Inorganic Chemistry
Forum Article
pubs.acs.org/IC

A Case for Molecular Recognition in Nuclear Separations: Sulfate Separation from Nuclear Wastes

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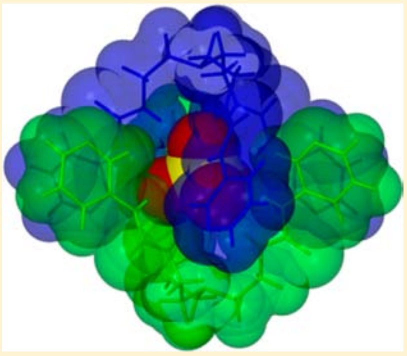


ABSTRACT: In this paper, we present the case for molecular-recognition approaches for sulfate removal from radioactive wastes via the use of anion-sequestering systems selective for sulfate, using either liquid−liquid extraction or crystallization. Potential benefits of removing sulfate from the waste include improved vitrification of the waste, reduced waste-form volume, and higher waste-form performance, all of which lead to potential cleanup schedule acceleration and cost savings. The need for sulfate removal from radioactive waste, especially legacy tank wastes stored at the Hanford site, is reviewed in detail and primarily relates to the low solubility of sulfate in borosilicate glass. Traditional methods applicable to the separation of sulfate from radioactive wastes are also reviewed, with the finding that currently no technology has been identified and successfully demonstrated to meet this need. Fundamental research in the authors' laboratories targeting sulfate as an important representative of the class of oxoanions is based on the hypothesis that designed receptors may provide the needed ability to recognize sulfate under highly competitive conditions, in particular where the nitrate anion concentration is high. Receptors that have been shown to have promising affinity for sulfate, either in extraction or in crystallization experiments, include hexaurea tripods, tetraamide macrocycles, cyclo[8]pyrroles, calixpyrroles, and self-assembled urea-lined cages. Good sulfate selectivity observed in the laboratory provides experimental support for the proposed molecular-recognition approach.

1. INTRODUCTION

Sulfur species in oxidation states 2− to 6+ have been of considerable concern with regard to the production and storage of nuclear waste. One of the outgrowths of this concern has been a recent body of research aimed at the binding and separation of sulfate from nuclear-waste media. While the specifics of this problem alone are sufficient to focus our attention in this review, from a different perspective it is also an opportunity to examine the role of molecular recognition in nuclear separations. Successful technologies must be competitive against a field of alternatives and therefore must fulfill a given industrial need with the least cost. It follows that research is necessitated if existing technologies are either economically unattractive for a given separation need or simply cannot effect the required separation. In this regard, the nuclear industry has provided impetus for an international community focused on solving a great diversity of inorganic separation problems. Because of the peculiar economics of the nuclear industry, in which full-scale separation plants cost \$1B−\$10B or more, the development of sophisticated separation agents based on molecular recognition has been relatively affordable when simple off-the-shelf reagents have not proven adequate. Research on molecular recognition has been further driven within this framework by the need for high efficiency and selectivity and for the very small footprint necessitated by use within expensive shielded cells. Even so, molecular recognition has not been needed for the majority of separations in the nuclear industry. Indeed, group separations have tended to be more valuable. As a famous example, nuclear-fuel reprocessing has evolved around the simultaneous extraction of tetra- and hexavalent actinides by tri-*n*-butylphosphate. Bias-type selectivity has been useful for large ions like Cs^+ and TcO_4^-, which are the least hydrated among univalent cations and anions in the waste, respectively, and therefore are the easiest to partition to ion-exchange resins or water-immiscible solvents. Sulfate separation is a unique case not targeted at removing radioactivity but rather solving a waste-vitrification issue, as will be described in detail below. The lack of attractive options for sulfate separation has driven the investigation of molecular-recognition approaches, and thus sulfate is an illustrative case for discussion.

Potential ramifications of sulfur species in nuclear technologies broadly include decreased effectiveness of vitrification and other waste-form production processes, increased volume of waste forms that must be produced and stored (i.e., limited waste loading), reduced geological waste-

Special Issue: Inorganic Chemistry Related to Nuclear Energy

Received: July 31, 2012
Accepted: October 19, 2012
Published: November 7, 2012

form performance, accelerated corrosion of waste-package materials, and unknown effects on the migration of radionuclides. Our entry into researching this problem area was motivated by the specific need for technologies to remove sulfate from alkaline radioactive salt waste.[1−3] A solution to this challenging problem has the potential to eliminate difficulties with waste vitrification stemming from the low solubility of sulfate in borosilicate glass. Although this opportunity pertains primarily to the U.S. Department of Energy (DOE) Hanford site, general benefits regarding the development of selective anion separations apply to a number of other DOE waste and environmental problems.[4] We were naturally drawn to such problems in connection with our long-term research on the design of new receptors for selective anion binding and extraction.[3] However, given that sulfur plays a larger role in the production and storage of nuclear waste than is reflected in our own focus area, sulfate separation processes in particular may have additional beneficial implications. Accordingly, this contribution examines these broader impacts of sulfur species in general and sulfate separation in particular and summarizes our progress to date in developing the fundamental chemistry needed to ultimately craft effective anion-separation processes applicable to removing sulfate from nuclear wastes. Particular focus will be devoted to synthetic anion receptors that might have a role to play as selective separation agents for the removal of sulfate from complex mixtures, especially those rich in nitrate.

2. ROLE OF SULFUR IN THE PRODUCTION AND STORAGE OF VITRIFIED NUCLEAR WASTE

The DOE has recently reported on the status of its cleanup mission,[5] including its implementation of plans for the remediation of 230 underground storage tanks containing cold-war-era high-level wastes (HLWs). Regarded as the single most important threat to the environment in the DOE complex, the 88 million gallons of wastes stored at the Hanford site, Idaho National Laboratory, and Savannah River Site (SRS) will require a life-cycle expenditure of \$87B−\$117B, representing 36−39% of the total program cost of the DOE Office of Environmental Management, which has the second largest budget within the DOE. Having been developed in large part well over a decade ago,[6] plans for the cleanup of legacy nuclear wastes in the United States have now advanced to the construction of large facilities for the pretreatment and vitrification of the tank wastes. The Hanford site and SRS have the preponderance of the waste and will be the focus of this summary. The Defense Waste Processing Facility (DWPF) at the SRS has been vitrifying HLW sludge since 1996, producing over 3000 canisters (2 m^3 apiece) of glass as of October 2010.[7] The Hanford Waste Treatment Plant (WTP) and the Savannah River Salt Waste Processing Facility (SWPF), currently scheduled to begin operation in 2019 and 2015, respectively, are both under construction. The WTP will pretreat the Hanford tank waste to produce HLW glass, originally destined for geological storage at Yucca Mountain, and low-activity-waste (LAW) glass, destined for on-site storage. At the SRS, the LAW waste stream from the SWPF will go into grout ("saltstone") for on-site storage, while the separated radionuclides (mainly ^{137}Cs and minor amounts of ^{90}Sr and actinides) will be vitrified at the DWPF for geological storage, also originally destined for Yucca Mountain. Loaded glass canisters are currently being stored on site at the SRS until the Yucca Mountain repository is opened, which is now uncertain, or another destination is determined. Interim salt-waste treatment has begun at the SRS as of May 2008[8] and will likely be implemented at Hanford.[9,10] Interim salt-waste treatment, which also serves to relieve near-term tank-space limitations, will accelerate the tank-waste cleanup by processing lower-activity waste streams in modular units in advance of operation of the WTP and SWPF.

Sulfate presents a problem for vitrification and storage in being relatively insoluble in borosilicate glass, the waste form selected for HLW disposition.[11] Chemically, the insolubility arises because sulfate does not contribute to the glass polymeric network, tending to remain as discrete ions in voids in the matrix.[12] The solubility is usually given as roughly 1 wt % SO_3 (as the formal sulfur-containing component), although allowing for variability with glass composition, the solubility limit can lie in the range 0.5−1.4 wt % SO_3.[13] Maintaining the waste loading of the glass to stay below the sulfate solubility limit avoids problems with processing and glass durability, and as a consequence, a 10−30% higher (possibly even more)[14] LAW glass volume must be produced at Hanford, extending the time of LAW treatment by up to 8 years and thereby compromising plans to accelerate the Hanford cleanup.[5,15,16] Even below its solubility limit, sulfate decreases glass durability.[17,18] Sulfate itself has a relatively high leach rate from the glass, comparable to Na^+ and Cs^+,[11] which follows from its weak inclusion in the glass. Above its solubility limit, sulfate solidifies in separate phases in the glass, and the sulfate leach rate increases an order of magnitude. Through complexation, sulfate increases the mobility of actinides,[19] although not as much as carbonate, and thus its release from glass through leaching could represent a factor in actinide transport.[20] Multiphase glass heterogeneity itself leads to degraded leaching performance.[11] Thus, the presence of sulfate in glass represents a general concern in terms of predicting glass and repository performance.

The greatest risk associated with excessive levels of sulfate in waste immobilization, at least insofar as issues recently driving the need for sulfate mitigation,[1,2] lies in the impact of sulfate on the vitrification process.[21,22] Above its solubility limit, sulfate has long been known to separate as a molten salt phase that migrates to the top of the molten glass phase.[23] Such sulfate segregation above its solubility limit has been observed in various laboratories, with multiple waste compositions, a wide range of glass compositions, and different types of melting equipment.[13,15,17,18,22−25] Often-cited potential problems associated with sulfate segregation include inhibition of the melt rate, corrosion of the melter and superstructure components, and short-circuiting of the melter electrodes.[1,2,21,22] Corrosion of the melter carries the safety risk of a steam explosion associated with the release of cooling water,[26] leading to strict limits and monitoring of sulfate loading into glass.[21] Plugging[27] and corrosion[21] of the off-gas handling system owing in part to the sulfate−SO_3 equilibrium (i.e., SO_3 volatility)[12,18] represent additional concerns. Because sulfate is a nonnegligible ionic constituent of tank wastes at the Hanford site, SRS, and Idaho National Laboratory, it follows that its concentration must be closely monitored overall to avoid these vitrification risks. At the SRS, the average sludge feeds expected at the DWPF corresponded to tolerable sulfate levels of several tenths of a percent of sulfate in the expected glass compositions.[28] However, recent sludge batches containing higher sulfate levels originating from ferrous sulfamate and hydroxylamine sulfate additions in solvent-extraction processes have led to further investigations examining the question of higher sulfate limits, whereupon it was found that at least 0.6% sulfate could be accepted.[22,29] The problem is most acute at Hanford, though, where it has been decided to vitrify even the LAW.[6] Elevated levels of sulfate in the Hanford LAW would cause the SO_3 loading to exceed the solubility limit at otherwise desirable waste loading, such that sulfate becomes the limiting constituent.[1,2,15,16] The impacts of sulfate loading on Hanford LAW vitrification received considerable attention in the 1990s[13,18,23,24] and were taken into account in the initial glass optimization, indicating that up to 1.0% SO_3 could be accommodated.[17] As the DOE nears a decision to employ bulk vitrification of Hanford LAW,[5] sulfate remains a limiting constituent and consideration in glass performance.[15,16] LAW glass durability does not represent a geological repository performance issue, though, because the LAW glass will be stored on the Hanford site.

To avoid simply tolerating an increased glass volume and longer overall cleanup schedule, an obvious sulfate mitigation strategy could entail reformulation of the glass or even adoption of a different waste form.[24,30] For example, it is known that high phosphate content increases the solubility of sulfate,[13,17] leading to examination of the sulfate retention in some phosphate glasses.[24] The increased sulfate solubility obtained was also associated with a higher volatility of SO_3, which was viewed as a potential benefit as being in effect a SO_3 separation.[24] However, it was noted that phosphate glasses promote melter corrosion,[11,24] and greater SO_3 evolution would also place a burden on off-gas treatment. By contrast, iron phosphate glasses have excellent durability and high sulfate compatibility,[31,32] and recent corrosion tests have shown good results.[14,31] Other borosilicate formulations involving CaO,[12] V_2O_5,[12] or barium[33] yield higher SO_3 solubility and have merits, although CaO or V_2O_5 did not prove effective with certain frit compositions.[22] Alternatively, ceramic waste forms for LAW are being examined, which effectively departs from the conventional vitrification paradigm.[30,34] Aluminosilicate hydroceramics based on metakaolin offer an advantage of economical processing and, by contrast to Portland cement saltstone, high salt compatibility, although calcination would be required for high nitrate−nitrite contents. Steam reforming also produces an aluminosilicate waste form of interest.[16,34] The available waste-form options have been summarized, and a downselected set has been evaluated from the point of view of reducing the large cost of vitirification of the Hanford tank waste.[30] While it will be a challenge to improve upon the advantages of the baseline borosilicate waste form and to overcome the inertia of decades of successful international experience, the study found that there is incentive to consider further other waste-form types, including alkali aluminosilicate glasses, iron phosphate glasses, and titanate-based ceramics, all of which can be produced in Joule heated melters.

Sulfur in its lower oxidation states plays a role in metal corrosion and therefore can affect waste-package and repository performance. Corrosion rates of the outer containers of waste packages ultimately determine the effective time that underground repositories can prevent release of their contained radionuclides into the environment. The effectiveness of waste containers in this regard depends upon the robustness of passive surface oxide films, and any chemical species that can disturb such films will therefore have an impact on the corrosion rates. Sulfur is thought to play such a role,[35] as considered at length in a recent review of the long-term corrosion of Alloy 22, the corrosion-resistant Ni-22Cr-13Mo-3W-4Fe alloy that has been intensively examined for use in the proposed Yucca Mountain repository.[36] Impurity sulfur atoms within the metal itself can form a surface layer, displacing the passivating oxide layer over many years. Depending on the starting assumptions, it is thought to take at least 500 years for corrosion to take place to the extent that sufficient sulfur atoms may be segregated at the surface in a monolayer. Experimental evidence for this process, called anodic sulfur segregation, has been presented in which the accumulated sulfur was found to be in its zero oxidation state.[37] During anodic sulfur segregation, corrosion may accelerate, although taking into account factors that could lead to repassivation and subsequent depassivation−repassivation cycles led to the conclusion that the waste-package lifetime was unlikely to be significantly reduced.[36,38] Nevertheless, this proposed complex corrosion mechanism and uncertainty in its conclusion remain to be demonstrated and experimentally validated for Alloy 22 under repository-relevant conditions. In view of the uncertainty, it was noted that the risk of anodic sulfur segregation could be reduced by decreasing the sulfur content of the alloy from its value of ca. 5 ppm.[36]

Other corrosion mechanisms related to Alloy 22 waste packages for Yucca Mountain disposal have been considered.[36,39] These can potentially involve sulfur as sulfate in the groundwater. It should at first be noted that the composition of Yucca Mountain water is considered to be relatively benign and is unlikely to cause localized corrosion of Alloy 22.[36] Further, sulfate was found to confer an inhibitory effect on localized corrosion on Alloy 22.[39,40] However, the variable behavior of sulfate under different conditions, where in some cases sulfate has been found to induce corrosion, led to the observation that there is no consensus yet on the role of sulfate in localized corrosion.[40] Moreover, the effect of microbial action on corrosion, particularly by the sulfate-reducing bacteria known to be present in Yucca Mountain groundwater, remains to be clarified and is under active examination.[39] The possibility of accelerated corrosion by displacement of the passivating oxide layer on Alloy 22 by reduced forms of sulfur deposited by the microbial reduction of sulfate does not seem to have been considered. Other questions remaining to be considered entail the effect of a high concentration of sulfate in the borosilicate glass waste form on waste-form integrity and on radionuclide migration upon eventual failure of the waste packages in the geological repository.

3. TRADITIONAL SEPARATION METHODS APPLICABLE TO SULFATE

Separation of sulfate represents a potential solution to the problems associated with the production and storage of vitrified nuclear waste as summarized above.[41] Techniques applicable at the industrial scale for sulfate removal from aqueous solution include bioreduction, chemical reduction, precipitation, anion exchange, adsorption, electrodialysis, reverse osmosis (RO), and liquid−liquid extraction. As discussed further below, most of these methods have been examined or used in a range of applications from dilute media such as groundwater[42,43] and mine drainage[44,45] to brines such as seawater,[46] chloralkali electrolyte,[47] and nuclear waste.[41] Reasons for removal are quite varied, including prevention of scale formation, wastewater treatment to meet environmental release standards, and mitigation of interference with industrial processes. Some of the leading technologies have been considered for sulfate removal from the alkaline nitrate tank wastes stored at the Hanford site,[16,41] but no technology has yet been found sufficiently promising to proceed with implementation.

On the basis of the same biochemistry that allows wetlands to efficiently reduce sulfate and nitrate inputs based on microorganisms,[48] particularly sulfate-reducing bacteria, bioreduction has attracted considerable interest for sulfate removal. The technology may be applied in either passive environmental systems[43,49] or bioreactors.[44,50] Production of sulfide, which can present corrosion or toxicity issues,[51] must be considered, but it can also be useful in the precipitation and coremoval of metals.[43,44,50]

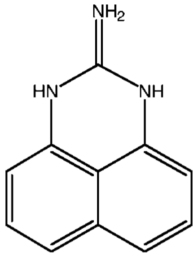
A number of membrane techniques have been used for different applications. RO has been examined and shown to be viable in applications where more-or-less all electrolytes are removed,[45,52] and thus this technique cannot be expected to be useful for selective electrolyte separation.[53] Nanofiltration, a variant of RO, employs negatively charged nanoporous membranes that exhibit charge discrimination based on Donnan exclusion and thereby can usefully concentrate sulfate (by rejection) from univalent anions like chloride.[42,45,47,53] Electrodialysis has been examined for sulfate concentration, but its application is limited to low ionic strengths and solutions where selectivity is not critical, such as in deionization or desalination applications.[54]

Inorganic materials functioning by ion exchange or adsorption have been examined, with mixed results. Layered double hydroxides as a class of inorganic ion exchangers exhibit good selectivity for sulfate in the absence of a high concentration of carbonate.[55] Feldspar and clay materials were only modestly effective,[56] and bentonite was at best poor.[42] Hydrous iron oxides are known to have an affinity for sulfate. In experiments in which sulfate was coprecipitated on increasing the pH of solutions of $FeCl_3$, good sulfate removal was observed at pH 4.[57] Binding appeared to occur by inner-sphere coordination of the sulfate anion as a ligand on the metal.

Having wide applicability to dilute as well as concentrated solutions, precipitation or crystallization is a widely used and potentially highly selective industrial technique for sulfate separation from aqueous electrolytes. It may be appreciated that the possibilities for crystallization of an insoluble sulfate salt largely depend on the composition of the electrolyte and the particular means for creating the insolubility condition, such as evaporation, temperature change, or addition of metal ions or other precipitating agents. Simple evaporation of Hanford LAW salt solutions has, in fact, been proposed based on expected crystallization of $Na_6(SO_4)_2CO_3$ (burkeite).[58] This fractional-crystallization approach has definite appeal in not adding more mass to the waste and potentially has the ability to bring down sulfate levels to well below the sulfate solubility limit of borosilicate glass. Depending on the waste composition, $NaNO_3$ and $Na_2CO_3{\cdot}H_2O$ crystallize also,[58,59] and it has turned out that fractional crystallization by evaporation has been of greater interest recently in terms of a bulk sodium removal from medium Curie waste streams.[60−62] Such a strategy concentrates radionuclides in the liquid supernatant phase, and redissolving the solid salts yields a LAW stream. When considered only as a sulfate removal process, though, evaporation is considered to be not sufficiently selective or efficient.[41,59] Nevertheless, it may be expected that burkeite crystallization would be selective from high-sulfate waste compositions, where it would be the first phase to crystallize, especially taking advantage of its retrograde solubility (i.e., decreases with increasing temperature, in contrast to that of $NaNO_3$).[58,60]

In general, the classical addition of alkaline earth and certain other divalent metal ions has been widely practiced for analytical to tonnage-scale sulfate separations in which the corresponding sulfate salts or sometimes double salts like ettringite,[63] $Ca_3Al_2O_3{\cdot}CaSO_4$, precipitate. The addition of a calcium ion to precipitate gypsum is a common low-cost industrial method for streams containing >1 g/L sulfate. It has been used for decontamination of anaerobic digesters,[64] textile wastewaters,[65] laboratory wastewaters,[66] and mine[45] and agricultural[67] drainage waters, for example. Sulfate precipitation using barium[65−67] and even lead[65] is commonly employed also, taking advantage of the exceptionally low solubilities of their sulfate salts. The use of alkaline-earth cations as precipitating agents was examined for sulfate removal from Hanford tank wastes.[16,41,68] The direct addition of alkaline-earth nitrates or chlorides to the alkaline waste proved ineffective, primarily owing to insufficient selectivity, resulting in excessive precipitated solids. Carbonate is the main competing bulk anion, but fluoride, chromate, and phosphate at lower concentrations were also found to precipitate. The use of barium required a prestrike with calcium nitrate to bring carbonate out of the solution, but selectivity remained an issue, and the limited solubility of barium nitrate in water led to undesirable dilution of the waste owing to the significant volume of the barium nitrate solution that had to be added. In addition, the use of toxic metal barium entails additional regulatory complications involving the generation of a mixed radioactive and hazardous waste. On the other hand, preacidification of the Hanford alkaline waste eliminates the competition from carbonate, and sulfate precipitation with a strontium ion under these conditions was found to be effective and recommended for further development.[16]

In addition to alkaline-earth metal precipitation approaches, several organic amine precipitants for sulfate may be usefully mentioned. As such, organic amines require acidic to neutral conditions to function as ammonium countercations for sulfate. Inspired by an older literature on analytical reagents,[69] workers tested 2-aminoperimidine for its ability to precipitate sulfate from Hanford alkaline tank waste.[41] Used under alkaline conditions where it would not be expected to function properly in any case, this compound quickly degraded and was therefore ineffective. This compound and related ones are worth noting, however, in view of both the low solubility of their sulfate salts and good selectivity versus nitrate and other competing anions.[70] Moreover, the crystal structure involving a related oxoanion, ethyl sulfate, has been examined to elucidate the origin of sulfate selectivity, revealing extensive hydrogen bonding together with $\pi-\pi$ stacking of two perimidines oriented in opposite directions so as to propagate the hydrogen-bonding network.[71] Thus, it may be argued that an elementary degree of sulfate "recognition" is exhibited by this system. Defining recognition in terms of complementary bonding with a function,[72] we may accordingly see this system as combining a strong $N-H\cdots O$ hydrogen-bonding interaction that gains strength from the relatively high charge density of sulfate and a functional aspect involving the $\pi-\pi$-stacking interaction that contributes to the lattice stability. This favorable combination of properties was already appreciated in developing an understanding of the sulfate selectivity in precipitation by related 4-amino-4′-halogenodiphenyls.[73] More recently, process development with simple amines including ethylamine and isopropylamine as precipitating solvents has been described for sulfate removal from seawater[45] and Hanford tank waste.[74]



2-Aminoperimidine

Cationic inorganic amine complexes, such as the hexamminecobalt(III) ion,[75] $[(NH_3)_6Co]^{3+}$, also have been useful as precipitants for sulfate.[76] Typical stoichiometries for crystallization of divalent anions with hexamminecobalt(III) include a halide, as in $[(NH_3)_6Co]ClX{\cdot}3H_2O$, X = SeO_4^{2-} and MoO_4^{2-},[77] where electrostatic and hydrogen-bonding interactions apparently stabilize the lattice.[78] The addition of solid $[(NH_3)_6Co]Cl_3$ to a Hanford tank supernatant waste solution was unfortunately unsuccessful in achieving significant removal of sulfate upon filtration of the mixture.[41]

Well-known in chromatographic analytical applications,[79] anion exchange is considered to be an effective and standard industrial method for the removal of sulfate up to several grams per liter where typically competition from other anions is not severe. In such applications, work has largely been limited to strong- and weak-base anion-exchange resins and regeneration with brine. Weak-base resins exhibit stronger sulfate affinity[80] in that the sulfate can more closely approach the cationic charge of the protonated amine and gain the benefit of hydrogen bonding. The affinity of styrene−divinylbenzene resins for sulfate follows the order polyamine > tertiary amine > quaternary amine.[80] Indeed, quaternary amine groups with longer chains, such a propyl, reject sulfate in preference for nitrate.[81] Typically, anion-exchange resins select charge-diffuse anions and for univalent anions follow the order, for example, $AuCl_4^- > ClO_4^- > I^- > Br^- > Cl^- > F^-$,[82] which may be said to be Hofmeister in nature. The connection between anion separation selectivity and Hofmeister's original order[83] of anion effects on salting-out of egg-white protein has been reviewed and is explained further below.[84] For anion-exchange resins, the selectivity has been explained primarily according to relative anion hydration and ion-pairing electrostatic interactions between the resin-immobilized cationic group and the anion,[85] although other factors are also operative.[82] Thus, it is possible to influence the anion selectivity by varying the structure of the ammonium group to control the ion pairing and also add hydrogen-bonding ability. For instance, type II resins have triethanolammonium groups. However, the effect is mainly to attenuate the Hofmeister bias rather than to reverse or change the order, at least for monovalent anions.[85] In terms of selectivity, divalent anions have an advantage called "electroselectivity", which refers to the inverse second-power dependence of divalent ion uptake on the concentration of the competing monovalent anion.[86] Accordingly, if the resin is in the nitrate form and not highly loaded with sulfate, the distribution ratio for sulfate will decrease to the second power of the nitrate concentration. However, these same considerations also mean that sulfate can be exchanged strongly if the aqueous nitrate concentration is sufficiently low, which is often the case. Although this consequence of mass action would appear to violate the Hofmeister selectivity, the thermodynamic exchange equilibrium constants for a trimethylammonium resin actually decrease for exchange of a monovalent anion with an anion of higher charge.[85]

Interestingly, polyamine backbone functionalities clearly confer relatively high sulfate selectivity over nitrate, as explained essentially by the complementarity of adjacent protonated sites for divalent versus monovalent anions.[80] The figure of merit in comparing the sulfate selectivity from system to system is the unitless selectivity factor, α_{SO_4/NO_3}, which in the present application is taken as the ratio of the sulfate distribution ratio D_{SO_4} to the nitrate distribution ratio D_{NO_3}. Whereas the selectivity factor is approximately constant for monovalent−monovalent exchange, for example, it is unfortunately dependent upon the composition for divalent−monovalent exchange because it becomes the product of the thermodynamic exchange constant K_{SO_4/NO_3} and the nitrate distribution ratio (neglecting activity coefficients). Thus, it is important to compare values of α_{SO_4/NO_3} for a defined composition or take into account its expected variation. Accordingly, if we expect an aqueous nitrate concentration of 3 M and a resin capacity of 2 mequiv/g, for example, the target selectivity factor needed would be $\alpha_{SO_4/NO_3} \geq 1.5$, assuming we require $D_{SO_4} \geq 1$ and the loading of sulfate is low. Commercial polyamine resins tested in an aqueous system containing 0.005 N $NaNO_3$−Na_2SO_4 exhibited particularly high sulfate selectivity, yielding α_{SO_4/NO_3} values in the 10-fold range 12.7−137.[80] Other resins gave much lower selectivity factors, with quaternary ammonium resins being the lowest. If α_{SO_4/NO_3} decreases with the first power of the aqueous nitrate concentration, then it will be expected to fall 2−3 orders of magnitude for tank-waste nitrate concentrations of 0.5−5 M. This would suggest a borderline performance but possibly one worth testing, albeit after neutralization or acidification of the waste.

Sulfate removal by anion exchange has been demonstrated in a number of applications. Using a type II strong-base resin, good sulfate removal was reported from groundwater, for example.[42] Sulfate removal from copper mine effluent was accomplished using a type I strong-base resin.[87] The use of a weak-base resin was reported for the removal of sulfate from seawater as a pretreatment for distillation,[88] where the rather inefficient sulfate removal was offset by a cheap stripping using recycled distillation brine and the lack of brine-disposal issues. Given the high competing nitrate concentration in the Hanford tank wastes, it may be expected that the usual anion-exchange approach using quaternary ammonium-type resins would be grossly inefficient; further, stripping by displacement would likely cause significant secondary-waste issues. No attempts to use strong-base resins for this application have been reported. However, a novel proprietary resin tested on Hanford supernatant tank waste turned out to be ineffective because of either a lack of sufficient sulfate affinity or its apparent degradation.[41,89]

Although liquid−liquid extraction is normally associated with high selectivity, it generally selects *against* sulfate and thus has not proved very useful for applications where the competitive extraction of sulfate from other electrolyte ions is required. Sulfate extraction is a challenge owing to the high hydration

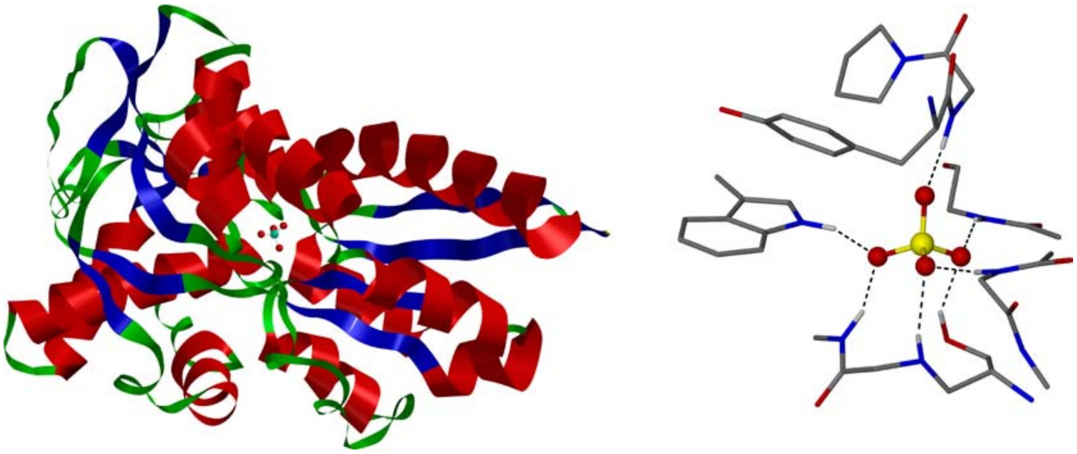


Figure 1. X-ray crystal structure at 1.7 Å resolution (left) and the anion-binding site in the *Salmonella typhimurium* sulfate-binding protein (right). Seven well-defined hydrogen-bonding interactions coordinate the anion. Structures were generated from coordinates taken from the Protein Data Bank.[105]

energy of this particular dianion, −1090 kJ/mol, compared with hydration energies of −306 kJ/mol for nitrate and −347 kJ/mol for chloride.[90] Generally, solvation of an ion by the solvent molecules is weaker than its hydration in the aqueous phase, and this effect is enhanced as the hydration energy increases.[91] As a result, the observed selectivity in simple liquid−liquid anion exchange follows Hofmeister behavior, meaning that charge-diffuse ions are preferred.[84,91] The generally observed order of extraction, commonly termed Hofmeister bias, is

$$PO_4^{3-} < CO_3^{2-} < SO_4^{2-} \ll Cl^- < Br^- < NO_3^- < SCN^- < I^- < ClO_4^-$$

In an application such as the removal of sulfate from the Hanford tank waste, nitrate is the typical bulk anion, and sulfate is consequently poorly extracted in competition. We earlier outlined the challenge of competitive sulfate extraction together with strategies for overcoming its high hydration energy.[3] In the absence of any anion-binding agents, as expected, we observed poor extraction of sulfate from a nitrate matrix using a quaternary ammonium nitrate extractant (see section 8). For completeness, one should be aware that sulfate can be made to distribute into an organic solvent using lipophilic amine extractants, such as trioctylamine or Alamine 336 (a tertiary amine with a mixture of octyl and decyl groups), where the driving force is protonation of the amine under fairly acidic conditions.[92,93] The organic-phase sulfate exchanges avidly for more charge-diffuse aqueous anions, making possible a number of industrially important hydrometallurgical processes for the recovery of metals such as uranium, molybdenum, and vanadium.[94−96]

4. ANION-RECOGNITION STRATEGIES TOWARD SULFATE SEPARATION

From the technology survey outlined above, elements of recognition for sulfate are largely absent in prior approaches to selective separation, although early thinking along these lines actually began over a half century ago in the study of selective precipitants[73] and over a quarter century ago in appreciation of the effect of complementarity of polyamine resins for divalent anions in ion exchange (see below for a further explanation of the concept of complementarity).[80] The basic challenge in developing a specific sulfate receptor has been the need to overcome the high hydration energy for this anion relative to competing anions.[90] That is, to bind sulfate inside an artificial cavity, the driving force of the binding must be at least as strong as the hydration energy lost by the anion. While not overlooking recent ideas regarding the role of entropic factors,[97] the approach taken here in proposing new receptor structures[3] has invoked now classical principles of complementarity[98] and preorganization.[99] According to these precepts, for maximal binding interaction, the cavity must match the size and tetrahedral shape of sulfate, and there should be a degree of rigidity[84] to this cavity to reduce the loss of entropy and conformational strain associated with the rearrangement of the receptor to the binding conformation. Further, if the fit and rigidity prevent other competing anions, including specifically the more abundant nitrate anion present in the waste, from being accommodated, selective removal of sulfate could be potentially achieved.

One inspiration for the design of artificial receptors is the sulfate-binding protein,[100−104] which effects the specific recognition of this anion through seven hydrogen bonds to the bound sulfate anion (Figure 1), as opposed to close-range Coulombic interactions. The protein exhibits an apparent binding constant for sulfate of 5.9×10^6 M[102] or higher.[103] This strong binding succeeds despite the competing strong hydration involving up to 12 hydrogen bonds supplied by water.[106] While it is difficult to prove in the absence of dedicated mutagenesis experiments, it is likely that the multiplicity of weak bonds endows the system with fast-exchange kinetics. Such fast exchange leads, presumably, to a high selectivity as the result of “error correction” in the event that a similar substrate, such as phosphate, is initially bound. To the extent such thinking is correct, it highlights design criteria that would be useful in the case of synthetic receptors and underscores the fact that a large number of hydrogen-bonding donors would be desirable to achieve optimal anion-recognition kinetics and thermodynamics. In the absence of such an idealized arrangement of hydrogen bonds, the use of charged interactions is expected to enhance the sulfate anion affinity, but likely at the price of slower-exchange kinetics (with other important factors being equal, such as rigidity). These are concepts whose merit is being reinforced as a result of our own efforts to develop synthetic receptors for sulfate anion recognition and extraction as described further below.

In the specific case of sulfate extraction, it is deemed particularly important to combine binding with function so as to achieve recognition.[72] Further, a receptor used for this purpose must be designed to move the captured sulfate selectively into another phase such that the resulting receptor−anion complex can be physically separated from the liquid waste. Given that designed receptors are likely to be expensive to produce, a means of releasing the captured sulfate and recycling the receptor is also needed. Available techniques include crystallization, liquid−liquid extraction, ion exchange, and membrane transport. Below we describe efforts in our laboratories to design and synthesize new receptors together with examples of strategies to employ the new receptors in selective sulfate separations using liquid−liquid extraction and crystallization approaches. For completeness, we should mention here that examples of sulfate receptors have also been reported by other groups, as recently reviewed.[107] However, because most of these studies gave little or no considerations to sulfate separation in general, or sulfate removal from nuclear waste in particular, they will not be covered here.

5. COMPUTER-AIDED DESIGN APPLIED TO SULFATE RECOGNITION

Molecular recognition usually requires the presence of multiple binding interactions between the host and guest.[108,109] In order to bind strongly, the host must have binding sites that are of the correct electronic character to complement those of the guest. Moreover, these binding sites must be spaced out to achieve optimal interaction with the guest in the binding conformation of the host molecule. Such a host is said to be complementary for the guest.[98] Host−guest interactions are further maximized when the complementary host architecture is constrained in the binding conformation. Such a host is said to be preorganized.[99]

Along these lines, the design of receptors that will recognize sulfate involves selecting an appropriate set of binding sites and linking them together to achieve a complementary and preorganized geometric arrangement. The design task entails a detailed understanding of both the molecular structure and the nature of host−guest interactions. Molecular models can be used to achieve this understanding. With respect to sulfate, electronic-structure calculations have been used to probe hydrogen-bonding directionality at the oxygen-atom acceptor,[110,111] the conformations of urea and thiourea hydrogen-bonding donor groups,[112,113] and the stable geometries for placing one to six urea groups about a tetrahedral anion.[114] In addition to providing criteria for host design, these data have been used to benchmark and refine a molecular-mechanics model, yielding a rapid method for the assessment of structure and energetics in sulfate−urea complexes.[115] As shown in the electrostatic potential-surface contour map for a positive point charge placed in one of the O−S−O planes of the sulfate anion (Figure 2), hydrogen bonds donated from suitable protic groups would be most favorable when directed along defined cones around each oxygen atom.[111] It is further seen that bidentate hydrogen-bonding donors, such as urea, thiourea, guanidinium, and amidinium groups, would have complementary two-point coordination along any of the six O−S−O edges of the sulfate tetrahedron. Ideally, 12 hydrogen bonds could be used to bind sulfate in this manner, and indeed one sees a collective donation of up to 12 hydrogen bonds in the hydration sphere of sulfate.[106]

Figure 2. (left) Contour map of the electrostatic potential surface for a positive point charge in one of the O−S−O planes of the SO_4^{2-} anion generated at the BP86/DN** level. The four low-energy regions are bound by contours at −275 kcal/mol. Contour lines are spaced at 30 kcal/mol intervals. (right) Most stable complexes formed when the hydrogen atom lies on the surface of one of the four cones attached to the oxygen atoms of the SO_4^{2-} anion. Figure and caption from Figure 7 of ref 111, reproduced with the kind permission of Springer Science and Business Media.

Even with an understanding of how to arrange hydrogen-bonding donor groups about sulfate, the rational design of host structures by assembling sets of disconnected binding sites in three dimensions is not a trivial task. The computer-aided molecular design software *HostDesigner (HD)* has been specifically created to address this issue.[116−119] *HD* generates and evaluates millions of candidate structures in minutes and identifies three-dimensional architectures that structurally organize binding sites for optimal guest interaction. Using a de novo structure-based design approach, building algorithms combine user-input host−guest fragments with linking fragments taken from a library containing hundreds of thousands of entries. During the building process, all possible connectivities, stereochemistries, and conformations are constructed, which generates large numbers of structures. Top candidates are identified after evaluation and ranking.

Following the development of these computer-aided molecular design tools, we have completed a first-of-a-kind study in which de novo structure-based design and high-throughput screening methods were deployed to identify promising anion-host architectures prior to synthesis and binding-affinity measurements.[120] Over 1.8 billion candidate geometries were built and evaluated, 12000 binding energies were calculated, and 3000 conformational analyses were performed to yield a short list of the best candidate architectures. Among this list were several structures known to complex sulfate as well as a number of novel structures that have yet to be explored.

The efficacy of the computational approach was recently demonstrated in the de novo computer-aided design of a self-assembled cage containing a cavity lined with urea groups arranged to give a high degree of complementary for sulfate. The basis for this cavity design came from electronic-structure calculations showing how sulfate can accommodate up to six urea groups, each chelating an edge of the tetrahedral anion.[114] *HD* was used to identify molecular building blocks (L) that could achieve this urea arrangement upon self-assembly with M^{2+} metal cations (M = Ni, Zn), leading to a M_4L_6 tetrahedral cage. Controlled and precise placement of hydrogen-bonding sites gave a host (Figure 3) with unprecedented sulfate affinity in aqueous solution ($K_a \geq 10^6$ M^{-1}),[121] rivaling that observed for the sulfate-binding protein.[102,103] Further studies indicated that, as designed, this cage receptor is shape-selective for tetrahedral oxoanions with charges greater than 2−. Thus,

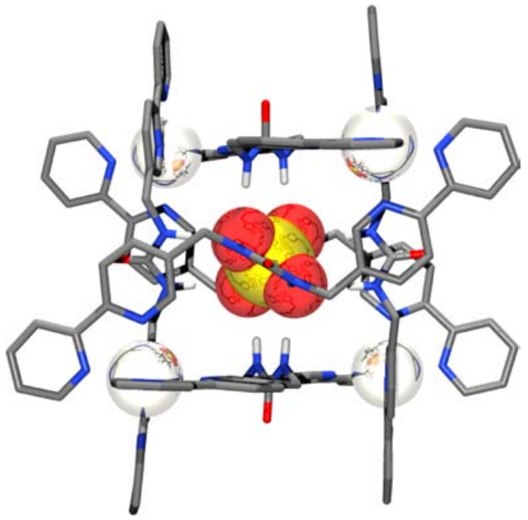


Figure 3. Six urea-containing bis(bipyridyl) ligands assembling with four Ni^{II} or Zn^{II} cations to form a tetrahedral cage that encapsulates sulfate in aqueous solution with exceptional binding affinity and selectivity.[121,122]

besides sulfate, the cage encapsulates PO_4^{3-}, CrO_4^{2-}, SeO_4^{2-}, and MoO_4^{2-} from aqueous solutions but excludes anions of different shapes and charges, such as F^-, Cl^-, Br^-, I^-, NO_3^-, BF_4^-, ClO_4^-, ReO_4^-, PF_6^-, CH_3COO^-, $CH_3SO_3^-$, $CF_3SO_3^-$, CO_3^{2-}, SO_3^{2-}, and SeO_3^{2-}.[122] The divalent tetrahedral oxoanions were found to template the cage self-assembly. Thus, in the absence of such anions, no M_4L_6 tetrahedral cages formed, and other coordination assemblies, such as M_2L_3, were observed instead.

6. SULFATE BINDING BY MACROCYCLIC POLYAZA AND POLYAMIDE RECEPTORS

Polyaza and polyamide macrocycles have been of interest to us as a classical framework for anion binding.[123−127] Reminiscent of the polyamine resins that show high selectivity for sulfate,[80] polyaza macrocycles tend to bind anions very strongly when the amine nitrogen atoms are protonated even in highly polar solvents like methanol and water. Crystal structures and binding studies of sulfate complexed to several polyaza macrocycles have been reported by us[124,125] and others.[128] Unfortunately, polyaza macrocycles have limited utility for extractive tank-waste separations because they are very soluble in water and highly pH-dependent, ultimately becoming neutral and inactive under the alkaline conditions of interest (although they would have revived interest in the context of neutralizing the waste). This problem was circumvented by incorporating amide groups into the macrocyclic framework. A systematic approach to designing these hosts produced the monocycles (**1** and **2**), bicycles (**3** and **4**), and tricycles (**5**) shown in Figure 4. These hosts incorporated either amine or mixed amine−amide hydrogen-bonding groups, 1,3-dimethylaminophenyl (**3**), 1,3-diamidophenyl (**a**), or 1,3-diamidopyridine (**b** and **c**) aromatic spacers, and ethyl ($n = 1$) or propyl ($n = 2$) linkers for these spacers to the secondary (R = H) or tertiary ($R = CH_3$) nitrogen bridgeheads.

Crystal structures were determined for the complexes of a majority of these hosts with sulfate. The amide monocycle **1a** revealed very selective binding for HSO_4^- and $H_2PO_4^-$ ($\log K = 4.50$ and $4.66\ M^{-1}$, respectively) in $CDCl_3$ using NMR titrations.[129] The solid-state structure for the $^nBu_4N^+$ salt of the sulfate complex with neutral **1a** had the anion sandwiched between two macrocycles through eight hydrogen bonds to four amide nitrogen atoms of each neutral monocycle [Figure 5 (**A**)]. The remaining structures for sulfate complexes involved protonated or quaternized amine nitrogen atoms in the macrocycles. The diprotonated pyridine monocycle **1b** binds a single sulfate [Figure 5 (**B**)] with hydrogen bonds from the six amine and amide protons. These protons are directed into a "pocket" that is formed when **1b** folds back onto itself at the two amine nitrogen atoms. Enhanced anion binding is generally observed when the *m*-xylyl group is replaced by pyridine.[126,130,131] The effect of monocycle amine substitution [tertiary (**2b**) vs secondary (**2c**)] on anion binding was also studied. Superior binding was observed with **2c** [$\log K$ of **2b** and **2c**, 1.86 and $4.81\ M^{-1}$ in dimethyl sulfoxide (DMSO)-d_6, respectively].

Bicyclic hosts can encapsulate sulfate as shown in Figure 6 (**E**−**G**), or they can bind it externally as in **H**. The sulfate complexes of diprotonated cryptands **4b** and **4c** crystallize as the sulfate salts $[H_2\mathbf{4b}(SO_4)]$[132] and $[H_2\mathbf{4c}(SO_4)(H_2O)_2]$.[133] Sulfate anions are held inside the cavity with eight and seven hydrogen bonds in **4b** and **4c**, respectively. Host **4b** showed very high binding for sulfate in nonpolar solvents such as $CDCl_3$ and CD_3CN ($\log K = 4.96$ and $4.74\ M^{-1}$, respectively), but the binding decreased substantially in DMSO ($\log K = 1.83\ M^{-1}$).[132] Cryptand **4c** showed better affinity for sulfate even in DMSO ($\log K = 3.43\ M^{-1}$), presumably because of the larger cavity produced by the propyl linkers.[133] Flexible propyl linkers allowed the neutral host **4c** to be readily quaternized by methylation of the two tertiary amines. $\mathbf{Q_24c^{2+}}$ gave a cryptand with a totally different conformation. Several water molecules

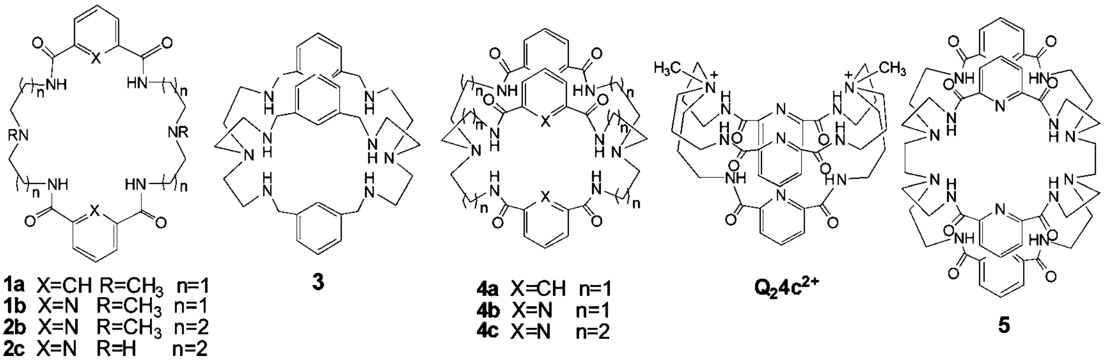


Figure 4. Monocyclic (**1**), bicyclic (**2**), and tricyclic (**3**) hosts.

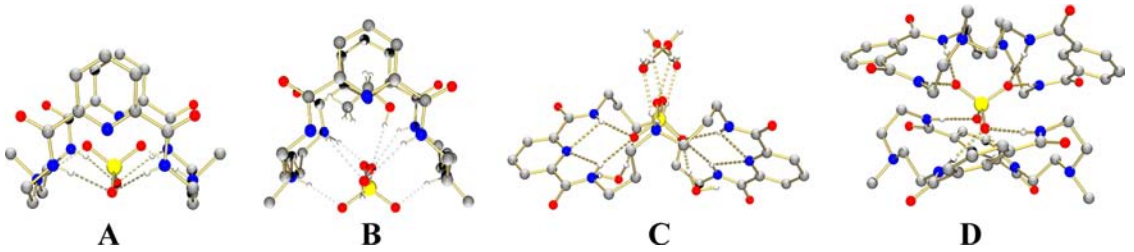


Figure 5. Crystal structures of sulfate complexes of **1a** (**A**), **1b** (**B**), **2b** (**C**), and **2c** (**D**).

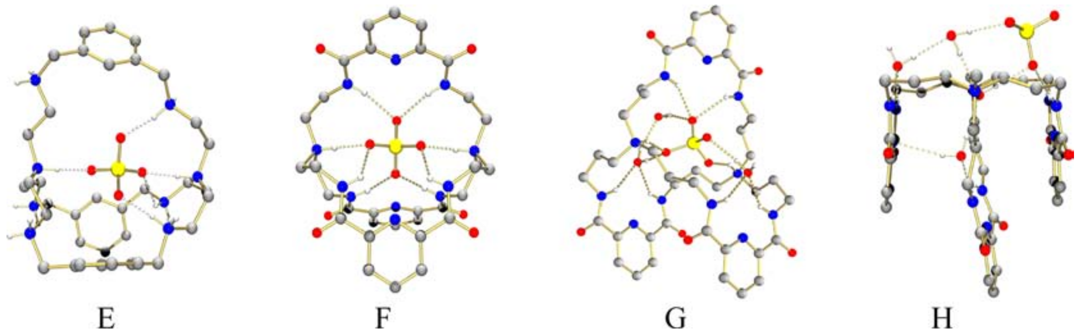


Figure 6. Crystal structures of sulfate complexes of **3** (**E**), **4b** (**F**), **4c** (**G**), and Q_2**4c**$^{2+}$ (**H**).

form a hydrogen-bonded network that threads through the inside of this bowl-shaped macrocycle and is hydrogen-bonded to the sulfate anion on the "top" of the macrocycle [Figure 6 (**H**)]. While sulfate binding to the polyaza host **3** resembles that for **4b**, the anion is held by only five hydrogen bonds in **E**.[132] This demonstrates the differences between nonpreorganized polyammonium cryptands and preorganized polyamide-based cryptands.

The tetraprotonated tricycle **5** also forms a 1:2 crystalline disulfate salt. Two sulfates and two water molecules are partially included in the cavity of the tricycle (Figure 7). The low affinity of this host for sulfate is presumably due to a guest−host mismatch of size and shape because this host was found to be very selective for linear anions such as FHF$^-$ and azide.[134]

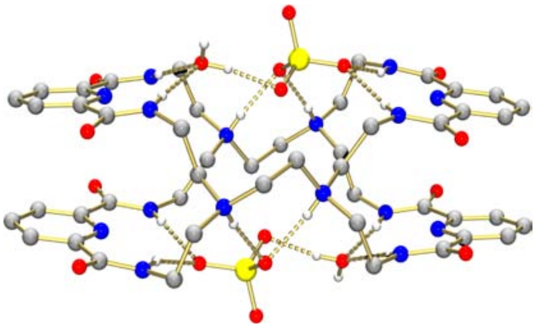
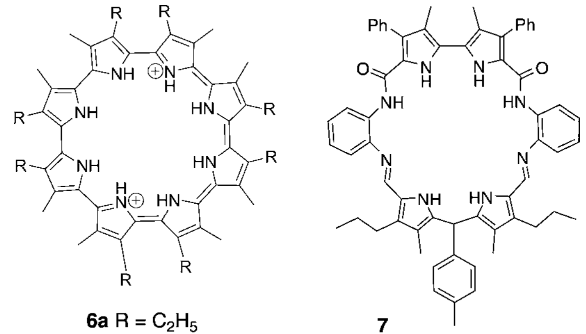


Figure 7. Crystal structure of the sulfate complex of **5**.

7. SULFATE BINDING AND EXTRACTION BY CALIXPYRROLES AND POLYPYRROLE MACROCYCLES

In 1990, we discovered that the diprotonated form of sapphyrin, a pentapyrrolic expanded porphyrin, formed a stable complex with the fluoride anion in the solid state.[135] This binding ability was found to be rather general in that it held for most expanded porphyrins and was applicable in a range of solvent environments, particularly those that were less polar. However, it was not until 2002 that a diprotonated form of the expanded porphyrin, cyclo[8]pyrrole (**6a**, Figure 8), was found to bind the sulfate anion, both in solution, as inferred from slow anion-exchange kinetics, and in the solid state.[136] A structural view of the sulfate complex of **6a** is shown in Figure 9, revealing involvement of all oxygen atoms of sulfate in hydrogen bonding. Owing to extensive electron delocalization, the cyclo[8]pyrrole remains relatively planar when complexed to sulfate, drawing two of the oxygen atoms more into the cavity with three hydrogen bonds each from the pyrrolic NH groups. The other two sulfate oxygen atoms lie above the receptor plane, each having a single hydrogen bond. The good complementarity of the cavity for sulfate and rigidity of the receptor led us to propose experiments to examine the sulfate selectivity in liquid−liquid anion exchange. However, the initial system **6a**, as prepared (R = C_2H_5 in Figure 8), was not sufficiently soluble in organic media (i.e., lacked a high enough organic/aqueous partition ratio) to make it suitable for use in



6a R = C_2H_5
6b R = $C_{11}H_{20}$

7

Figure 8. Cyclic pyrroles, including two alkyl-substituted derivatives of cyclo[8]pyrrole, **6a** and **6b**, and diamidodipyrromethane **7**. Whereas **6a** and **6b** receptors bind sulfate in their diprotonated forms, **7** functions as a neutral receptor and therefore requires a countercation.

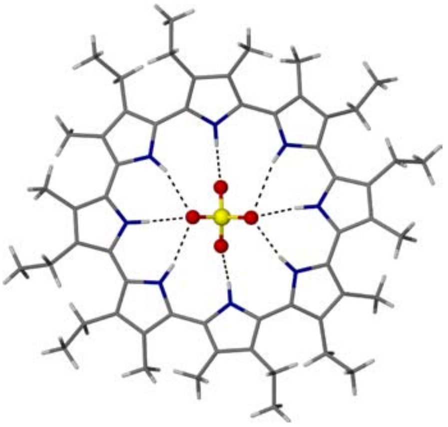
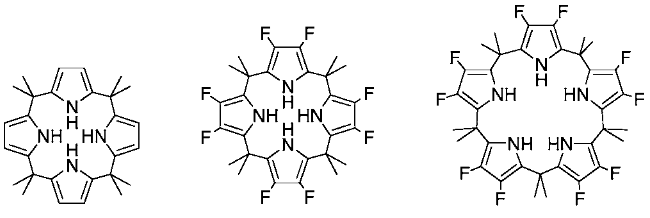


Figure 9. Solid-state structure of the sulfate complex of **6a** stabilized by the diprotonated form of cyclo[8]pyrrole.[136].

extraction. Therefore, a more soluble version (**6b**, R = $C_{11}H_{23}$) was prepared. This system proved highly effective as a sulfate anion extractant under neutral conditions and behaved as expected for exchange, with an inverse second-power dependence of the sulfate distribution ratio versus the competing nitrate concentration being observed.[137] At concentrations of sodium nitrate up to 3 mM, sulfate distribution ratios exceeding unity were seen using 0.5 mM $[H_2\mathbf{6b}]^{2+}(NO_3)_2$ in toluene as the extractant; these values increased to 1000 when the competing nitrate concentration was reduced to 0.3 mM. The selectivity factor (α_{SO_4/NO_3}) at 10 mM aqueous $NaNO_3$ was 3.4. This value compares favorably with those found for anion-exchange resins[80] and is 1 order of magnitude higher than that found for the best synergized liquid–liquid anion-exchange system examined (see the next section). While representing an important step forward, this first-generation extractant was plagued by slow-exchange kinetics, even when a phase-transfer catalyst was added. While further studies are warranted and desirable, one explanation, inspired by the example of the sulfate-binding protein,[100−104] is that the cationic charge present in the system serves to impede fast anion exchange, even though it presumably plays a critical role in enhancing the binding thermodynamics and hence the overall extraction process. Additional factors may be equally important; these include the weak solvating environment of the organic phase and the rigidity of the receptor, both of which would be expected to lead to a sizable activation energy for the exchange process.

The consideration that one or more positive charges within the receptor system, an inherent feature of most expanded porphyrins, were correlated with less-than-ideal kinetic performance has inspired the study of neutral sulfate anion receptors containing pyrrolic entities. In recent years, we have prepared and studied several of these, including **7** (Figure 8), where the sulfate anion is coordinated by multiple hydrogen-bonding interactions.[138−140] However, as yet, these systems have not been explored as sulfate anion extractants.

Neutral, pyrrole-based receptors that have been studied for anion extraction include the so-called calix[*n*]pyrroles (Figure 10).[141] These compounds, whose spatial properties are subject to modification through synthesis, feature pyrrole units bridged by alkylated methylene carbon atoms. Lacking delocalization across these sp^3 bridges, the pyrrole units have rotational freedom, endowing these receptors with the potential for three-dimensional anion recognition. In the calix[4]pyrroles, four convergent N−H vectors are complementary for halides, which perch at the top of a square pyramid of hydrogen bonds. The convergence of the N−H vectors leads to binding of sulfate through a single oxygen atom, as shown in Figure 11.[143] This figure also features the now well-known ability of the cup of **8** (Figure 10) to accommodate cations or cationic groups of appropriate size, making **8** an elegant ion-pair receptor.[144] Fluorination at the *β*-pyrrolic positions makes these compounds especially avid anion receptors capable of overcoming the Hofmeister bias among monovalent anions and even able to effect ion-pair extractions of 1:1 cesium salts without a cation receptor.[142] Extraction experiments will be described in more detail below.



8 **9** **10**

Figure 10. Members of the calix[*n*]pyrrole family with *n* = 4 and 5. In three dimensions, the pyrrole groups have rotational freedom and can bind anions by tilting all N−H bonds toward the anion. Among the many synthetic variations possible, the pyrrole rings may be substituted with halogens in their *β* positions, as in the fluorinated analogues **9** and **10**.

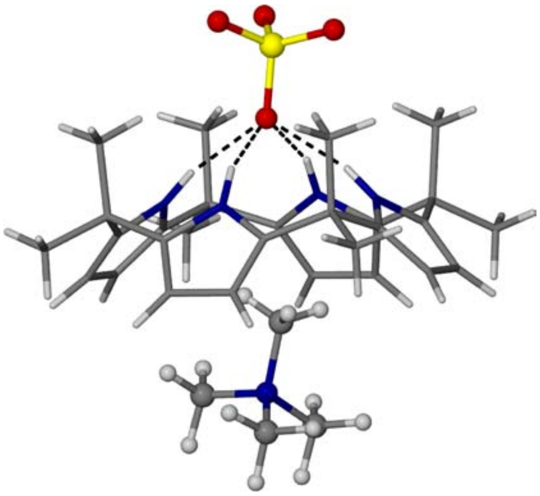


Figure 11. Crystal structure of the ion-pair complex of **8** with tetramethylammonium sulfate, $\mathbf{8}\cdot(TMA)_2SO_4\cdot(CH_2Cl_2)_2\cdot(EtOH)_2$.[143]

8. SULFATE SEPARATION BY LIQUID–LIQUID EXTRACTION

Its powerful advantages of high throughput and all-liquid handling, especially helpful for remote operation, would immediately make solvent extraction a competitive technology for sulfate separations provided a suitable extractant could be found. As discussed above, selective extraction of the highly hydrated sulfate ion from a nitrate-containing aqueous matrix presents a formidable thermodynamic challenge for receptor design. Whereas the applicable principles of molecular design have been outlined above for the selective *binding* of sulfate, the functional attributes of such a receptor adapted for sulfate *extraction* require additional design elements. Among many desirable attributes, a successful extractant must possess solubility in a water-immiscible diluent, water insolubility, and a provision for maintaining phase charge neutrality. The resulting ion recognition as designed for application in a liquid–liquid system should result in the extraction of sulfate from the initial waste stream, preferably without feed adjustment of any sort. The process cycle should be closed in a subsequent stripping or back-extraction step, depositing the sulfate anion into a preferably concentrated stream acceptable in composition to the downstream unit operations toward final waste disposal. For the purposes of estimation, if we expect an aqueous nitrate concentration of 3 M and an extractant concentration of 0.6 M, the target selectivity factor needed would be $\alpha_{SO_4/NO_3} \geq 5$, assuming we require $D_{SO_4} \geq 1$ and the loading of sulfate is low. We may note that this is of comparable magnitude to the selectivity factor estimated for ion-exchange resins above. Although progress has been made toward the selective binding of sulfate and even selective extraction, including an elegant tripodal hexaurea receptor (Figure 12),[145] a functional solvent-extraction system for practical use has yet to be reported.

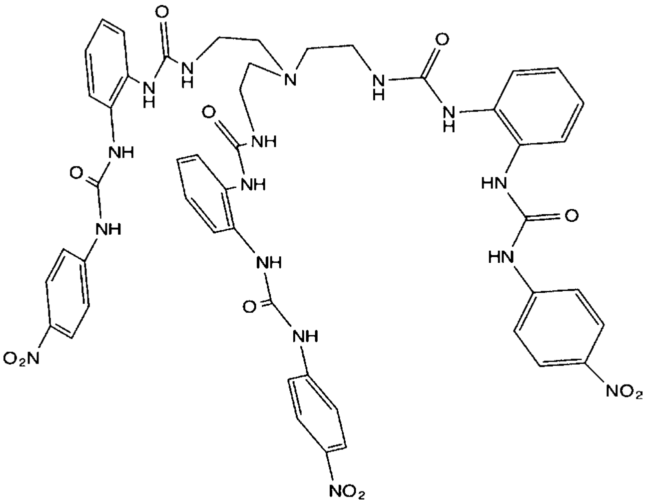


Figure 12. Schematic view of powerful tripodal hexaurea sulfate receptor, reported to extract sulfate quantitatively into chloroform in competition with nitrate.[145] It binds sulfate in the solid state by 12 hydrogen bonds, with each urea occupying an edge of the sulfate tetrahedron.

Organic-phase solubility and weak partitioning to the aqueous phase are generally achieved in an extractant by ensuring that polar groups in the receptor are balanced by sufficiently lipophilic groups but without deleterious side effects such as high interfacial activity. This was achieved, for example, by lengthening the ethyl chains in **6a** to undecyl in **6b** (see above).[137] Whereas this seems trivial, the substitution of hydrocarbon groups onto otherwise effective ion-binding agents normally entails a complex interplay of difficult-to-predict effects related to phase compatibility, self-association, interfacial activity, hydrodynamics, and kinetics in addition to steric effects on conformation, coordination, and solvation. Receptor **6b**, in fact, exhibited severely slow kinetics, which was partially mitigated with the use of phase-transfer catalysis. Indeed, much of the science of solvent extraction has grown around the understanding and sorting out of such phenomena, all associated with the desire to make polar molecules function as extractants in nonpolar diluents.

Another essential functional attribute of an extractant revolves around satisfying the condition of charge neutrality, which requires that each sulfate anion in the organic phase be accompanied by two cationic equivalents. These cationic equivalents may reside permanently in the organic phase, as in the case of lipophilic quaternary ammonium cations like those in Aliquat 336 (methylated Alamine 336 tri-C_8,C_{10}-amine), or they may be extracted, as in the case of extraction of alkali-metal cations by crown ethers or in the case of protonation of lipophilic amines like Alamine 336. These two basic approaches correspond to anion exchange or ion-pair extraction, with or without the involvement of lipophilic receptors, as outlined previously.[3,146] Each approach has its merits. However, further experiments will be needed to determine whether one is to be preferred in the removal of sulfate from radioactive waste.

Given that the Hanford tank-waste composition is essentially a concentrated highly alkaline sodium nitrate matrix, the ion-pair approach would logically take the form of sodium sulfate extraction. In one conception, sodium is accommodated in an appropriate neutral receptor of its own together with a separate neutral sulfate receptor (dual-host approach). Alternatively, one could design an ion-pair receptor that recognizes the combination of sodium and sulfate simultaneously. We previously demonstrated a dual-host system for sulfate extraction using the dansyl analogue (substituting dansyl, 5-(dimethylamino)naphthalene-1-sulfonyl, for methyl) of the tetraamide macrocycle **1a**. This host was mixed with a neutral calix-crown extractant for cesium as a means of driving the extraction.[3] In this example, a cesium receptor was employed for experimental convenience, whereas a receptor with a good affinity for sodium would be needed in more practical approaches. Ion-pair extraction has merit in that stripping can be accomplished by contacting the loaded solvent with water, which would thus create no secondary waste. It should be appreciated, however, that ion-pair extraction systems still tend to function by anion exchange in effect. This is because the large concentrations of nitrate in the aqueous phase act to force sodium nitrate to load the extractant, which then in effect functions by sulfate–nitrate exchange. Such a phenomenon was noticed in the development of a solvent-extraction process for extraction of sodium pertechnetate by a crown ether.[147,148]

Experiments demonstrated that liquid–liquid anion exchange using the quaternary ammonium nitrate salt Aliquat 336N is strongly enhanced by the addition of neutral anion receptors.[3,149] Extraction of sulfate by anion exchange using a lipophilic quaternary ammonium nitrate alone is very weak and difficult to measure. We obtained $D_{SO_4} = <1 \times 10^{-4}–4.4 \times 10^{-3}$ for 10 mM Aliquat 336N in various diluents and 10 mM $NaNO_3$ in the aqueous phase.[3,149] The addition of several neutral anion receptors led to significant enhancement in sulfate exchange. Fluorinated calix[4]pyrrole **9** was especially effective in this system, with an enhancement factor of 1200 (ratio of D_{SO_4} with added receptor to D_{SO_4} with no receptor) on adding 10 mM receptor to 10 mM Aliquat 336N in 2:1 hexane–chloroform; the value of α_{SO_4/NO_3} was 0.20.[3] Fluorinated calix[5]pyrrole **10** displayed larger selectivity factors for sulfate over nitrate relative to that for **9** in toluene, with $\alpha_{SO_4/NO_3} = 0.36$ and 0.21, respectively. It was possible using 100 mM of **9** together with 100 mM Aliquat 336N in toluene to reach a D_{SO_4} value of 1.63 for trace sulfate exchange from 10 mM $NaNO_3$, showing that process-suitable distribution ratios are obtainable in dilute competitive systems. Note that the selectivity factor for this system, 0.163, is approximately unchanged, because $D_{NO_3} = 10$. For solubility reasons, neutral tetraamide macrocycles could not be tested in toluene, but a comparison was possible in chloroform. In this medium, the analogue of **1a** with R = dansyl gave the strongest enhancement among the tested receptors (**9**, **10**, and two other tetraamide macrocycles) over most of the range of conditions tested. Fluorinated calix[5]pyrrole **10** was somewhat stronger in terms of enhancement at 10 mM receptor concentration; surprisingly, **9** was nearly 1 order of magnitude weaker than **10** in this system compared with their similar strength in toluene. An even more curious result was observed with a series of eight receptors including **1a** with R = dansyl and **8**−**10** in 1,2-dichloroethane.[150] In this study, extraction and binding constants were determined for sulfate extraction from nitrate media by receptors combined with Aliquat 336N. Both 1:1 and 2:1 receptor−sulfate complexes were implicated in the extraction. Fluorinated calix[5]pyrrole **10** again emerged as the strongest receptor (strongest enhancement), but interestingly, the unfluorinated parent **8** was stronger than fluorinated calix[4]pyrrole **9**. This and other anomalies led us to suggest that supramolecular interactions involving the receptors and anion exchanger were occurring. This conclusion was strongly supported by the structure of the ion-pair complex of **8** with tetramethylammonium sulfate showing insertion of the methyl group of the quaternary ammonium cation into the cup of **8** bound to sulfate (Figure 11).[143] The putative ability of **8** to function as a simple ion-pair receptor provides additional binding strength, and a thermodynamic model has been developed.[143,144] Overall, the mixing of an anion exchanger with a neutral anion receptor, which we term "synergized anion exchange", has appeal in its simplicity and in being able to manipulate the exchange and binding functions separately. It also avoids the coupling of sulfate extraction with cation extraction that characterizes ion-pair extraction approaches. However, anion exchange inescapably forces the uphill exchange of organic-phase nitrate into a concentrated nitrate solution, and stripping must be effected by a reverse exchange that can increase secondary waste. Further, results may not be easily rationalized or predicted from simple binding behavior.

As an alternative to synergized anion exchange, the anion receptor itself may be charged under the conditions of interest so that it supplies both the cationic equivalents and the needed complementary hydrogen bonding. The cyclo[8]pyrrole **6b**[137] discussed above is a good example of this approach. However, like many anion receptors, it gains its positive charge via protonation and therefore is not functional under alkaline conditions. Positively charged receptors for extraction from alkaline solution must necessarily involve additional synthesis to add permanently charged groups such as quaternary ammonium or phosphonium groups. Recalling the extraction results for octapyrrole **6b** described in the previous section, particularly slow-exchange kinetics, the question naturally arises as to the efficacy of having the cationic charges as part of the macrocyclic ring structure. Given the limited experimental data available to date, the answer is unclear and must take into account multiple effects such as rigidity and solvation. Further research will be needed to inform future receptor design for liquid−liquid extraction.

9. SULFATE SEPARATION BY SELECTIVE CRYSTALLIZATION OF UREA-FUNCTIONALIZED CAPSULES

As an alternative approach to achieving sulfate-specific recognition and separation, we have explored selective crystallization of organic frameworks from competitive aqueous environments.[84,151,152] In this case, the challenge has been to design the sulfate receptor so that it not only binds sulfate efficiently but also provides for linking interactions in the solid phase, leading to crystallization of sulfate within an insoluble compound. One particular advantage of such anion-binding solids is that the stiffer environment normally associated with a crystalline state provides superior organizational rigidity[84] compared to molecular receptors in solution, thereby minimizing or preventing altogether the accommodation of competing anions. Another attractive feature of crystalline hosts is that they are easily self-assembled in one step from simple building blocks, thus creating complex binding sites that may otherwise be difficult to achieve in traditional organic hosts assembled by multistep synthesis.

Sulfate recognition in crystalline materials can be achieved by functionalizing the organic ligand components with complementary hydrogen-bonding donor groups, such as urea.[153] Crystallization studies indicated that urea-functionalized frameworks can selectively bind and separate sulfate from a variety of competing anions.[154−161] Maximum recognition of sulfate and its effective sequestration from water, however, require complete encapsulation of this anion.[121,122,162,163] The results of electronic-structure calculations[114] and X-ray crystallography[164−178,121] indicate that sulfate ideally accommodates 12 hydrogen bonds from six urea groups, which approximately correspond to the number of hydrogen bonds lost from the initial hydration shell of sulfate in water.[106] In addition to such ideal complementarity, efficient and selective sulfate crystallization requires a ligand capable of forming a robust, water-insoluble framework that is rigid enough to exclude competing anions.

As it turned out, all of the above requirements were met by the tripodal tris(urea) ligand **11** (Figure 13). Two molecules of **11**, in the presence of Mg^{2+} (or other M^{2+} cations: M = Ca, Zn, Cd, Co, Mn) and water, selectively encapsulate SO_4^{2-} from competitive aqueous anionic mixtures by crystallization into rigid hydrogen-bonded capsules with the composition $MgSO_4(\mathbf{11})_2(H_2O)_6$.[173,174] Structural analysis by single-crystal X-ray diffraction revealed that the crystalline capsules match the

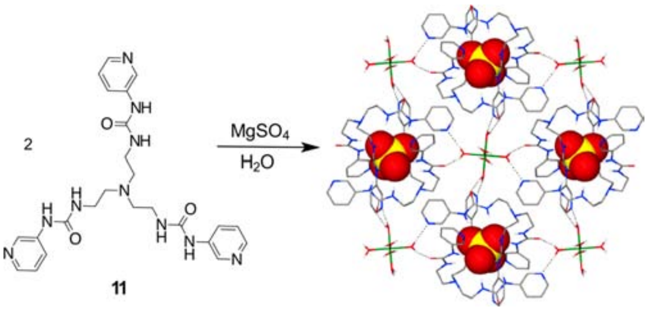


Figure 13. Sulfate encapsulation in crystalline $MgSO_4(\mathbf{11})_2(H_2O)_6$.[173−175]

size and shape of the tetrahedral sulfate anion, binding it by 12 complementary hydrogen bonds. The capsules are interlinked in a three-dimensional hydrogen-bonded framework with NaCl topology, involving pyridyl groups as acceptors and the $Mg(H_2O)_6^{2+}$ cations as donors (Figure 13). Despite the inherent flexibility of ligand **11**, the capsules are remarkably rigid in the crystalline state, retaining their shape even in the presence of strongly competitive anions like CO_3^{2-} and SO_3^{2-}. We concluded that these capsules are templated by sulfate (or other divalent oxoanions, e.g., SeO_4^{2-}, CrO_4^{2-}, SO_3^{2-}, and CO_3^{2-}), because no structures could be isolated in the absence of such anions. A detailed thermodynamic study revealed that crystallization of the capsules is highly exothermic, with the most favorable enthalpy of crystallization corresponding to tetrahedral SO_4^{2-} (−99.1 kJ/mol) and SeO_4^{2-} (−108.5 kJ/mol) anions.[175] In direct contrast, the pyramidal-shaped SO_3^{2-} has a significantly less favorable enthalpy of crystallization (−64.6 kJ/mol), which may be attributed to its poor fit inside the capsules, as found by X-ray structural analysis. However, entropy proved to play a critical role, strongly favoring sulfite over sulfate and selenate. Overall, this enthalpy−entropy interplay favored crystallization of the sulfate capsules, whose measured solubility of 2×10^{-5} M is in the same range as that of $BaSO_4$. Competition experiments also confirmed that carbonate, a major component of alkaline nuclear waste, neither effectively competes nor interferes with crystallization of sulfate.

Encouraged by these fundamental results, we recently investigated the crystallization of $MgSO_4(\mathbf{11})_2(H_2O)_6$ as a means for sulfate separation from aqueous alkaline solutions simulating Hanford waste compositions.[176] We found that, up to pH 9.5, sulfate can be removed essentially quantitatively in one step, by selective crystallization in the presence of more than 100-fold excess of $NaNO_3$. The ligand **11** can also be easily recovered in more than 90% yield by dissolution of the crystalline cages in dilute nitric acid and subsequent precipitation with NaOH. This also demonstrates that the organic ligand **11** is reasonably stable under both acidic and basic conditions, as was found in various nuclear waste streams. Unfortunately, under more basic conditions (pH > 9.5), the magnesium-based capsules do not form, and precipitation of $Mg(OH)_2$ is observed instead. Although this system is not applicable to the highly alkaline conditions found in the Hanford waste, its simplicity coupled with the high crystallization efficiency and excellent ligand recyclability qualifies it as a viable approach to other industrial sulfate separations from neutral or mildly alkaline aqueous solutions.

Moving away from the magnesium-based system, we began exploring the ability of alkali-metal cations to form similar crystalline capsules in the presence of sulfate and **11**. The impetus was that such capsules would be more stable under highly alkaline conditions because of the much higher solubility of the corresponding metal hydroxides. We first discovered that Li_2SO_4 crystallizes with **11** from water to yield crystalline $Li_2SO_4(\mathbf{11})_2(H_2O)_2$.[177] Crystal structure analysis revealed that this compound contains $SO_4(\mathbf{11})_2^{2-}$ anionic capsules similar to those previously found in the magnesium-based system, which, however, are linked by $Li(H_2O)^+$ cations into a three-dimensional framework with pyrite topology (Figure 14).

More recently, we found that the alkaline-metal cations Na^+ and K^+ can self-assemble with **11** from aqueous solutions into crystalline solids with the compositions $Na_2SO_4(\mathbf{11})_2(H_2O)_4$ and $K_2SO_4(\mathbf{11})_2(H_2O)_2$, respectively.[178] Single-crystal X-ray structural analysis revealed that both compounds display NaCl-type frameworks similar to the magnesium-based structure, where the $Mg(H_2O)_6^{2+}$ units are replaced by $Na_2(H_2O)_4^{2+}$ or $K_2(H_2O)_2^{2+}$ cationic clusters, respectively (Figure 15). Once again, the sulfate anion is encapsulated by two embracing molecules of ligand **11**, providing 12 hydrogen bonds from six urea groups.

Figure 14. Sulfate encapsulation in crystalline $Li_2SO_4(\mathbf{11})_2(H_2O)_2$.[177]

The sodium-based crystalline capsules appeared to us particularly promising for sulfate separation from nuclear wastes because sodium is the most abundant cation in such wastes. Employing this system, we reasoned, would not only circumvent the need for adding additional ionic components to the waste but would also decrease the solubility of the capsules through the common ion effect. Indeed, crystallization of $Na_2SO_4(\mathbf{11})_2(H_2O)_4$ from highly alkaline (pH 14) aqueous solutions that simulate the Hanford waste compositions proved very efficient, resulting in up to 90% sulfate removal in one step.[176,178] The ligand **11** can be easily recovered for reuse by recrystallization from water, leaving sodium sulfate in solution (Figure 16). These results thus may lead in the near future to much-needed technology for selective sulfate separation from Hanford tank wastes. However, further research will be needed to understand the selectivity and thermodynamics of crystallization, enhance the crystallization kinetics, and develop and scale-up a process cycle.

10. CONCLUSIONS

From the point of view of a specific application, a clear need has been presented for the development of effective technologies for the removal of sulfate from legacy radioactive wastes destined for vitrification. Potential cost savings and schedule acceleration could be anticipated based on consequent improvements in vitrification processing, reduction in waste-form volumes, and higher waste-package performance. Various industrial technologies have been employed for sulfate separation from a range of dilute to concentrated electrolyte aqueous feed streams, but a suitable technology has not yet been identified for the removal of sulfate from the problem wastes stored in tanks at the Hanford site. Experimental results from the authors' laboratories support the hypothesis that approaches based on anion recognition using selective sulfate receptors have potential in this application. A molecular-design approach has led to selective sulfate binding, which has been expressed in selective sulfate crystallization and liquid−liquid extraction. Although such results remain in the domain of fundamental research, the needed selectivity for technology development is viewed as obtainable.

The thrust of this review has purposely dealt with molecular recognition as the major criterion in developing a separation

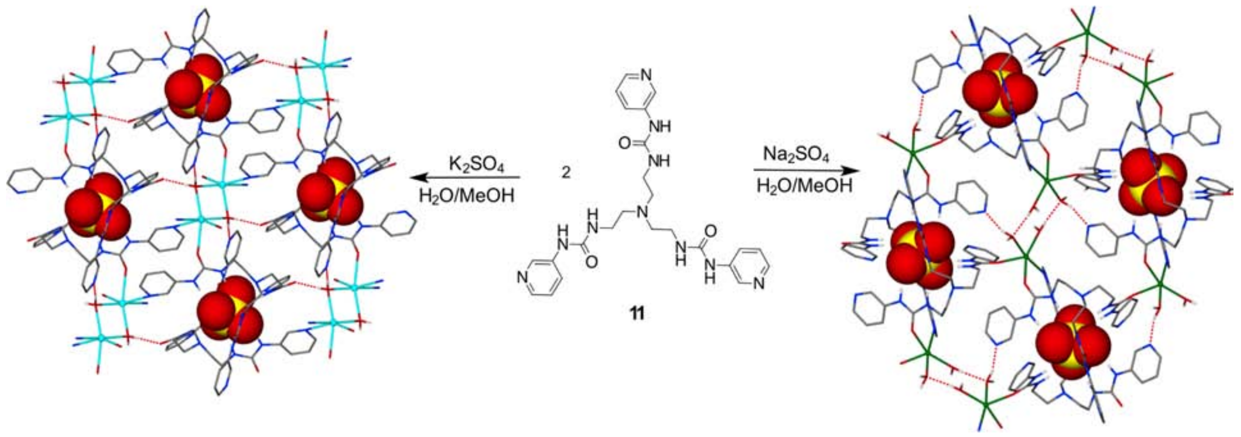


Figure 15. Sulfate encapsulation in crystalline $Na_2SO_4(\mathbf{11})_2(H_2O)_4$ (right) and $K_2SO_4(\mathbf{11})_2(H_2O)_2$ (left).[178]

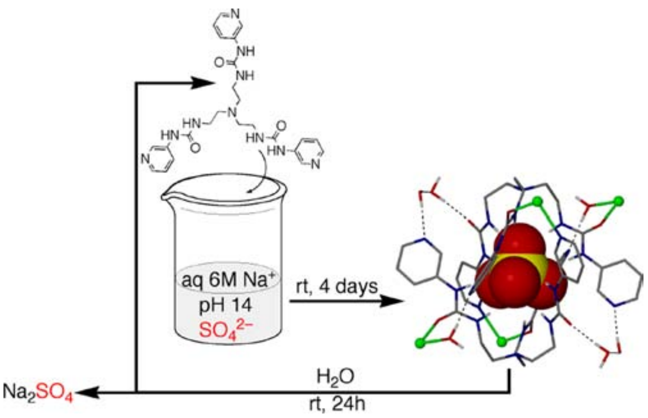


Figure 16. Separation cycle for sulfate removal from aqueous alkaline solutions.[178]

technology concept. However, a progression of other requirements must be met for successful deployment. The release of the bound species from the receptor complex is perhaps the next most important consideration so that a closed process cycle can be obtained. Because most molecular-recognition agents used in separation processes are typically valuable materials, economics dictates that they be recycled rapidly thousands of times with low loss. Accordingly, issues of kinetics and reagent stability must be faced. For example, we found that sulfate self-exchange of the sulfate complex of cyclo[8]pyrrole **6a** is slow,[136] implying the need for phase-transfer catalysis. Classically, a price paid for preorganization has often been slow kinetics of binding and especially release, and while high binding constants are often prized, the task of engineering thermodynamically and kinetically efficient release becomes that much harder. Reagent stability also plays a key role in process economics, both in terms of the loss rate of the valuable molecular-recognition agent and the chemical mischief that the degradation products can inflict on the carefully designed process. The receptor molecules discussed in this review have for the most part been designed with reasonably robust functional groups and building blocks so that experimental studies have not been compromised by instability. However, in reality, dedicated studies of stability have not been performed, and the information at hand is largely qualitative. For instance, organic solutions of simple, nonfluorinated calix[4]pyrroles will discolor over the course of hours or days when contacted with aqueous acidic media, with the rate of discoloration depending on the pH. In general, octafluorocalix[4]pyrrole is much more stable than its nonfluorinated analogue.[179] Typically, no evidence of decomposition is seen even under conditions of prolonged contact with weakly acidic environments. Pentafluorocalix[5]pyrrole displays intermediate stability and will convert to the corresponding calix[4]pyrrole upon treatment with acid at reflux in methanol or other organic solvents.[180] All of the calixpyrroles examined appear stable when contacted with aqueous alkaline media. Nevertheless, it is clear that robustness to process conditions must be tested and possibly ameliorated in the course of technology maturation. In general, much work needs to be done in examining the applied aspects of molecular recognition in real-world industrial separations, and considerations such as efficient binding-release cycles, rapid kinetics, and reagent stability should be approached at an early stage in the design of the molecular-recognition agent and its chemical system.

Finally, while this review has made a case for molecular recognition in the very specific and perhaps unusual application involving sulfate removal from nuclear waste, we believe that it serves as a positive model for the use of molecular recognition in many other applications for industrial separations. The nuclear industry, with its peculiar economics in which expensive reagents are not necessarily cost prohibitive, has, in fact, proven to be a breeding ground for molecular-recognition technologies.[181] A number of examples demonstrate a growing presence of molecular recognition for metal separations industry-wide.[182,183] In all of these instances, the molecular-recognition agent is efficiently recovered and recycled, and the price paid for the reagent is recovered in performance that could not be otherwise achieved. As separation problems become more stringent in the nuclear, environmental, electronics, and pharmaceutical sectors, it is certainly expected that molecular recognition will continue to grow and add value in industry.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Research at Oak Ridge National Laboratory was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office Basic Energy Sciences, U.S. Department of Energy. Research at The University of Texas at Austin was supported by the U.S. Department of Energy (Grants DE-FG02-04ER63741 and DE-FG02-01ER15186 to J.L.S.). Work at the University of Kansas was supported by the U.S. Department of Energy (Grant DE-FG02-04ER63745 to K.B.-J.) and the National Science Foundation (Grant CHE-0316623 to K.B.-J.). Acknowledgement is also made to the Robert A. Welch Foundation (grant F-1018 to J.L.S.).

■ REFERENCES

(1) *Research Needs for High-Level Waste Stored in Tanks and Bins at U.S. Department of Energy Sites*; National Research Council, National Academy Press: Washington, DC, 2001; p 55.

(2) Allen, R. W.; Josephson, G. B.; Westsik, J. H.; Nickola, C. L. *Tanks Focus Area Site Needs Assessment*; Report PNNL-13518; Pacific Northwest National Laboratory: Richland, WA, Apr 2001.

(3) Moyer, B. A.; Delmau, L. H.; Fowler, C. J.; Ruas, A.; Bostick, D. A.; Sessler, J. L.; Katayev, E.; Pantos, G. D.; Llinares, J. M.; Hossain, M. A.; Kang, S. O.; Bowman-James, K. In *Supramolecular Chemistry of Environmentally Relevant Anions, Advances in Inorganic Chemistry, Template Effects and Molecular Organization*; van Eldik, R., Bowman-James, K., Eds.; Elsevier: Oxford, U.K., 2007; Vol. 59, p 177.

(4) Lumetta, G. J. In *The Problem with Anions in the DOE Complex, Fundamentals and Applications of Anion Separations*; Moyer, B. A., Singh, R. P., Eds.; Kluwer Academic/Plenum: New York, 2004; p 107.

(5) *Report to Congress: Status of Environmental Management Initiatives to Accelerate the Reduction of Environmental Risks and Challenges Posed by the Legacy of the Cold War*; Report DOE/EM-0001; U.S. Department of Energy, Office of Environmental Management: Washington, DC, Jan 2009.

(6) *Nuclear Wastes: Technologies for Separations and Transmutation*; National Research Council, National Academy Press: Washington, DC, 1996.

(7) Campbell, D. *DWPF Pours Its 3,000th Canister of Radioactive Glass*; News Release; Savannah River Remediation: Aiken, SC, Oct 10, 2010; available on the internet at http://srremediation.com/milestone_dwpf.html (accessed July 15, 2012).

(8) Peterson, J.; Giusti, J. *DOE Marks Key Cleanup and Closure Milestones at its Savannah River Site*; News Release SR-08-01; U.S. Department of Energy, Savannah River Operations Office: Aiken, SC, June 19, 2008; available on the internet at http://sro.srs.gov/nr_2008/sr0801.pdf (accessed July 15, 2012).

(9) Conrad, K. A.; Dunford, G. L.; Schaus, S. *Project W-551 Interim Pretreatment System Technology Selection Summary Decision Report and Recommendation*; Report RPP-RPT-38057; CH2M HILL Hanford Group (for the U.S. Department of Energy): Richland, WA, Aug 2008.

(10) Certa, P. J. *River Protection Project System Plan*; Report ORP-11242; CH2M HILL Hanford Group (for the U.S. Department of Energy): Richland, WA, July 2008.

(11) Ojovan, M. I.; Lee, W. E. *An Introduction to Nuclear Waste Immobilisation*; Elsevier: Amsterdam, The Netherlands, 2005; Chapter 17.

(12) Manara, D.; Grandjean, A.; Pinet, O.; Dussossoy, J. L.; Neuville, D. R. *J. Non-Cryst. Solids* **2007**, *353*, 12.

(13) Li, H.; Langowski, M. H.; Hrma, P. R.; Schweiger, M. J.; Vienna, J. D.; Smith, D. E. *Minor Component Study for Simulated High-Level Nuclear Waste Glasses*; Report PNNL-10996; Pacific Northwest National Laboratory: Richland, WA, Feb 1996.

(14) Kim, D. S.; Buchmiller, W. C.; Schweiger, M. J.; Vienna, J. D.; Day, D. E.; Kim, C. W.; Zhu, D.; Day, T. E.; Neidt, T.; Peeler, D. K.; Edwards, T. B.; Reamer, I. A.; Workman, R. J. *Iron Phosphate as an Alternative Waste-Form for Hanford LAW*; Report PNNL-14251; Pacific Northwest National Laboratory: Richland, WA, Feb 2003.

(15) Mahoney, L. A.; Vienna, J. D. *Feed Variability and Bulk Vitrification Glass Performance Assessment*; Report PNNL-14985; Pacific Northwest National Laboratory: Richland, WA, Jan 2005.

(16) Allen, D. I.; Raymond, R. E.; Brouns, T. M.; Mauss, B. M. *Recommendation for Supplemental Technologies for Hanford River Protection Project Potential Mission Acceleration*; Report RPP-11838-FP; CH2M HILL Hanford Group (for the U.S. Department of Energy): Richland, WA, Jan 2003.

(17) Feng, X.; Hrma, P. R.; Westsik, J. H., Jr.; Brown, N. R.; Schweiger, M. J.; Li, H.; Vienna, J. D.; Chen, G.; Piepel, G. F.; Smith, D. E.; McGrail, B. P.; Palmer, S. E.; Kim, D.; Peng, Y.; Hahn, W. K.; Bakel, A. J.; Ebert, W. L.; Peeler, D. K.; Chang, C. *Glass Optimization for Vitrification of Hanford Site Low-Level Tank Waste*; Report PNNL-10918; Pacific Northwest National Laboratory: Richland, WA, Mar 1996.

(18) Li, H. *Letter Report—Minor Component Study for Low-Level Radioactive Waste Glasses*; Report PNNL-11053; Pacific Northwest National Laboratory: Richland, WA, Mar 1996.

(19) Pirlet, V. *J. Nucl. Mater.* **2001**, *298*, 47.

(20) Ebert, W. L.; Bates, J. K.; Buck, E. C.; Gong, M.; Wolf, S. F. *Disposition of Actinides Released from High-Level Waste Glass*; Proceedings of the American Ceramic Society 96th Annual Meeting, Indianapolis, IN, Apr 24–28, 1994; Argonne National Laboratory: Argonne, IL, 1994.

(21) Marra, J. C.; Andrews, M. K.; Schumacher, R. F. *Vitrification in the Presence of Salts*; Proceedings of the American Ceramic Society 96th Annual Meeting, Indianapolis, IN, Apr 24–28, 1994; Westinghouse Savannah River Company: Aiken, SC, 1994; WSRC-MS-93-621 (P).

(22) Lorier, T. J.; Reamer, I. A.; Workman, R. J. *Initial Sulfate Solubility Study for Sludge Batch 4 (SB4)*; Report WSRC-TR-2005-00213; Savannah River National Laboratory: Aiken, SC, Apr 2005.

(23) Langowski, M. H. *The Incorporation of P, S, Cr, F, Cl, I, Mn, Ti, U, and Bi into Simulated Nuclear Waste Glasses: Literature Study*; Report PNNL-10980; Pacific Northwest National Laboratory: Richland, WA, Feb 1996.

(24) Merrill, R. A.; Whittington, K. F.; Peters, R. D. *Vitrification of High Sulfate Wastes*; Report PNL-SA-24672; Pacific Northwest National Laboratory: Richland, WA, Sept 1994.

(25) Vienna, J. D.; Schweiger, M. J.; Smith, D. E.; Smith, H. D.; Crum, J. V.; Peeler, D. K.; Reamer, I. A.; Musick, C. A.; Tillotson, R. D. *Glass Formulation Development for INEEL Sodium-Bearing Waste*; Report PNNL-12234; Pacific Northwest National Laboratory: Richland, WA, July 1999.

(26) Schumacher, R. F.; Smith, M. E.; Sproull, J. F. *Review of Background Applicable to the Potential for a Steam Explosion in the DWPF Melter*; Report WSRC-RD-91-15; Westinghouse Savannah River Company: Aiken, SC, 1991.

(27) Jantzen, C. M. *Glass Melter Off-Gas System Pluggages: Cause, Significance, and Remediation*; Report WSRC-MS-91-009; Westinghouse Savannah River Company: Aiken, SC, 1991.

(28) Plodinec, M. J. *Glass Technol.* **2000**, *41*, 186.

(29) Fox, K. M.; Edwards, T. B.; Peeler, D. K. *Sulfate Retention in High Level Waste (HLW) Sludge Batch 4 (SB4) Glasses: A Preliminary Assessment*; Report WSRC-STI-2006-00038; Savannah River National Laboratory: Aiken, SC, Dec 2006.

(30) Perez, J. M., Jr.; Bickford, D. F.; Day, D. E.; Kim, D.-S.; Lambert, S. L.; Marra, S. L.; Peeler, D. K.; Strachan, D. M.; Triplett, M. B.; Vienna, J. D.; Wittman, R. S. *High-Level Waste Melter Study Report*; Report PNNL-13582; Pacific Northwest National Laboratory: Richland, WA, July 2001.

(31) Day, D. D.; Ray, C. S.; Kim, C.-W. *Iron Phosphate Glasses: An Alternative for Vitrifying Certain Nuclear Wastes*; Final Report for DE-FG07-96ER45618, Environmental Management Science Program, U.S. Department of Energy; University of Missouri—Rolla, Rolla, MO, Sept 2004.

(32) Kim, C. W.; Day, D. E. *J. Non-Cryst. Solids* **2003**, *331*, 20.

(33) Mishra, R. K.; Sudarsan, K. V.; Sengupta, P.; Vatsa, R. K.; Tyagi, A. K.; Kaushik, C. P.; Das, D.; Raj, K. *J. Am. Ceram. Soc.* **2008**, *91*, 3903.

(34) Bao, Y.; Grutzeck, M. W.; Jantzen, C. M. *J. Am. Ceram. Soc.* **2005**, *88*, 3287.

(35) Marcus, P. *J. Chim. Phys. Phys.-Chim. Biol.* **1991**, *88*, 1697.

(36) Ahn, T.; Jung, H.; He, X.; Pensado, O. *J. Nucl. Mater.* **2008**, *379*, 33.

(37) Windisch, C. F.; Baer, D. R.; Jones, R. H.; Engelhard, M. H. *Corros. Sci.* **2007**, *49*, 2497.

(38) Passarelli, A.; Dunn, D.; Pensado, O.; Bloomer, T.; Ahn, T. *Metall. Mater. Trans. A* **2005**, *36A*, 1121.

(39) Pan, Y. M.; Chiang, K. T.; Dunn, D. S.; He, X.; Pensado, O.; Shukla, P.; Yang, L. *Nucl. Technol.* **2008**, *163*, 85.

(40) Llevbare, G. O. *The Effect of Sulfate Anions on Crevice Corrosion in Alloy 22*; Report UCRL-TR-206271; Lawrence Livermore National Laboratory: Livermore, CA, Feb 2004.

(41) Hay, M.; Coleman, C.; Hassan, N.; McCabe, D.; King, B.; Nash, C.; Saito, H.; Calloway, B.; Crawford, C. *Sulfate Removal Studies for River Protection Project Part B1*; Report WSRC-TR-2000-00489; Westinghouse Savannah River Company: Aiken, SC, Mar 2001.

(42) Darbi, A.; Viraraghavan, T.; Jin, Y. C.; Braul, L.; Corkal, D. *Water Qual. Res. J. Can.* **2003**, *38*, 169.

(43) Sappington, F. C.; Phifer, M. A.; Denham, M. E.; Millings, M. R.; Turick, C. E.; McKinsey, P. C. *D-Area Sulfate Reduction Study Comprehensive Final Report (U)*; Report WSRC-TR-2005-00017; Savannah River National Laboratory: Aiken, SC, Feb 11, 2005.

(44) McCauley, C. A.; O'Sullivan, A. D.; Milke, M. W.; Weber, P. A.; Trumm, D. A. *Water Res.* **2009**, *43*, 961.

(45) Gerber, M. A.; Orth, R. J.; Elmore, M. R.; Monzyk, B. F. *Clean Option—Berkeley Pit Water Treatment and Resource Recovery Strategy*; Report PNL-10786; Pacific Northwest National Laboratory: Richland, WA, Feb 1995.

(46) Bader, M. S. H. *J. Pet. Sci. Eng.* **2007**, *55*, 93.

(47) Wang, K. Y.; Chung, T. S.; Rajagopalan, R. *Ind. Eng. Chem. Res.* **2007**, *46*, 1572.

(48) Whitmire, S. L.; Hamilton, S. K. *J. Environ. Qual.* **2005**, *34*, 2062.

(49) Vangelas, K.; Albright, W. H.; Becvar, E. S.; Benson, C. H.; Early, T. O.; Hood, E.; Jardine, P. M.; Lorah, M.; Majche, E.; Major, D.; Waugh, W. J.; Wein, G.; West, O. R. *Enhancements to Natural Attenuation: Selected Case Studies*; Report WSRC-STI-2007-00250; Savannah River National Laboratory: Aiken, SC, 2007.

(50) Jong, T.; Parry, D. L. *Water Res.* **2003**, *37*, 3379.

(51) Lens, P. N. L.; Visser, A.; Janssen, A. J. H.; Pol, L. W. H.; Lettinga, G. *Crit. Rev. Environ. Sci. Technol.* **1998**, *28*, 41.

(52) Malaiyandi, M.; Sastri, V. S. *Sep. Sci. Technol.* **1981**, *16*, 371.

(53) Bhattacharya, A.; Ghosh, P. *Rev. Chem. Eng.* **2004**, *20*, 111.

(54) Lee, H. J.; Oh, S. J.; Moon, S. H. *Water Res.* **2003**, *37*, 1091.

(55) Tsuji, M. In *Evaluation and Molecular Design of Inorganic Anion Sieves, Fundamentals and Applications of Anion Separations*; Moyer, B. A., Singh, R. P., Eds.; Kluwer Academic/Plenum: New York, 2004; p 293.

(56) Priyantha, N.; Perera, S. *Water Res. Manage.* **2000**, *14*, 417.

(57) Boukhalfa, C.; Mennour, A.; Reinert, L.; Fuzellier, H. *Desalination* **2007**, *214*, 38.

(58) Geniesse, D. *Hanford Aqueous Waste Minimization via Burkeite Evaporative Crystallization*; COGEMA-BURKEITE-RPT-001; COGEMA Engineering Corp.: Richland, WA, 2002.

(59) Lumetta, G. J.; Klinger, G. S.; Kurath, D. E.; Sell, R. L.; Darnell, L. P.; Greenwood, L. R.; Soderquist, C. Z.; Steele, M. J.; Urie, M. W.; Wagner, J. J. *Removal of Sulfate Ion from AN-107 by Evaporation*; Reports PNWD-3036 and BNFL-RPT-018; Pacific Northwest National Laboratory: Richland, WA, July 2000.

(60) Geniesse, D. J.; Nelson, E. A.; Hamilton, D. W.; Majors, J. H.; Nordahl, T. K. *Fractional Crystallization of Hanford Single Shell Tank (SST) Wastes from Concept to Plant*; Proceedings of the WM'07 Conference, Tucson, AZ, Feb 25−Mar 1, 2007; AREVA: Richland, WA, 2006; RPP-30995-FP.

(61) Herting, D. L.; Nelson, E. A.; Rousseau, R. W. *Fractional Crystallization of Hanford Single-Shell Tank Wastes—Laboratory Development*; Proceedings of the WM'07 Conference, Tucson, AZ, Feb 25−Mar 1, 2007; CH2M HILL Hanford Group, Inc.: Richland, WA, 2006; RPP-31983-FP.

(62) Hamilton, D. W. *Hanford Medium/Low Curie Waste Pretreatment Project−Pretreatment Process Plan*; Report RPP-PLAN-27238; CH2M HILL Hanford Group, Inc.: Richland, WA, 2006.

(63) Pehlivanoglu, E.; Kabdasli, I.; Tunay, O. *Fresenius Environ. Bull.* **1998**, *7*, 826.

(64) Tait, S.; Clarke, W. P.; Keller, J.; Batstone, D. J. *Water Res.* **2009**, *43*, 762.

(65) Kabdasli, I.; Tunay, O.; Orhon, D. *Water Sci. Technol.* **1995**, *32*, 21.

(66) Benatti, C. T.; Tavares, C. R. G.; Lenzi, E. J. *Environ. Manage.* **2009**, *90*, 504.

(67) Jegadeesan, G.; Mondal, K.; Lalvani, S. B. *Environ. Technol.* **2005**, *26*, 1181.

(68) Fiskum, S. K.; Kurath, D. E.; Rapko, B. M. *Development and Demonstration of a Sulfate Precipitation Process for Hanford Waste Tank 241-AN-107*; Reports PNWD-3050 and BNFL-RPT-029; Pacific Northwest National Laboratory: Richland, WA, Aug 2000.

(69) Williams, W. J. *Handbook of Anion Determination*; Butterworth: London, 1977; pp 535−565.

(70) Stephen, W. I. *Anal. Chim. Acta* **1970**, *50*, 413.

(71) Yokoyama, T.; Masuo, T.; Akashi, H.; Zenki, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1331.

(72) Lehn, J.-M. Alkali Metal Complexes with Organic Ligands. In *Design of Organic Complexing Agents. Strategies Towards Properties*; Dunitz, J. D., Ed.; Springer-Verlag: New York, 1973; pp 1−69.

(73) Belcher, R.; Stephen, W. I.; Nutten, A. J. *J. Chem. Soc.* **1953**, 1334.

(74) Bader, M. S. H. *J. Hazard. Mater.* **2001**, *82*, 139.

(75) Mahr, C.; Krauss, K. Z. *Z. Anal. Chem.* **1948**, *128*, 477.

(76) Belcher, R.; Gibbons, D. *J. Chem. Soc.* **1952**, 4216.

(77) Sharma, R. P.; Bala, R.; Sharma, R.; Bhasin, K. K.; Chadha, R. K. *J. Coord. Chem.* **2004**, *57*, 313.

(78) Sharma, R. P.; Bala, R.; Sharma, R.; Ferretti, V. *Inorg. Chim. Acta* **2005**, *358*, 3457.

(79) Weiss, J. *Ion Chromatography*, 2nd ed.; VCH: Weinheim, Germany, 1995.

(80) Clifforde, D. A.; Weber, W. *J. React. Polym.* **1983**, *1*, 77.

(81) Gu, B.; Ku, Y.-K.; Jardine, P. M. *Environ. Sci. Technol.* **2004**, *38*, 3184.

(82) Harland, C. E. *Ion Exchange: Theory and Practice*, 2nd ed.; The Royal Society of Chemistry: Cambridge, U.K., 1994; pp 128−132.

(83) Hofmeister, F. *Arch. Exptl. Pathol. Pharmakol.* **1888**, *24*, 247.

(84) Custelcean, R.; Moyer, B. A. *Eur. J. Inorg. Chem.* **2007**, 1321.

(85) Diamond, R. M.; Whitney, D. C. Resin Selectivity in Dilute to Concentrated Aqueous Solutions. In *Ion Exchange, A Series of Advances*; Marinsky, J., Ed.; Marcel Dekker: New York, 1966; Vol. *1*, pp 277−302.

(86) Helfferich, F. G. *Ion Exchange*; McGraw-Hill: New York, 1962.

(87) Haghsheno, R.; Mohebbi, A.; Hashemipour, H.; Sarrafi, A. *J. Hazard. Mater.* **2009**, *166*, 961.

(88) Boari, G.; Liberti, L.; Santori, M.; Spinosa, L. *Desalination* **1976**, *19*, 283.

(89) Kurath, D. E.; Bontha, J. R.; Blanchard, D. L., Jr.; Fiskum, S. K.; Rapko, B. M. *Ion Exchange Studies for Removal of Sulfate from Hanford Tank Waste Envelope C (241-AN-107) Using Superlig® Resin*; Reports PNWD-3053 and BNFL-RPT-036; Pacific Northwest National Laboratory: Richland, WA, Aug 2000.

(90) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997.

(91) Moyer, B. A.; Bonnesen, P. V. Supramolecular Chemistry of Anions. In *Physical Factors in Anion Separations*; Bianchi, A., Bowman-James, K., García-España, E., Eds.; Wiley-VCH: New York, 1997; pp 1−44.

(92) Marcus, Y.; Kertes, A. S. *Ion Exchange and Solvent Extraction of Metal Complexes*; Wiley Interscience: New York, 1969.

(93) Högfeldt, E. Solvent Extraction Research. In *Some Aspects on Amine Extraction*; Marcus, Y., Kertes, A. S., Eds.; Wiley-Interscience: Jerusalem, 1968; pp 157−175.

(94) Coleman, C. F. *Nucl. Sci. Eng.* **1963**, *17*, 274.

(95) Coleman, C. F. Process Chemistry. *Amine Extraction in Reprocessing*; Pergamon Press: Oxford, U.K., 1969; pp 233−285.
(96) Coleman, C. F.; Brown, K. B.; Moore, J. G.; Crouse, D. J. *Ind. Eng. Chem.* **1958**, *50*, 1756.
(97) Schmidtchen, F. P. In *The Role of Entropy in the Design of Molecular Hosts*; Proceedings of the International Solvent Extraction Conference, ISEC 2008, Tucson, AZ, Sept 15−19, 2008; Moyer, B. A., Ed.; Metallurgical Society of CIM: Ottawa, Canada, 2008; Vol. *1*, pp 59−82.
(98) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.
(99) Cram, D. J. *J. Inclusion Phenom.* **1988**, *6*, 397.
(100) Pflugrath, J. W.; Quiocho, F. A. *Nature* **1985**, *314*, 257.
(101) He, J. J.; Quiocho, F. A. *Protein Sci.* **1993**, *2*, 1643.
(102) He, J. J.; Quiocho, F. A. *Science* **1991**, *251*, 1479.
(103) Jacobson, B. L.; Quiocho, F. A. *J. Mol. Biol.* **1988**, *204*, 783.
(104) Quiocho, F. A. *Kidney Int.* **1996**, *49*, 943.
(105) Sack, J. S.; Quiocho, F. A. *1.7 Angstroms Refined Structure of Sulfate-Binding Protein Involved in Active Transport and Novel Mode of Sulfate Binding*; Protein Data Bank (http://www.wwpdb.org/), PDB ID: 1sbp, http://dx.doi.org/10.2210/pdb1sbp/pdb .
(106) Vchirawongkwin, V.; Rode, B. M.; Persson, I. *J. Phys. Chem. B* **2007**, *111*, 4150.
(107) Ravikumar, I.; Ghosh, P. *Chem. Soc. Rev.* **2012**, *41*, 3077−3098.
(108) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: New York, 2000.
(109) Schneider, H.-J.; Yatsimirsky, A. *Principles and Methods in Supramolecular Chemistry*; Wiley: New York, 2000.
(110) Hay, B. P.; Dixon, D. A; Bryan, J. C.; Moyer, B. A. *J. Am. Chem. Soc.* **2002**, *124*, 182.
(111) Hay, B. P.; Dixon, D. A.; Lumetta, G. J.; Vargas, R.; Garza, J. Structural Aspects of Hydrogen Bonding with Nitrate and Sulfate: Design Criteria for Polyalcohol Hosts. In *Fundamentals and Applications of Anion Separations*; Moyer, B. A., Singh, R. P., Eds.; Kluwer Academic/Plenum: New York, 2004; Chapter 3, pp 43−56.
(112) Bryantsev, V. S.; Firman, T. K.; Hay, B. P. *J. Phys. Chem. A* **2005**, *109*, 832.
(113) Bryantsev, V. S.; Hay, B. P. *J. Phys. Chem. A* **2006**, *110*, 4678.
(114) Hay, B. P.; Firman, T. K.; Moyer, B. A. *J. Am. Chem. Soc.* **2005**, *127*, 1810−1819.
(115) Bryantsev, V. S.; Hay, B. P. *THEOCHEM* **2005**, *725*, 177.
(116) Hay, B. P.; Firmane, T. K. *Inorg. Chem.* **2002**, *41*, 5502.
(117) Hay, B. P.; Firmane, T. K.; Lumetta, G. J.; Rapko, B. M.; Garza, P. A.; Sinkov, S. I.; Hutchison, J. E. *J. Alloys Compd.* **2004**, *374*, 416.
(118) Hay, B. P.; Oliferenko, A. A.; Uddin, J.; Zhang, C.; Firmane, T. K. *J. Am. Chem. Soc.* **2005**, *127*, 17043.
(119) Reyheller, C.; Hay, B. P.; Kubic, S. *New J. Chem.* **2007**, *31*, 2095.
(120) Bryantsev, V. S.; Hay, B. P. *J. Am. Chem. Soc.* **2006**, *128*, 2035.
(121) Custelcean, R.; Bosano, J.; Bonnesen, P. V.; Kertesz, V.; Hay, B. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 4025.
(122) Custelcean, R.; Bonnesen, P. V.; Duncan, N. C.; Zhang, X.; Watson, L. A.; Van Berkel, G.; Parson, W. B.; Hay, B. P. *J. Am. Chem. Soc.* **2012**, *134*, 8525.
(123) *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., Garcia-Espana, E., Eds.; Wiley-VCH: New York, 1997.
(124) Llinares, J. M.; Powell, D.; Bowman-James, K. *Coord. Chem. Rev.* **2003**, *240*, 57.
(125) Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671.
(126) Kang, S. O.; Hossain, M. A.; Bowman-James, K. *Coord. Chem. Rev.* **2006**, *250*, 3038.
(127) Kang, S. O.; Begum, R. A.; Bowman-James, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7882.
(128) McKee, V.; Nelson, J.; Town, R. M. *Chem. Soc. Rev.* **2003**, *32*, 309.
(129) Hossain, M. A.; Llinares, J. M.; Powell, D.; Bowman-James, K. *Inorg. Chem.* **2001**, *40*, 2936.
(130) Chimielewski, M. J.; Jurczak, J. *Chem.—Eur. J.* **2005**, *11*, 6080.
(131) Hossain, M. A.; Kang, S. O.; Powell, D.; Bowman-James, K. *Inorg. Chem.* **2003**, *42*, 1397.
(132) Kang, S. O.; Hossain, M. A.; Powell, D.; Bowman-James, K. *Chem. Commun.* **2005**, 328.
(133) Kang, S. O.; Powell, D.; Bowman-James, K. *J. Am. Chem. Soc.* **2005**, *127*, 13478.
(134) Kang, S. O.; Powell, D.; Day, V. W.; Bowman-James, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 1921.
(135) Sessler, J. L.; Cyr, M. J.; Lynch, V.; McGhee, E.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 2810.
(136) Sessler, J. L.; Seidel, D.; Lynch, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 1422.
(137) Eller, L. R.; Stępień, M.; Fowler, C. J.; Lee, J. T.; Sessler, J. L.; Moyer, B. A. *J. Am. Chem. Soc.* **2007**, *129*, 11020. Correction: *J. Am. Chem. Soc.* **2007**, *129*, 14523.
(138) Sessler, J. L.; Katayev, E.; Pantos, G. D.; Ustynyuk, Y. A. *Chem. Commun.* **2004**, 1276.
(139) Sessler, J. L.; Katayev, E.; Pantos, D. G.; Scherbakov, P.; Reshetova, M. D.; Khrustalev, V. N.; Lynch, V. M.; Ustynyuk, Y. A. *J. Am. Chem. Soc.* **2005**, *127*, 11442.
(140) Katayev, E. A.; Boev, N. V.; Khrustalev, V. N.; Ustynyuk, Y. A.; Tananaev, I. G.; Sessler, J. L. *J. Org. Chem.* **2007**, *72*, 2886.
(141) Gale, P. A.; Sessler, J. L.; Kral, V. *Chem. Commun.* **1998**, 1.
(142) Levitskaia, T. G.; Marquez, M.; Sessler, J. L.; Shriver, J. A.; Vercouter, T.; Moyer, B. A. *Chem. Commun.* **2003**, 2248.
(143) Borman, C. J.; Custelcean, R.; Hay, B. P.; Bill, N. L.; Sessler, J. L.; Moyer, B. A. *Chem. Commun.* **2011**, *47*, 7611.
(144) Borman, C. J.; Bonnesen, P. V.; Moyer, B. A. *Anal. Chem.* **2012**, *84*, 8214−8221.
(145) Jia, C. D.; Wu, B. A.; Li, S. G.; Huang, X. J.; Zhao, Q. L.; Li, Q. S.; Yang, X. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 486.
(146) Moyer, B. A.; Bonnesen, P. V.; Custelcean, R.; Delmau, L. H.; Hay, B. P. *Kem. Ind.* **2005**, *54*, 65.
(147) Bonnesen, P. V.; Moyer, B. A.; Presley, D. J.; Armstrong, V. S.; Haverlock, T. J.; Counce, R. M.; Sachleben, R. A. *Alkaline-Side Extraction of Technetium from Tank Waste Using Crown Ethers and Other Extractants*; Report ORNL/TM-13241; Oak Ridge National Laboratory: Oak Ridge, TN, June 1996.
(148) Moyer, B. A.; Bonnesen, P. V.; Burns, J. H.; Delmau, L. H.; Haverlock, T. J.; Presley, D. J.; Sachleben, R. A.; Sloop, F. V. *Investigating the Solvent Extraction of Technetium(VII) from Alkaline Nitrate by Crown Ethers*; Proceedings of the Third International Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Cadarache, France, Dec 12−14, 1994; OECD Nuclear Energy Agency: Paris, France, 1995; pp 425−437.
(149) Fowler, C. J.; Moyer, B. A.; Shriver, J. A.; Gross, D. E.; Sessler, J. L.; Bowman-James, K. *J. Am. Chem. Soc.* **2008**, *130*, 14386.
(150) Moyer, B. A.; Sloop, F. V., Jr.; Fowler, C. J.; Haverlock, T. J.; Kang, H.-A.; Delmau, L. H.; Bau, D. M.; Hossain, A.; Bowman-James, K.; Shriver, J. A.; Bill, N.; Gross, D. E.; Marquez, M.; Sessler, J. L. *Supramol. Chem.* **2010**, *22*, 653.
(151) Custelcean, R. *Curr. Opin. Solid State Mater. Sci.* **2009**, *13*, 68.
(152) Custelcean, R. *Chem. Soc. Rev.* **2010**, *39*, 3675.
(153) Custelcean, R. *Chem. Commun.* **2008**, 295.
(154) Custelcean, R.; Sellin, V.; Moyer, B. A. *Chem. Commun.* **2007**, 1541.
(155) Adarsh, N. N.; Kumar, D. K.; Dastidar, P. *CrystEngComm* **2008**, *10*, 1565.
(156) Adarsh, N. N.; Kumar, D. K.; Dastidar, P. *CrystEngComm* **2009**, *11*, 796.
(157) Xia, Y.; Wu, B.; Liu, Y.; Yang, Z.; Huang, X.; He, L.; Yang, X.-J. *CrystEngComm* **2009**, *11*, 1849.
(158) Zhuge, F. Y.; Wu, B. A.; Liang, J. J.; Yang, J.; Liu, Y. Y.; Jia, C. D.; Janiak, C.; Tang, N.; Yang, X. J. *Inorg. Chem.* **2009**, *48*, 10249.
(159) Adarsh, N. N.; Dastidar, P. *Cryst. Growth Des.* **2010**, *10*, 483.
(160) Banerjee, S.; Adarsh, N. N.; Dastidar, P. *Eur. J. Inorg. Chem.* **2010**, 3770.
(161) Adarsh, N. N.; Tocher, D. A.; Ribas, J.; Dastidar, P. *New J. Chem.* **2010**, *34*, 2458.

(162) Arunachalam, M.; Ghosh, P. *Chem. Commun.* **2011**, *47*, 8477.
(163) Fernando, I. R.; Surmann, S. A.; Urech, A. A.; Poulsen, A. M.; Mezei, G. *Chem. Commun.* **2012**, *48*, 6860.
(164) Custelcean, R.; Moyer, B. A.; Hay, B. P. *Chem. Commun.* **2005**, 5971.
(165) Wu, B.; Liang, J.; Yang, J.; Jia, C.; Yang, X. J.; Zhang, H.; Tang, N.; Janiak, C. *Chem. Commun.* **2008**, 1762.
(166) Ravikumar, I.; Lakshminarayanan, P. S.; Arunachalam, M.; Suresh, E.; Ghosh, P. *Dalton Trans.* **2009**, 4160.
(167) Andrews, N. J.; Haynes, C. J. E.; Light, M. E.; Moore, S. J.; Tong, C. C.; Davis, J. T.; Harrell, W. A.; Gale, P. A. *Chem. Sci.* **2011**, *2*, 256.
(168) Yang, Z.; Wu, B.; Huang, X.; Liu, Y.; Li, S.; Xia, Y.; Jia, C.; Yang, X.-J. *Chem. Commun.* **2011**, *47*, 2880.
(169) Busschaert, N.; Wenzel, M.; Light, M. E.; Iglesias-Hernandez, P.; Perez-Tomas, R.; Gale, P. A. *J. Am. Chem. Soc.* **2011**, *133*, 14136.
(170) Akhuli, B.; Ravikumar, I.; Ghosh, P. *Chem. Sci.* **2012**, *3*, 1522.
(171) Dey, S. K.; Chutia, R.; Das, G. *Inorg. Chem.* **2012**, *51*, 1727.
(172) Custelcean, R.; Bonnesen, P. V.; Roach, B. D.; Duncan, N. C. *Chem. Commun.* **2012**, *48*, 7438.
(173) Custelcean, R.; Remy, P.; Bonnesen, P. V.; Jiang, D.; Moyer, B. A. *Angew. Chem., Int. Ed.* **2008**, *47* (10), 1866.
(174) Rajbanshi, A.; Custelcean, R. *Supramol. Chem.* **2012**, *24*, 65.
(175) Custelcean, R.; Bock, A.; Moyer, B. A. *J. Am. Chem. Soc* **2010**, *132*, 7177.
(176) Rajbanshi, A.; Moyer, B. A.; Custelcean, R. *Sep. Sci. Technol.* **2012**, DOI: 10.1080/01496395.2012.697512.
(177) Custelcean, R.; Remy, P. *Cryst. Growth. Des.* **2009**, *9*, 1985.
(178) Rajbanshi, A.; Moyer, B. A.; Custelcean, R. *Cryst. Growth. Des.* **2011**, *11*, 2702.
(179) Anzenbacher, P.; Try, A. C.; Miyaji, H.; Jursikova, K.; Lynch, V. M.; Marquez, M.; Sessler, J. L. *J. Am. Chem. Soc.* **2000**, *122* (42), 10268.
(180) Sessler, J. L.; Anzenbacher, P., Jr.; Shriver, J. A.; Jurisíková, K.; Miyaji, H.; Lynch, V. M.; Marquez, M. *J. Am. Chem. Soc.* **2000**, *122*, 12061.
(181) Moyer, B. A., Ed. *Ion Exchange and Solvent Extraction*; Taylor and Francis: Philadelphia, PA, 2010; Vol. *19*.
(182) Goken, G. L.; Bruening, R. L.; Krakowiak, K. E.; Izatt, S. R. In *Metal-Ion Separation and Preconcentration*; Bond, A. H., Dietz, M. L., Rogers, R. D., Eds.; American Chemical Society: Washington, DC, 1999; pp 251−259.
(183) Izatt, S. R.; Bruening, R. L.; Izatt, N. E. *J. Met.* **2012**, Nov issue, DOI: 10.1007/s11837-012-0452-8.