Using carbon dioxide and calix[4]arenes to separate sodium†

Hexiang Zhang* and Dmitry M. Rudkevich‡

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Reversible CO_2-induced precipitation of a calix[4]arene-based complex leads to selective separation of Na^+ salts.

Public attention to greenhouse carbon dioxide (CO_2) is constantly growing,[1] and there is a need for its chemical utilization. We use CO_2 to make switchable, supramolecular polymers.[2] More recently, we found that such polymers can be employed for metal ion separation.[3] Separation of ions through molecular recognition typically involves extraction.[4] Macrocyclic receptors have been synthesized that selectively complex metal salts and solubilize them in organic solvents. Polymer-supported macrocyclic receptors have also been introduced. One significant problem here is the handling and storage of large quantities of organic solvents that are often expensive and/or environmentally toxic. This is particularly important for storage of toxic metal wastes in solution after the extraction. On the other hand, when polymers with appended receptors are used, the complexation takes place not in homogeneous solution but at the solid–liquid interface, which is often not effective. We are developing an approach which eliminates these problems. It combines solution complexation/extraction by macrocyclic receptors and subsequent CO_2-induced precipitation of the complexes (Fig. 1).[3]

In this communication, we demonstrate selective separation of Na^+ salts using CO_2 and calix[4]arene-based receptors. There is significant interest in Na^+ separation in industry, including nuclear waste treatments and desalination of seawater.

Calix[4]arene **1** has four $CH_2C(O)NH$ amide groups at the lower rim (Fig. 2).§ The carbonyl oxygen atoms and four ether oxygens provide eight preorganized coordination sites for binding Na^+. According to the literature, such a structural arrangement offers a very high affinity towards Na^+ cation; binding constants $> 10^5\ M^{-1}$ and selectivities of $Na^+/K^+ > 10^4$ have been documented.[5] Receptor **1** also possesses four primary amino groups on the periphery that are capable of reacting with CO_2 to form cross-linked ammonium carbamates.[6]

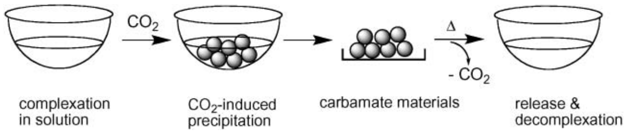

Fig. 1 Separation strategy using CO_2.

We found that receptor **1** selectively extracts Na^+ salts *vs.* K^+ and Cs^+ and complex **2** can subsequently be precipitated upon reacting with CO_2 (Fig. 2). In detail, a TFA salt of calixarene **1** was dissolved in $CHCl_3$ in the presence of Et_3N ($\sim$15 equiv.) and, as expected, quantitatively extracted $Na^+ClO_4^-$ from the solid phase. Complex **2** was characterized by ^1H NMR spectroscopy in DMSO-d_6, showing significant changes compared to free receptor **1** (Fig. 3). For example, the aromatic protons shifted from 6.83 in free **1** to 7.12 ppm in **2**, which is attributed to the electron-withdrawing nature of Na^+. The CH_2 protons of the methylene bridges between the aromatic rings shifted from 4.52 and 3.22 in **1** to 4.34 and 3.34 ppm in **2**, respectively. This phenomenon is known and is caused by fixation of Na^+ cation at the lower rim.[7] Under the same conditions, no extraction of $K^+ClO_4^-$ and $Cs^+ClO_4^-$ was observed; no changes in the ^1H NMR spectra were detected. Similar selectivity was also observed for Na^+Pic^- over K^+Pic^- and Cs^+Pic^-.

After the extraction, the solution was separated and CO_2 gas was introduced (rt, 1 atm). A fine white precipitate quickly formed (Fig. 4), which was identified as cross-linked carbamate polymer **3**.¶ While the ^1H NMR spectrum was broad, ^{13}C NMR

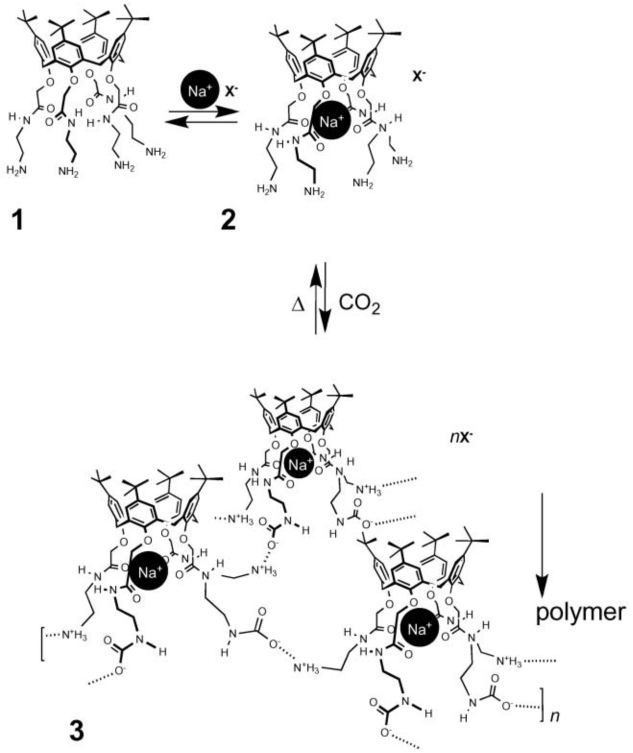

Fig. 2 Separation of Na^+ involves selective calix[4]arene tetraamide receptor **1** and CO_2 gas.

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019-0065, USA.
E-mail: zhanghx7997@yahoo.com; Tel: 1 817 272 6063

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‡ Passed away 4th August 2007.

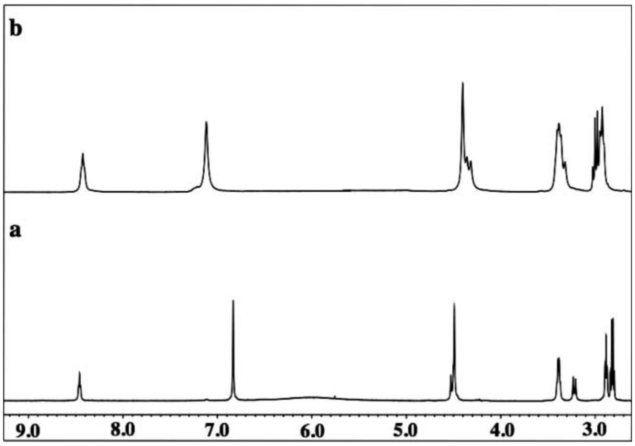

Fig. 3 Portions of the ^{1}H NMR spectra (500 MHz, rt, DMSO-d_6) of: a) receptor **1**; b) Na^+-complex **2**. The residual Et_3N quartet is at ~2.8 ppm.

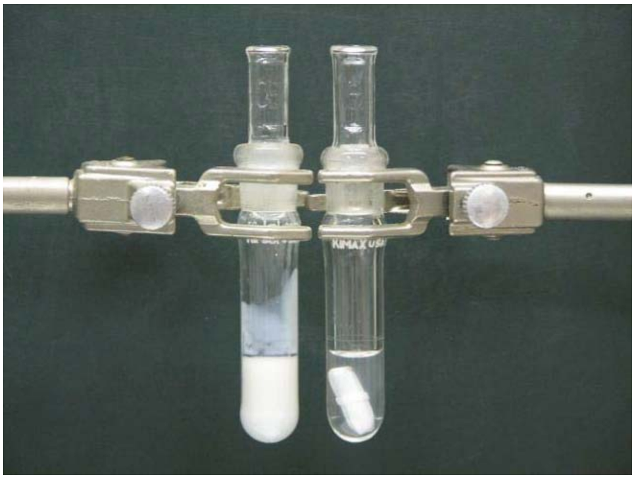

Fig. 4 Right: Na^+-complex **2** in $CHCl_3$ after the extraction. Left: same solution after bubbling CO_2.

spectroscopy provided an unambiguous proof of the carbamate formation. Specifically, when ^{13}C-labeled CO_2 was used, a strong carbamate *C*=O signal at ~160 ppm was clearly seen (in DMSO-d_6).|| In additional experiments, metal-free receptor **1** also reacted with CO_2 both in $CHCl_3$ and DMSO, yielding the corresponding carbamate precipitate and carbamic acid, respectively (see ESI†). For example, when CO_2 was bubbled through the DMSO-d_6 solution of **1**, the carbamic C*H*$_2$NHC(O) methylene and NH signals were detected at 3.03 and 6.68 ppm in the ^{1}H NMR spectrum, respectively. In the COSY, a cross-peak between these two signals was observed. Prior to CO_2, the C*H*$_2$NH$_2$ methylene protons in **1** were recorded at 2.88 ppm. These data agree well with the published spectra for alkylammonium carbamates.[8]

Importantly, polymer **3** incorporates the Na^+ cations. The process thus separates the complexed species from the bulk solution. Considering that neither K^+ nor Cs^+ was complexed under the described conditions, the proposed approach offers a selective Na^+ separation.** Precipitate **3** was collected and stored for several weeks. On the other hand, it released CO_2 and dissociated back to the monomers simply upon heating and flushing with nitrogen (40–50 °C). The Na^+ can subsequently be released in the pure form simply upon washing with water.

In conclusion, it is possible to selectively separate Na^+ salts through binding in solution and subsequent precipitation with CO_2. The Na^+-storage can now be accomplished without solvent, which is economically preferred and prevents environmentally dangerous leaching. Combined with the increasing role of CO_2 in separations[9] and green chemistry,[10] our approach offers a means for creating environmentally responsive processes.

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Notes and references

§ Calixarene **1** was prepared as a TFA salt. For the subsequent experiments, Et_3N was added to liberate the free amino groups. See ESI.

¶ According to ^{1}H NMR, in the reaction between **2** and CO_2, in addition to polymer **3**, triethylammonium carbamates of **2** also form. In these, the calixarene-$CH_2NHC(O)O^-$ units are coordinated to one or more Et_3NH^+ residues.

|| After precipitation by CO_2, the resulting clear solution was separated off and analyzed by NMR spectroscopy (*cf.* ESI, p. 21). Only triethylamine was found in the organic phase.

** Control experiments, involving the use of $KClO_4$ and $CsClO_4$, revealed no entrapment of these cations (*cf.* ESI, pp. 19–20).

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