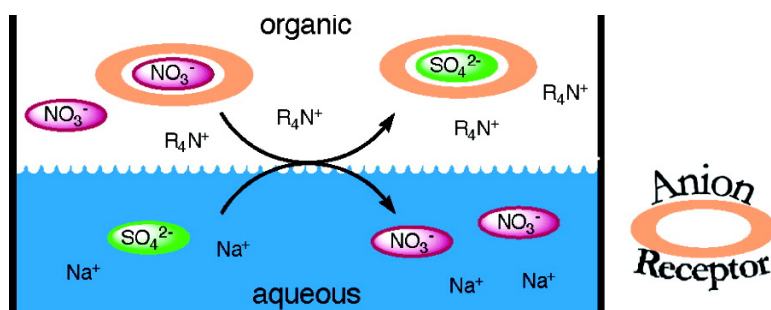## Communication

Enhanced Anion Exchange for Selective Sulfate Extraction: Overcoming the Hofmeister Bias

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Enhanced Anion Exchange for Selective Sulfate Extraction: Overcoming the Hofmeister Bias

Christopher J. Fowler, Tamara J. Haverlock, Bruce A. Moyer,* James A. Shriver, Dustin E. Gross, Manuel Marquez, Jonathan L. Sessler,* Md. Alamgir Hossain, and Kristin Bowman-James*

Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, Department of Chemistry and Biochemistry, Institute for Cellular and Molecular Biology, The University of Texas, Austin, Texas 78712, Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, and Harrington Department of Bioengineering, Arizona State University, Tempe, Arizona 85287

Received August 16, 2008; E-mail: moyerba@ornl.gov; sessler@mail.utexas.edu; kbjames@ku.edu

Synergism in liquid−liquid (L−L) extraction, typified by the combination of a neutral extractant with a cation exchanger to enhance selectively cation extraction strength, has been used and understood for over five decades.[1] Surprisingly, analogous enhancements in anion extraction have yet to be reported. Here, we present a simple way to achieve non-Hofmeister selectivity in L−L anion exchange by combining a synthetic H-bond-donating (HBD) anion receptor with a standard quaternary ammonium type extractant. Specifically, we show that fluorinated calixpyrroles **1** and **2**[2] and the tetraamide macrocycles **3**−**5**[3] may be used to enhance the solvent extraction of sulfate from nitrate by Aliquat 336-nitrate ($CH_3N[(CH_2)_{7-9}CH_3]_3NO_3$; A336N).

1. n = 1
2. n = 2
3. R^1 = H, R^2 = CH$_3$
4. R^1 = H, R^2 = dansyl
5. R^1 = t-butyl, R^2 = CH$_3$
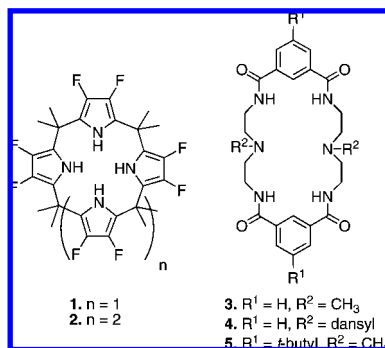
L−L anion exchange is an established industrial technology for anion separations[4] that is rapidly progressing[5] driven in part by advances in understanding anion binding.[6,7] In traditional practice, extraction-based anion exchange relies on the use of lipophilic cationic sites, such as ammonium, phosphonium, imidazolium, or pyridinium centers (protonated or quaternary), whose associated anions exchange in favor of more charge-diffuse anions. Despite its many uses, this solvation-based selectivity,[6b] a manifestation of the ubiquitous Hofmeister bias,[8] inhibits the anion exchange of hydrophilic anions. This limitation has deterred broader application of this technology, which might otherwise provide alternative solutions to such problems as nuclear waste and environmental remediation.[3b,5b]

Based on earlier results,[9] we recently suggested that the use of appropriately chosen anion receptors might allow the Hofmeister bias to be overcome.[3b] Whereas a number of examples are known for receptors containing non-HBD Lewis acid sites,[6a,7,10] non-Hofmeister selectivity has been rarely seen in extractive systems based on receptors possessing only HBD sites. This is particularly true in the case of sulfate,[11] a highly hydrated anion whose selective removal from nitrate-rich matrices is particularly difficult (hydration energies $\Delta G_h = -1103$ vs -314 kJ mol^{-1} for sulfate and nitrate,

respectively[12]), but which would be potentially beneficial in the context of current nuclear waste remediation.[3b,5b] Recently, we demonstrated that the extraction of sulfate from nitrate-rich mixtures could be achieved through the use of a charged oligopyrrolic receptor.[11] However, a potentially simpler approach to this and a multitude of other anion-separation problems involves combining a neutral HBD receptor, whose anion-recognition properties could be separately optimized, with a traditional quaternary ammonium extractant.

The choice of receptors **1**−**5** for the present studies was based on their neutral charge, ability to bind preferentially various anions through HBD interactions, and the fact that they represent two separate classes of anion-binding agents.[7] Since their "rediscovery" in 1996, calix[4]pyrroles have been shown to be good receptors for anions and certain neutral substrates.[13] Moreover, the use of β-pyrrolic fluorine substitution and expansion of the core has led to the generation of systems, such as **1** and **2**, with enhanced affinities and modulated selectivities.[2] Tetraamide macrocycles **3**−**5** are noteworthy for their ability to bind nitrate and sulfate in organic solution and the solid state.[3] We considered that systems **1**−**5** would allow the concept of receptor-mediated enhancement to be tested as a general phenomenon in anion exchange.

The ability to enhance sulfate anion extraction was tested using ^{35}S-labeled sulfate to monitor the exchange of sulfate from an aqueous matrix, consisting of sodium sulfate and excess sodium nitrate, into an organic solvent containing A336N and varying concentrations of **1**−**5**. Toluene and chloroform were chosen as the water-immiscible organic-phase diluents, as they lack strong HBD strength and were expected to minimize competitive anion-solvation effects. Standard beta liquid-scintillation counting techniques were used to determine the distribution of sulfate between the aqueous and organic phases.

Figure 1 illustrates the distribution ratio ($D_{\text{sulfate}} = [\text{SO}_4]_{\text{org}}/[\text{SO}_4]_{\text{aq}}$) recorded for various concentrations of **1** and **2** with A336N in the organic (toluene) phase. The ion exchange between nitrate and the more hydrophilic sulfate was notably increased in the presence of both of the receptors (**1** or **2**) and the quaternary ammonium salt. For the stronger receptor **2**, we showed through use of higher reagent concentrations that D_{sulfate} could be pushed to technologically useful values above 1 (i.e., where stagewise extraction is generally considered viable). We ascribe this apparent enhancement to the specific binding interactions between the calixpyrroles and sulfate anion. However, the matter of stoichiometry, expected to involve competitive binding of both nitrate and sulfate in the organic phase and aggregation phenomena, is not easily inferred from the data without detailed equilibrium modeling, which is the object of ongoing investigation.
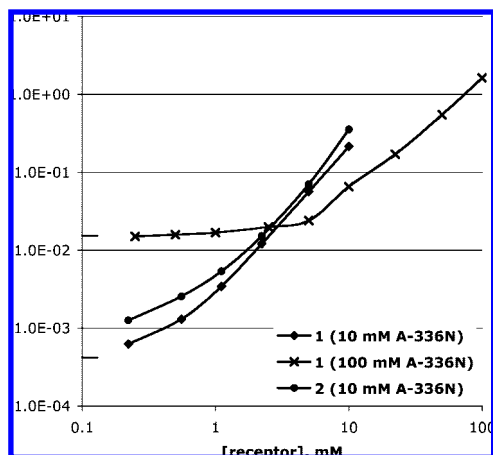
Figure 1. Extraction of sulfate from water using a toluene solution with 10 or 100 mM A336N and varying concentrations of **1** and **2**. Aqueous phase: 10 mM NaNO$_3$, 0.1 mM Na$_2$SO$_4$ (spiked with ^{35}SO$_4$), and 0.1 mM HNO$_3$. Equal volumes of organic and aqueous phases were placed on a rotating wheel for 1 h at 25 °C. Experimental uncertainty in the sulfate distribution ratio, $D_{sulfate}$, is ±5−10%. The heavy tics on the Y-axis indicate the position at the limit of zero receptor concentration.
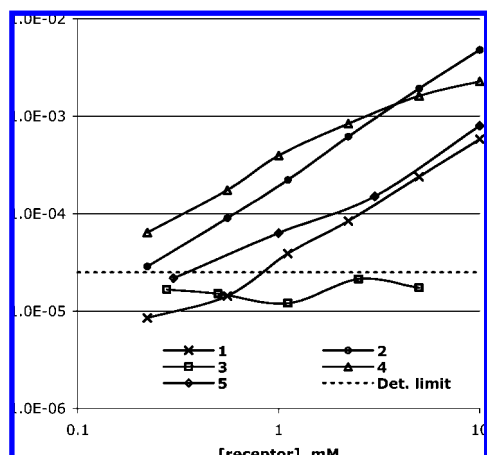

Figure 2. Extraction of sulfate from water using a chloroform solution with 10 mM A336N and varying concentrations of **1−5**. Aqueous phase: 10 mM NaNO$_3$, 0.1 mM Na$_2$SO$_4$ (spiked with ^{35}SO$_4$), and 1.0 mM NaOH. Other conditions are as described in Figure 1. Values of $D_{sulfate}$ < 2.5 × 10^{-5} (dotted line) are considered below the detection limit (1.3 × background count rate).

The enhancement was extended to chloroform as a diluent (Figure 2). This was done to demonstrate the generality of the effect in other solvent environments and for the practical necessity of overcoming solubility limitations of **3−5**. The aqueous phase was made slightly alkaline with 1 mM NaOH to ensure that **3−5** were in their neutral form. While both **3** and **4** bind sulfate strongly in chloroform,[3] the less-lipophilic system **3** did not show any significant sulfate extraction behavior (below detection limit), but **4** was quite effective. The butyl-substituted analogue of **3**, receptor **5**, showed intermediate behavior.

In the case of **1** and **2**, comparison of the extraction behavior in chloroform and toluene was possible; this serves to highlight a significant solvent dependence (cf. Figures 1 and 2). In toluene the behavior of these two fluorinated calixpyrrole receptors was essentially identical, whereas in chloroform the larger system was ca. 10× more effective. While further work is required to rationalize these findings, they could reflect differences in aggregation, con-

formational effects, or specific ion-pairing interactions, for which a strong solvent dependence has been suggested in the case of nonfluorinated calix[4]pyrrole.[14]

In summary, we have shown that the use of specifically chosen neutral anion receptors can be used to overcome the Hofmeister bias in L−L extraction. This finding is noteworthy given the weak nature of the recognition forces involved and the expectation that little direct anion−receptor interaction would be observed in purely aqueous environments. This approach is attractive given its inherent simplicity and the fact that various anion receptors could be made and tested as extractants without having to incorporate them into more complicated bifunctional receptors.

Supporting Information Available: Procedures for extraction studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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