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Novel Approach to Sodium Hydroxide Separation: Synergistic Pseudo-Hydroxide Extraction by a Fluorinated Alcohol and Cage-Functionalized Crown Ethers

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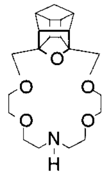
Synergistic pseudo-hydroxide extraction is demonstrated for the first time based on the cooperative effect of a proton-ionizable fluorinated alcohol and cage-annulated crown ethers in nitrobenzene. Synergism was selective for hydroxide compared with normally more extractable inorganic anions. Unexpectedly, the crowns gave unequal synergistic effects, and the strongest sodium salt extraction did not correspond to the strongest synergism.

Significant effort has been expended over the past decade toward understanding anion recognition and transport in liquid−liquid separation systems.[1] However, OH^- ion has received limited attention in this regard, one example being the adduct formation between OH^- and electrophilic boranes.[2] Interest in the chemistry of alkaline solutions has been intensified by the need to treat alkaline nuclear wastes stored in underground tanks at several U.S. Department of Energy sites.[3] One problem of special interest is the selective separation of OH^- ion itself for possible recycle applications.[4,5] Separation of OH^- represents a particular challenge because the Hofmeister effect[6] favors extraction of large charge-diffuse anions.[7]

One approach to hydroxide separation avoids the Hofmeister effect by employing a cation-exchange principle.[4] Termed pseudo-hydroxide extraction, this approach employs weak hydroxy acids such as phenols or fluorinated alcohols dissolved in a water-immiscible diluent to afford proton exchange with aqueous alkali cations at elevated pH.[4,5] On contact with water, the phenoxide or alkoxide molecules release their cation and hydroxide equivalents via hydrolysis to generate a salt-free aqueous solution of the metal hydroxide.

Use of a cation receptor in synergistic combination with a weak hydroxy acid has been proposed to allow control of the strength and cation selectivity of pseudo-hydroxide extraction.[4] Such a strategy lowers the net barrier to cation partitioning otherwise governed solely by cation solvation[8] and follows from related systems employing stronger organic acids.[9,10] Here, we experimentally demonstrate the principle of synergistic pseudo-hydroxide extraction, making use of novel cage-annulated crown ethers[11,12] **1**−**3** of varying flexibility in combination with fluorinated alcohol[13] **4** in nitrobenzene. Regarding the crown ethers, cage-annulation provides both lipophilicity and ring-rigidification, and the amine groups serve as potential pivot points for eventual sidearm substitution. Three spacers $-(CH_2)_{n=1-3}-$ were examined to reveal the most efficient attachment of the cage moiety within the macrocycle. Fluorinated alcohol **4** was chosen for its requisite ionizability and lipophilicity.[5] Possessing a high dielectric constant ($\epsilon = 34.8$),[14] nitrobenzene as a model diluent minimizes ion-pairing effects in the organic phase. It also lacks hydrogen-bond donor strength,[14] minimizing specific anionic solvation and ion-pair extraction by the crowns used alone; a marked Hofmeister bias is thus expected (cf., Gibbs energies of anion transfer[15]).[7]



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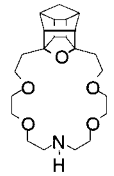

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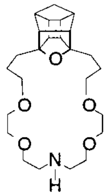

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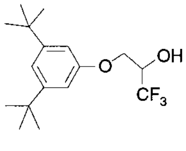

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Figure 1 compares the distribution behavior of Na^+ ion observed using each combination of crown ether and **4** versus the corresponding behavior for the crown ether used alone. A data point falls on the diagonal line when the D_{Na} value for a crown ether remains unchanged upon addition of **4** in the NB phase. This condition is met or nearly so for all anions other than hydroxide, suggesting that **4** interacts weakly with the salt anions. Data points rise above the diagonal line in the case of NaOH, however, indicating a synergistic effect. Synergistic factors [$S = D_{Na,CE+\mathbf{4}} / (D_{Na,CE} + D_{Na,\mathbf{4}})$] for NaOH were 24.5, 3.5, and 3.4 using **1**, **2**, and **3**, respectively. It may be noted for combination of **1** and **4** that the enhancement for OH^- ion puts the pseudo-hydroxide extraction nearly on par with sodium perchlorate ion-

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(13) Compound **4** was prepared by the reaction of 3,5-di-*tert*-butylphenol with 1,1,1-trifluoro-2,3-epoxypropane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 18H, $-C(CH_3)_3$), 2.95 (s, 1H, OH), 4.18 (dd, $J = 6.2$, 9.9 Hz, 1H, OCH*H*CH(CF_3)OH), 4.26 (dd, $J = 3.2$, 9.9 Hz, 1H, OC*H*HCH(CF_3)OH), 4.37 (m, 1H, OCHHC*H*(CF_3)OH), 6.78 (d, $J = 1.6$ Hz, 2H, ArH_2, ArH_6), 7.10 (t, $J = 1.6$ Hz, 1H, ArH_5).

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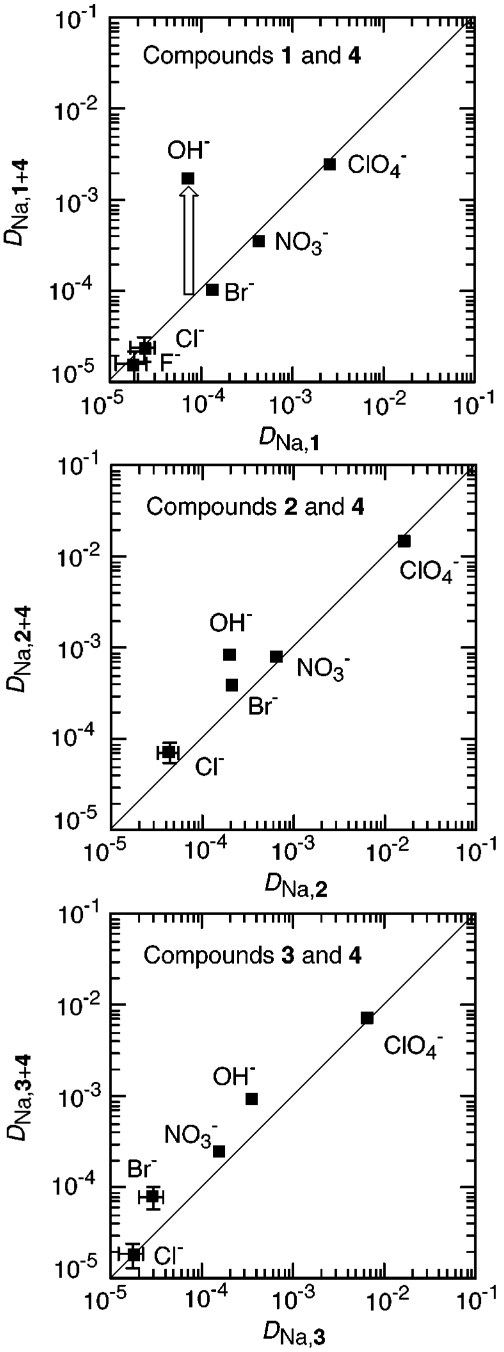

Figure 1. Each plot shows the Na^+ ion distribution ratios (D_{Na}) for a combination of 22 mM crown ether **1**, **2**, or **3** with 44 mM fluorinated alcohol **4** vs D_{Na} for the corresponding crown ether used alone at 22 mM in nitrobenzene. Aqueous phase: 1 M NaX ($X^- = ClO_4^-$, NO_3^-, Br^-, Cl^-, F^-, or OH^-). Equal phase volumes were gently agitated for 2 h at 25 °C, and values of D_{Na} ($[Na^+]_{org}/[Na^+]_{aq}$) were determined by ^{22}Na radiotracer techniques. Experimental uncertainty is approximately ±5% unless otherwise indicated by error bars. Values of $D_{Na,CE+\mathbf{4}}$ and $D_{Na,\mathbf{CE}}$ for ClO_4^- and OH^- were corrected for slight extraction by **4**.[18] Values of D_{Na} for NaF using receptors **2** and **3** were not obtained, owing to the formation of a third liquid phase in the extraction system.

pair extraction, perchlorate being highly extractable, owing to its diffuse charge density.[7,10]

Interestingly, the synergistic factors were not all the same, as would be expected by the simplest possible hypothetical model reaction (CE = crowns **1**, **2**, or **3**; ROH = alcohol **4**):

$$ROH_{(org)} + CE_{(org)} + Na^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons RO^-_{(org)} + NaCE^+_{(org)} + H_2O_{(aq)} \quad (1)$$

The elevation of a point above the diagonal reflects the strength of this reaction, extraction otherwise occurring via ion-pair extraction. Accordingly, this model predicts that the synergistic enhancement depends only on the properties of the ion exchanger and thus is expected to be the same for hosts **1**, **2**, and **3**.[16] Thus, additional interactions that depend on the structure of the host molecule must occur. Hydrogen-bonding of **4** to the crowns may be ruled out, because such antagonism would also be seen for the other anions (points falling below the diagonal). A more likely possibility is ion-pairing between the complex cation and the alkoxide anion, which would depend on the structure of the crown compound and, though minimized by nitrobenzene, may still be important. In this context, ineffective encapsulation of the metal cation by the host often fosters stronger ion-pairing.[8] Thus, the strongest host may not necessarily be the one that gives the strongest synergism.

Finally, the distribution results demonstrate that the length of the spacer linking the cage moiety with the remainder of the macrocycle has a marked effect on Na^+ binding (Figure 1). It may be seen that **2** possesses the strongest overall extraction strength toward the various salts. As found from the crystal structure of **1** and molecular-modeling simulation,[11] the dipole moments of the −COC− units in the calculated low-energy conformation align in different directions relative to the plane of the crown ether cavity, implying costly conformational reorganization in Na^+ ion binding. The lower conformational rigidity of **2** together with the likely more favorable bite of the −OCCCO− unit[17] may allow formation of a less strained Na^+ complex. Highly flexible crown **3** presumably suffers from the least preorganization. Encapsulation of Na^+ by crown **1** is thus expected to be least efficient, leading to strongest ion-pairing and greatest synergism.

In conclusion, model distribution studies have demonstrated the principle of synergistic pseudo-hydroxide extraction, in which cation host molecules synergistically enhance liquid−liquid cation exchange of sodium ion by a weakly acidic hydroxy acid at high pH. This novel approach based on the simultaneous utilization of ion-exchange and recognition principles suggests possible advances in hydroxide recovery and recycle in industrial applications.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Note that a stronger host molecule only moves the point up the diagonal line. It is the effective acidity of the hydroxy acid that moves the point above the diagonal.

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[18] D_{Na} was 1.0(±0.1) × 10^{-4} for $NaClO_4$ and NaOH and <(1 × 10^{-5}) for other sodium salts.