holes are cone-shaped (*vide supra*). On the "aqueous" side the diameter is 22 μm, and on the "organic" side 13 μm (**Figure 5**). The membrane is mounted on the cell also shown in **Figure 5**. It is of critical importance to mount the membrane so that there is no parallel path for current flow that might subsequently interfere with the processes of interest. As indicated, a two-electrode system is employed, the two electrodes, one in each aqueous phase, being AgCl/Ag.

The cell configurations can be represented as follows:

Cell I:
Ag/AgCl | BTPPACl $_{aq}$ (1mM) + LiCl (10 mM) | BTPPATPBCl (10 mM) || Li_2SO_4 (10 mM) + $LiNO_3$ (x mM)$_{aq}$| Ag_2SO_4/Ag

Cell II:
Ag/AgCl | BTPPACl $_{aq}$ (1 mM) + LiCl (10 mM)| BTPPATPBCl (10 mM) || Li_2SO_4 (10 mM) + TMACl (x mM)$_{aq}$ | Ag_2SO_4/Ag

Cell III:
Ag/AgCl | BTPPACl $_{aq}$ (1 mM) + LiCl (10 mM) | BTPPATPBCl (10 mM) + TTB (10 mM)||Li_2SO_4 (10 mM) + $LiNO_3$ (x mM)$_{aq}$ | Ag_2SO_4/Ag

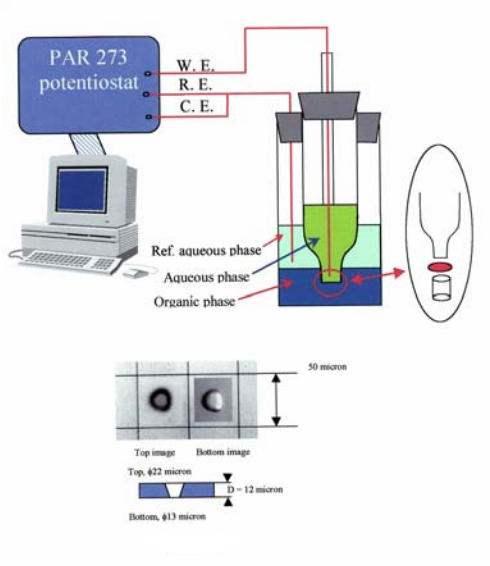


Figure 5. Experimental apparatus for ITIES experiments.

BTPPACl is *bis*(triphenylphosphoranylidene) ammonium chloride; BTPPATPBCl corresponds to *bis*(triphenylphosphoranylidene) ammonium *tetrakis*(4-chlorophenyl) borate; and TTB to a tripodal triamide nitrate host related to **3**, with a *p*-$C_6H_4C(CH_3)_3$ appendage (**Figure 3,** *vide supra*). The receptors, which form the basis for the selectivity of the system, are essentially soluble only in the organic phase, 1,2 dichloroethane.

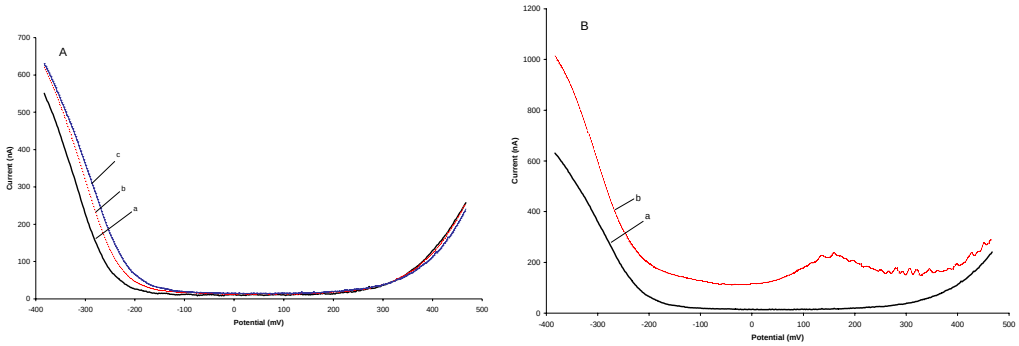


Figure 6. Background measurements and scale setting for ITIES experiment.

Figure 6A shows the differential pulse voltammogram (DPV) for Cell I. Curve *a* corresponds to the background current whereas curves *b* and *c* correspond to increasing nitrate 0.91 mM and 1.67 mM, respectively. Note that there is a slight increase in the current, but at the negative discharge limit, which for this reason is difficult to measure. The relatively weak dependence on concentration suggests that NO_3^- is being transferred into the organic layer, but only with difficulty. **Figure 6B** of Cell II again shows the DPV background (curve *a*) and the voltammogram of TMA^+ (tetramethylammonium ion) (curve *b*), which is assigned a potential of 160 mV. The scale is set from this experiment. **Figure 7A** of Cell III shows facilitation of nitrate transport to the organic phase. Compared to the background current (curve *a*), the DPV peaks are shifted in the positive

direction indicating more facile transfer. They correspond (curves *b-d*) to aqueous nitrate concentrations of 0.57, 1.53 and 3.15 mM, respectively. **Figure 7B** shows the differential pulse voltammograms for a cell similar to Cell III, except that K^+ is added to the aqueous phase as K_2SO_4 and dibenzo-18-crown-6 (DB18C6) is added to the organic phase, i.e., the dual host concept.

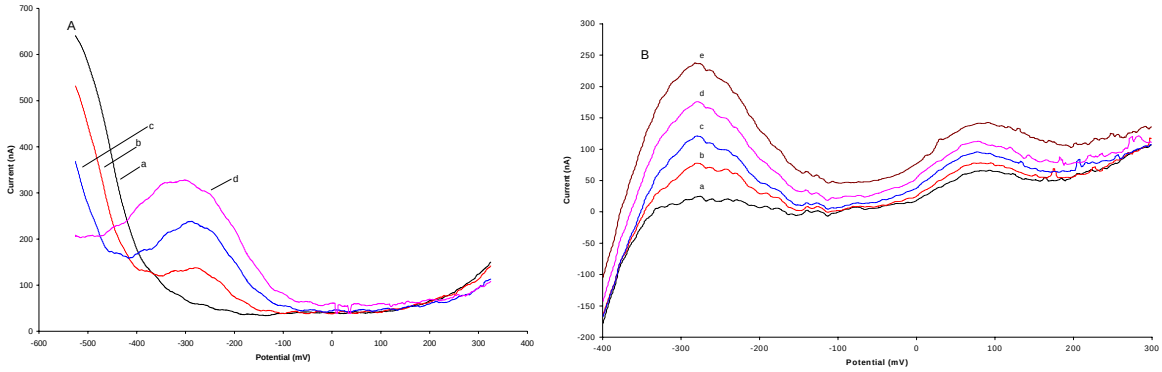


Figure 7. Transfer of nitrate with assistance of the tripod receptor (A) and with added crown ether (B) the facilitated transfer of both nitrate (negative voltage) and potassium (positive voltage).

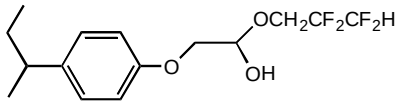
III. Extraction Studies Efforts focused on a systematic survey of sulfate extraction behavior in the context of the 11 approaches (**Table 2**). The results confirmed generally that the use of anion receptors weakens, and in can even overcomes, Hofmeister bias.

Table 2. Eleven approaches to recognition and extraction.

Case	Name	Description
#1	No host	A polar solvent (e.g., 1-octanol) is used to solvate both cation and anion.
#2	Cation host	A cation host (e.g., crown ether) binds the cation. Anion remains primarily solvated.
#3	Anion host	An anion host binds the anion. Cation remains primarily solvated.
#4	Dual hosts	Cation host and anion host are used in synergistic combination.
#5	Ion-pair host	A single host binds both the cation and anion.
#6	Cation exchange	A lipophilic weak organic acid is employed to effect cation exchange. No hosts are used.
#7	Synergistic cation exchange	A cation host is used in synergistic combination with a lipophilic weak organic acid.
#8	Ditopic cation exchange	A weakly acidic functionality is incorporated into the cation host.
#9	Anion exchange	A salt of a lipophilic cation is employed to effect anion exchange. No hosts are used.
#10	Synergistic anion exchange	An anion host is used in synergistic combination with an anion exchanger.
#11	Ditopic anion exchange	An anion-exchange functionality is incorporated into the anion host.

Experimental techniques employed radiometric counting methods for the determination of cation and anion distribution on equilibrating organic and aqueous phases at 25 °C. Tracers included gamma isotopes ^{22}Na and ^{137}Cs, as we have often used previously, and methods were worked out for employing $^{35}SO_4^{2-}$ tracer for a direct measurement of sulfate distribution. Following the cation is useful for surveys of many anions, as it gives an indirect measure of the co-anion distribution by a single methodology, whereas following sulfate is needed for anion exchange. The sulfate distribution ratio D_{SO4} was measured by beta liquid scintillation counting.

Several experiments were conducted in which sodium sulfate extraction into 1-octanol was measured (Case #1). 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, a feeble D_{SO4} of 2×10^{-6} was obtained. As it is known that anion partitioning, particularly that of small anions, is influenced mostly by the hydrogen-bond donor ability of the solvent, it was postulated that addition of hydrogen-bond donors more acidic than 1-octanol to the 1-octanol solvent would enhance extraction. This modification may be thought of as a primitive Case #3 with a monofunctional anion receptor or perhaps just Case #1 with enhanced solvation. The simple monofunctional hydroxy compounds tested are given below:



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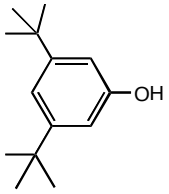

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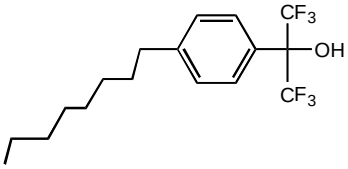

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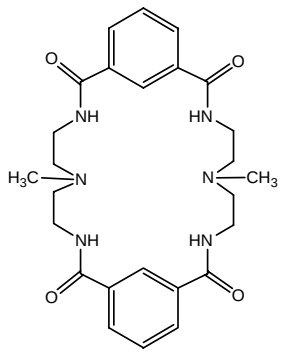
Compound **9** is the diluent modifier used in the CSSX process for $CsNO_3$ extraction by a calixcrown and is thought to function by solvation of the anion based on solvatochromic data. On adding **9**, **10**, or **11** at 0.2 M to 1-octanol, D_{SO4} values were obtained as follows: 1.9×10^{-4}, 1.3×10^{-4}, and 3.4×10^{-4}, respectively. Although these are still very low distribution ratios, considerable extraction enhancement was observed. Sodium distribution was measured in parallel by gamma counting of ^{22}Na tracer. The hydroxy proton of **9** is not significantly exchangeable with sodium under the experimental conditions used, and thus, the enhancement of extraction is interpreted as being due to enhanced solvation of sulfate by hydrogen bonding. On the other hand, the hydroxy protons of **10** and **11** are sufficiently acidic that an appreciable fraction of each compound is converted to its sodium salt, 70% in the case of **10** and 98% in the case of **11**. The enhanced sulfate extraction observed for these two compounds must therefore involve some other mechanism involving ionic interactions.



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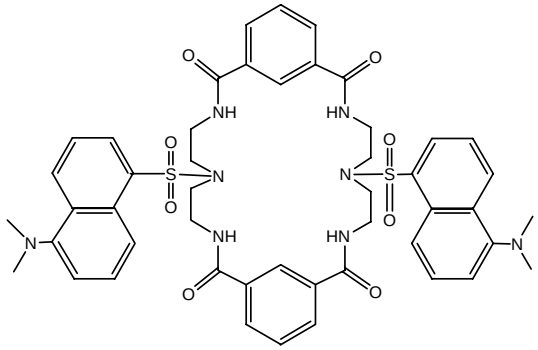

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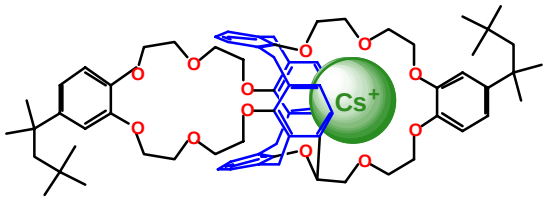
In accordance with expectations, Case #3 was confirmed to be weak. Addition of the anion receptor **4** (MMEAM), to 1-octanol weakly enhances sodium sulfate extraction from an aqueous solution containing 1 M NaOH, 0.1 mM Na_2SO_4, and tracer. On adding 10 mM **4** to 1-octanol, D_{SO4} increases from 2×10^{-6} to 3×10^{-5}. This is a feeble extraction, but the anion receptor does appear to have a noticeable effect. In other experiments, it was also demonstrated that **12** (DSMEAM) used alone effects cesium salt extraction into nitrobenzene (again Case #3, no cation receptor present). Cesium salts are weakly extractable by nitrobenzene alone without any receptor at all, and it is therefore possible to detect the enhancement of the cesium salt extraction when an anion receptor is added. Receptor **12** at 3 mM in NB was used to extract cesium salts to which was added 1 mM NaOH and ^{137}Cs tracer. Distribution ratios of cesium salts of univalent anions were low but measurable; extraction of salts of divalent anions were too low for reliable determination. As an example, the distribution ratio for cesium nitrate was 0.0058 with **12** vs 0.0019 without. Apparently, the anion receptor must be exceptionally strong to overcome the unfavorable cation partitioning.



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

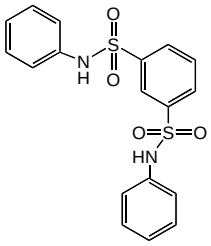
Dual-host extraction systems (Case #4) exhibited reasonably strong salt extraction with a synergistic effect being observed. Extraction experiments were conducted with **4** and **12** as anion receptors in synergistic combination with the cesium-selective calixcrown, calyx[4]arene-bis(*t*-octylbenzo)crown-6 (BOBCalixC6) in nitrobenzene (NB). In general, **4** was found to be somewhat weaker in enhancing cesium salt extraction than **12**, but the observed behavior was otherwise similar. In dual-host systems, the expected synergism is ideally ascribable to a new reaction in which the cation receptor B binds the cation M^+ and the anion receptor R binds the anion X^{q-}, resulting in extraction of the M*q*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:

$$qM^+\,(aq) + X^{q-}\,(aq) + qbB\,(org) + rR\,(org) == qMB_b^{\,+}\,(org) + R_rX^{q-}\,(org) \qquad (1)$$

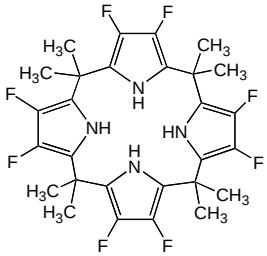
The polar diluent NB was chosen so as to minimize any effect of ion-pairing interactions. The cation receptor BOBCalixC6 was chosen for convenience as a strong cesium extractant with simple well-characterized extraction reactions that for univalent anions conforms to:

$$Cs^+ (aq) + X^- (aq) + B (org) == CsB^+ (org) + X^- (org) \qquad (2)$$

In many cases, including the present case, the anion receptor has negligible ability to extract CsX salts by itself. When this is true, on addition of an anion receptor to the cation receptor BOBCalixC6, an enhancement of extraction may be interpreted in terms of anion binding according to the new reaction given in eq. 1. Extraction surveys were performed with various concentrations of **4** or **12** 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. Results for **12** are illustrated in **Figure 8**. In general, it was found that **12** 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 the univalent anions, the enhancement is strictly anti-Hofmeister. That is, anion binding increases as the anions become smaller or more hydrated. This effect is typical, as the smaller the anion is, the stronger is the hydrogen bond with a given hydrogen-bond donor. Among all the anions, enhancement of sulfate extraction was one of the strongest (11-fold for **12**, 4-fold for **4**). At 3 mM, **12** exhibited a higher enhancement (16-fold), which was the highest seen for any of the anions at that receptor concentration. It is not clear whether the selectivity for sulfate is due to special complementarity (e.g., sandwich formation or simply to the higher charge density on sulfate). We should keep in mind that we have been discussing enhancement, whereas the small anions are difficult to extract in absolute terms, owing to their large hydration energies. Note the low salt distribution ratios D_{Cs} for small anions and the decreasing trend with increasing size from left to right in **Figure 8**. The anti-Hofmeister *enhancement* that we observe is therefore not of sufficient magnitude to offset the dominant Hofmeister effect of eq. 2. The net extraction observed thus follows Hofmeister behavior. Relevant to the problem of sulfate removal from nitrate waste, cesium nitrate is overall two orders of magnitude more strongly extracted than cesium sulfate in the dual-host system with **12**. Selected survey results for different receptors and different diluents are given in **Table 3**. In addition to compounds **9-13**, a 1,3-benzene disulfonamide **14** and the octafluorinated calix[4]pyrrole **15** have been examined.



14



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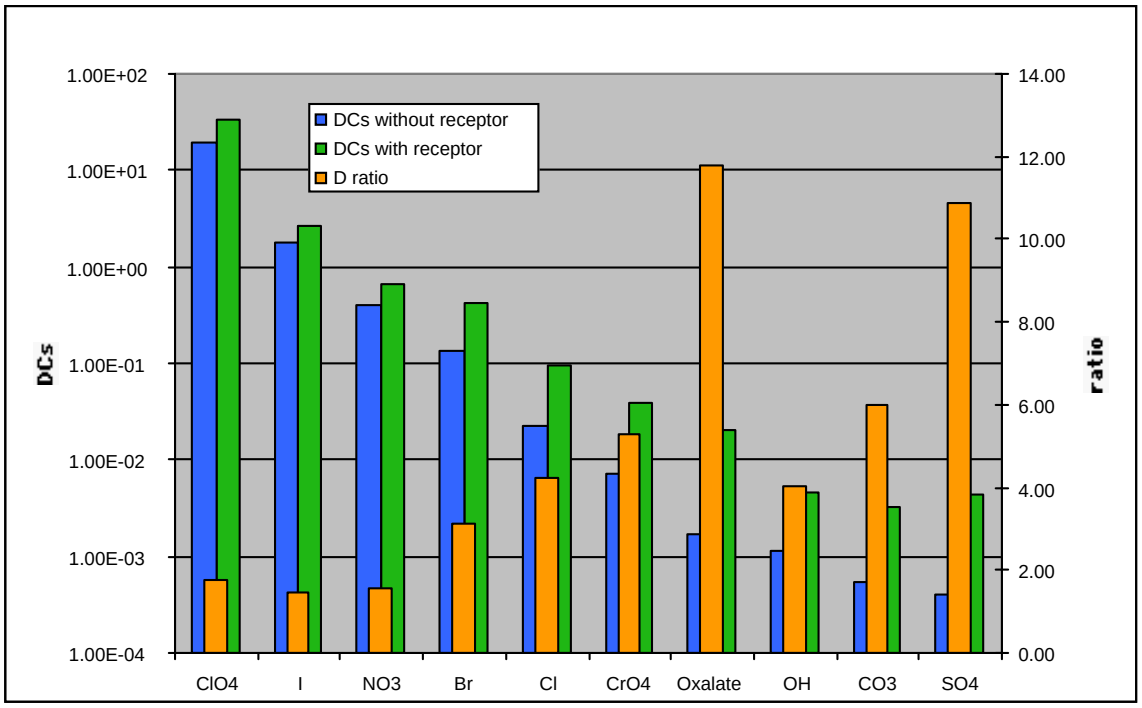


Figure 8. Synergistic extraction of cesium salts into nitrobenzene by dual hosts **13** and BOBCalixC6. The cesium distribution ratio is shown on the left Y-axis, and the enhancement ratio D_{Cs}(**13** + BOBCalixC6)/D_{Cs}(BOBCalixC6 alone) is shown on the right Y-axis.

It was intended to examine the two disparate diluents 1-octanol and toluene most extensively, with more limited extension to other diluent systems. Solubility limitations were encountered for **4** and **13** in toluene. Enhancement of anion exchange is taken quantitatively as the ratio of D_{SO4} in the system with receptor vs the system without the receptor. In no case was extraction by the anion receptor alone sufficient to be taken into account. One may see at once a striking effect of both diluent and receptor type. In 1-octanol, enhancements tend to be weak, which is interpreted in terms of the ability of this diluent to act as both a hydrogen-bond donor and acceptor. Hence, the diluent competes with the receptor for anion binding and with the anion for receiving hydrogen bonds from the receptor. In this medium, **4** somewhat outperforms **14**, and **13** exhibits no activity. Addition of hydroxy hydrogen-bond donors at elevated concentration produces a positive effect. Selected tests were performed at 0.1 M quaternary ammonium salt in 1-octanol (not tabulated), where it was noted, for example, that addition of 10 mM of **4** approximately halved the value of D_{SO4} from 3.6×10^{-1} to 1.9×10^{-1}. This apparent dependence of the enhancement on the exchanger concentration strongly suggests an effect of aggregation.

Quaternary ammonium salts are notorious for aggregating in organic solvents due to their high dipole moments. Hence, the exchanger is presumably at a higher state of aggregation when it is at 100 mM vs. 10 mM. **12** apparently interacts more strongly with nitrate at the higher aggregation state. Unfortunately, it was not possible to examine the

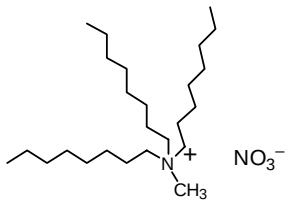
effect of **4** in toluene, as it was not soluble in the presence of the quaternary ammonium nitrate salt. For fluorinated calix[4]pyrrole **14**, the ordering of diluents with increasing enhancement of anion exchange was 1-octanol < 0.5 M tributylphosphate (TBP) in dodecane < 1,2-dichloroethane < toluene < 2:1 hexane:chloroform. It makes sense that in the TBP system, the good hydrogen-bond accepting ability of the phosphoryl oxygen ties up the anion receptor, giving weak enhancement. Enhancements for **14** in toluene and 2:1 hexane:chloroform were quite striking, exceeding three orders of magnitude for the latter. In these two systems, the diluents are not polar nor are they capable of engaging in significant hydrogen bonding. Enhancement tended to correlate inversely with the sulfate distribution ratio without receptor, as anion binding and hence enhancement will be favored in the absence of competing strong solvation effects, which are otherwise favorable for sulfate relative to nitrate.

Table 3. Survey of anion receptors as synergists for anion exchange for various diluents.[a]

Receptor	[Receptor] mM	Diluent	D_{SO4}	Enhancement factor
None	0	1-octanol	4.4×10^{-3}	
9	200	"	9.7×10^{-3}	2.2
10	200	"	1.0×10^{-2}	2.3
11	200	"	1.1×10^{-2}	2.5
12	10	"	7.3×10^{-3}	1.7
13	10	"	4.4×10^{-3}	1.0
14	10	"	6.4×10^{-3}	1.5
None	0	Toluene	3.9×10^{-4}	
10	200	"	3.6×10^{-3}	9.2
14	3	"	2.1×10^{-3}	5.4
15	3	"	2.4×10^{-2}	62
15	10	"	1.9×10^{-1}	490
None	0	1,2-Dichloroethane	1.6×10^{-4}	
15	10	"	7.8×10^{-4}	4.9
None	0	2:1 Hexane/$CHCl_3$	1.7×10^{-4}	
15	10	"	2.0×10^{-1}	1200
None	0	0.5 M TBP, dodecane	2.3×10^{-3}	
15	10	"	5.5×10^{-3}	2.4

[a] All systems run at 10 mM Aliquat 336 in the indicated diluent. The aqueous phase contained 10 mM $NaNO_3$ plus 0.1 mM Na_2SO_4 and $^{35}SO_4^{2-}$ tracer. Contacting at 1:1 phase ratio at 25 °C.

Further efforts have now gone toward understanding the synergistic anion exchange in the presence of a quaternary ammonium nitrate salt **Q**NO_3 with **4** (MMEAM) Experiments were performed in $CHCl_3$. Preliminary equilibrium analysis confirmed synergistic anion exchange for MMEAM (**Figure 9**).



QNO_3

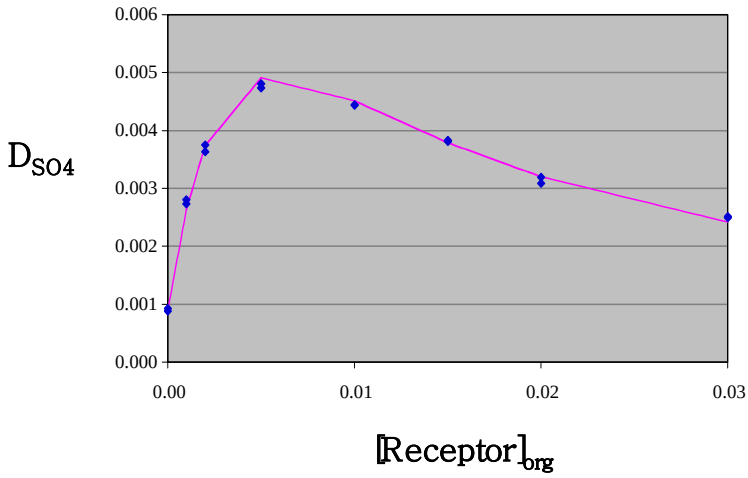


Figure 9. Distribution coefficient as a function of concentration of MMEAM (M) with 10 mM **QNO$_3$** in $CHCl_3$. Aqueous layer = 5 mM $NaNO_3$ and 0.1 mM Na_2SO_4.

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