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Communication

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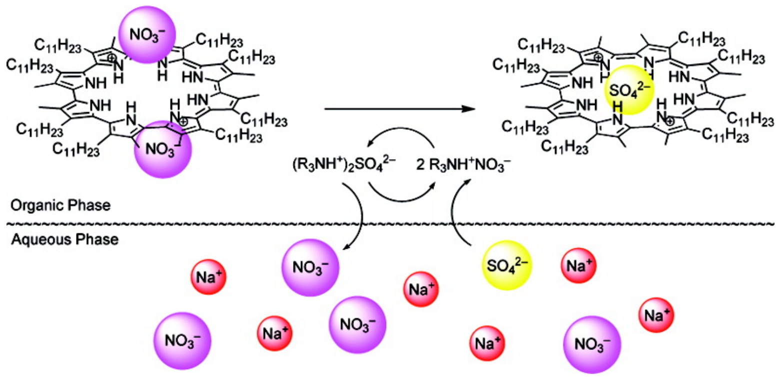

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Octamethyl-octaundecylcyclo[8]pyrrole: A Promising Sulfate Anion Extractant

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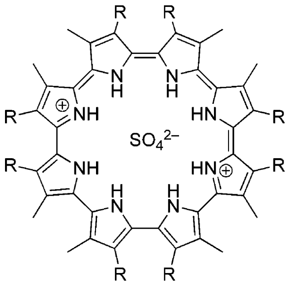
Weapons production during the Cold War era has left a worrisome legacy of radioactive waste, much of it stored in underground tanks.[1] One proposed means of disposing of this waste involves vitrification, namely, incorporation into transportable glass "logs" that can be stored for millennia in a geologic repository. Sulfate, because of its low solubility (typically ca. 1%) in borosilicate glass, has been identified as especially problematic in the vitrification of tank wastes and in long-term glass performance.[2] Although this difficulty has prompted the testing of methods for sulfate removal from the nitrate-rich mixtures that constitute most tank waste, a satisfactory separation remains to be found.[2] One of the strategies that appears particularly promising involves solvent extraction, requiring the use of a highly selective extractant.[3] This is because both the inherent preference for nitrate over sulfate under aqueous−organic partition conditions (the so-called Hofmeister bias)[4] and the high nitrate/sulfate ratios present in tank waste militate against effective sulfate extraction in the absence of such adjuvants. In this Communication, we describe fundamental anion-exchange studies of a system that shows particular promise in this regard, namely the organic-soluble expanded porphyrin, octamethyl-octaundecylcyclo[8]pyrrole (**1**).[5] To the best of our knowledge, this system represents the first anion receptor with which high sulfate-over-nitrate selectivity has been demonstrated in solvent extraction.[6]



1 R = $C_{11}H_{23}$
2 R = C_2H_5

Cyclo[8]pyrroles represent a relatively new class of expanded porphyrins that are noteworthy both for their ease of synthesis (ferric ion-mediated oxidative coupling of bipyrroles in the presence of dilute sulfuric acid) and for their ready crystallization in the form of diprotonated-sulfate salts.[7] Such observations led us to consider that these systems could prove attractive as extractants if they could be rendered soluble in hydrocarbon solvents. Derivative **1**, a system originally developed as a potential liquid crystal,[5] bears eight undecyl β-pyrrolic "side chains" and meets this key solubility criterion, which was problematic in initial work with the short-chain cyclo[8]pyrrole, **2**.[7] In analogy to such less hydrophobic cyclo[8]pyrroles, it was expected that **1** would contain a highly basic core and exist in its diprotonated-anion bound form ($[\mathbf{1}{\cdot}2H]^{2+}{\cdot}X^{2-}$) when in contact with aqueous salt solutions at or near neutral pH. The high rigidity of this system also led us to believe that it would be able to overcome the Hofmeister bias for complementary anions, such as sulfate.[4]

Initial tests of **1** as a potential anion extractant, involving the use of toluene solutions of $[\mathbf{1}{\cdot}2H]^{2+}$ in contact with various aqueous phases, gave results that were consistent with slow-exchange kinetics. Such an interpretation seemed reasonable given the highly hydrophobic nature of the cyclo[8]pyrrole and its likely resultant low interfacial activity. Thus, it was considered that this problem could be overcome through the use of a phase-transfer catalyst as shown for isotopic exchange in Scheme 1.

To test this hypothesis, a simple isotopic-exchange experiment was designed. It involved contacting a solution of $[\mathbf{1}{\cdot}2H]^{2+}{\cdot}SO_4^{2-}$, 0.5 mM in toluene, with an equal volume of a 0.5 mM aqueous Na_2SO_4 solution spiked with $^{35}SO_4^{2-}$ tracer (0.5 μCi/mL). Under these conditions, the actual sulfate distribution ratio D_{SO4} ($= [SO_4^{2-}]_{org}/[SO_4^{2-}]_{aq}$) is set by experiment to unity, and the apparent value of D_{SO4}, as determined from $[^{35}SO_4^{2-}]_{org}/[^{35}SO_4^{2-}]_{aq}$, approaches unity as the isotope exchange reaches completion.[8] Very slow sulfate exchange was indeed seen, reaching only 5.5% completion by 72 h, as shown in Figure 1. However, when Aliquat 336-nitrate (A336N), a commercially available phase-transfer catalyst consisting of a mixture of tri(C_8,C_{10}-*n*-alkyl)methylammonium nitrates, was added to the organic layer at 0.1 mM, equilibrium was reached in 4 h. As expected, little exchange was seen when A336N was used on its own (i.e., in the absence of $[\mathbf{1}{\cdot}2H]^{2+}{\cdot}SO_4^{2-}$). On this basis, we concluded that phase-transfer catalysis is critical to the practical use of **1** for anion exchange.

As selectivity is of primary interest, subsequent efforts were devoted to measuring sulfate exchange with other anions. It was logical to proceed by simply measuring the displacement of sulfate from $[\mathbf{1}{\cdot}2H]^{2+}{\cdot}SO_4^{2-}$ by adding various sodium salts to the aqueous phase under conditions of the phase-transfer-catalyzed isotopic-exchange experiment described above. However, it proved difficult to achieve equilibrium in such systems in a manageable time frame (see Supporting Information). It is reasonable to infer from the slowed kinetics that competing anions compromise the phase-transfer catalyst by reducing the concentration of its sulfate form in the organic phase.

Given the slow exchange kinetics observed for displacing sulfate from $[\mathbf{1}{\cdot}2H]^{2+}{\cdot}SO_4^{2-}$ under the above-described conditions, we felt it was important to prepare other anion-bound forms of $[\mathbf{1}{\cdot}2H]^{2+}$, particularly the bisnitrate salt, $[\mathbf{1}{\cdot}2H]^{2+}{\cdot}(NO_3^-)_2$. In this way, the sulfate exchange could be carried out in a more normal manner, that is, with $[\mathbf{1}{\cdot}2H]^{2+}{\cdot}(NO_3^-)_2$ as the effective form of the extractant and possibly with less hindered kinetics. With this goal in mind, the free-base form of **1** was prepared by contacting toluene solutions containing 0.5 mM $[\mathbf{1}{\cdot}2H]^{2+}{\cdot}SO_4^{2-}$ and 0.1 mM A336N repeatedly with aqueous NaOH solutions (0.1 M) until all the sulfate initially present in $[\mathbf{1}{\cdot}2H]^{2+}{\cdot}SO_4^{2-}$ was transferred to the aqueous phase

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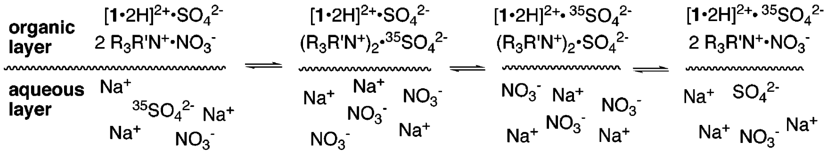
Scheme 1. Phase-Transfer Catalyzed Anion Exchange[a]



[a] $R_3R'N^+$ = Aliquat 336-nitrate (A336N) or trioctylamonium cation ($TOAH^+$).

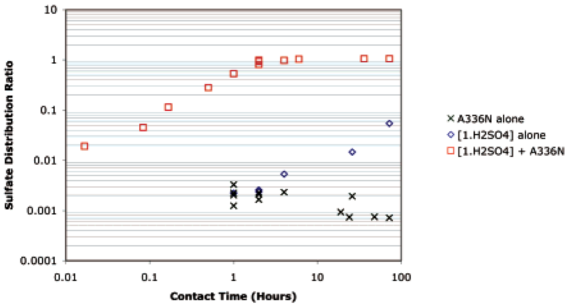


Figure 1. Kinetic enhancement observed using a phase-transfer catalyst. Organic phase: [A336N] = 0.1 mM, $[\mathbf{1}\cdot 2H]^{2+}\cdot SO_4^{2-}$ = 0.5 mM in toluene. Aqueous phase: $[Na_2SO_4]$ = 0.5 mM. O/A = 1, T = 25 °C.

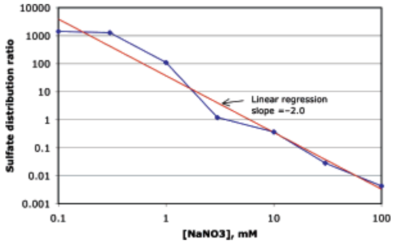


Figure 2. Effect of aqueous $[NO_3^-]$ on D_{SO4}. Organic phase: $[(TOAH)^+(NO_3^-)]$ = 0.1 mM, $[\mathbf{1}\cdot 2H]^{2+}\cdot(NO_3^-)_2$ = 0.5 mM in toluene. Aqueous phase: $[NaNO_3]$ = 0.1−100 mM, $[Na_2SO_4]$ = 0.02 mM. O/A = 1, T = 25 °C, t = 24 h.

(as confirmed by ICP−AES analysis). Unfortunately, little evidence that **1** could be reprotonated was observed, even in the presence of A336N. For instance, no detectable uptake of $^{35}SO_4^{2-}$ into the organic phase was seen upon treatment of toluene solutions of **1** containing A336N (0.5 and 0.1 mM, respectively) with aqueous sulfuric acid (0.1−1.0 M) spiked with $^{35}SO_4^{2-}$ tracer (0.5 μCi/mL). This result is not surprising. Although recognized as an efficient phase-transfer catalyst for anions, A336 is unlikely to mobilize protons into the organic phase effectively.

Given the apparent need to facilitate proton transfer, trioctylamine (TOA; 0.1 mM) was substituted for A336. Under these conditions, it was found that toluene solutions of $[\mathbf{1}\cdot 2H]^{2+}\cdot SO_4^{2-}$ (0.5 mM) could then be stripped of sulfate anion and recharged to produce again $[\mathbf{1}\cdot 2H]^{2+}\cdot SO_4^{2-}$ by successive contact with aqueous NaOH and H_2SO_4 solutions. This process could be repeated without significant degradation, as judged from the near-quantitative transfer of sulfate to the aqueous layer after stripping. It was found possible to produce the dichloride salt of the cyclo[8]pyrrole, $[\mathbf{1}\cdot 2H]^{2+}\cdot(Cl^-)_2$, using this same basic approach by simply substituting HCl for H_2SO_4. However, reprotonation with nitric acid proved too sluggish to produce $[\mathbf{1}\cdot 2H]^{2+}\cdot(NO_3^-)_2$ effectively from the free-base form of **1**.

Fortunately, organic phases containing 0.5 mM $[\mathbf{1}\cdot 2H]^{2+}\cdot(NO_3^-)_2$ and 0.1 mM $(TOAH)^+(NO_3^-)$ could be obtained by repeatedly contacting toluene solutions of $[\mathbf{1}\cdot 2H]^{2+}\cdot SO_4^{2-}$ (0.5 mM) and TOA (0.1 mM) with aqueous 0.1 M HNO_3 until sulfate was no longer detected in the aqueous phase. The resulting solutions were found to re-equilibrate effectively when contacted for 16 h with aqueous solutions containing 0.02 mM Na_2SO_4 and $NaNO_3$ spiked with a $^{35}SO_4^{2-}$ tracer at 1 μCi/mL. Under these conditions, the D_{SO4} values were seen to vary from 0.001 (at 1 M $NaNO_3$) to 1000 (at 0.3 mM $NaNO_3$). In particular, as expected given the relative charges of the anions involved, an inverse second-power mass-action dependence on nitrate concentration was found for the uptake of sulfate from aqueous phases containing an excess of nitrate (Figure 2). The simplest stoichiometry for this exchange is

$$SO_4^{2-}\ (aq) + [\mathbf{1}\cdot 2H]^{2+}\cdot(NO_3^-)_2\ (org) \rightleftharpoons 2NO_3^-\ (aq) + [\mathbf{1}\cdot 2H]^{2+}\cdot SO_4^{2-}\ (org) \quad (1)$$

From the data, the corresponding conditional exchange constant, $\log(K'_{exch})$, valid under the experimental conditions, could be determined; it was found to be 4.9 ± 0.4.

The high K'_{exch} value produced with **1** is remarkable given the challenge imposed by the Hofmeister bias. It effectively means that the more highly hydrated sulfate anion can be usefully extracted from a much higher concentration of a much less hydrated competing anion, such as nitrate. To the best of our knowledge, no other synthetic system has been reported that shows such selectivity. We thus propose that **1** and its congeners may have a role to play, albeit with anticipated improvements in the kinetics, as sulfate-specific anion extractants.

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Supporting Information Available: Experimental procedures and additional extraction results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Except for the kinetics experiment (Figure 1), no distinction is made between actual and apparent D_{SO4}. The limit of detection of the tracer technique corresponds to a value of ca. 1 × 10^{-4}.

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