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CO$_2$ Capture by a Task-Specific Ionic Liquid

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There is little doubt that petroleum, coal, and natural gas will continue to be the primary global fuel and chemical feedstock sources for some years to come.[1] The lattermost—natural gas—is regarded as the cleanest of these materials, and as such is being consumed at an accelerating pace.

Despite its reputation as a clean fuel, natural gas is usually contaminated with a variety of undesirable materials, especially CO$_2$ and H_2S. While this level of contamination is very low in gas from certain sources (sweet gas), it is much higher in others (sour gas). As sweet gas reserves are depleted, pressures will build for the increased utilization of sour gas.[2] Since admixed CO$_2$ lowers the fuel value of natural gas, the large amount of it present in sour gas compels its removal prior to combustion. The lower fuel value for sour gas, coupled with the connection between CO$_2$ and global warming, makes CO$_2$ capture a commercially important and environmentally desirable process.

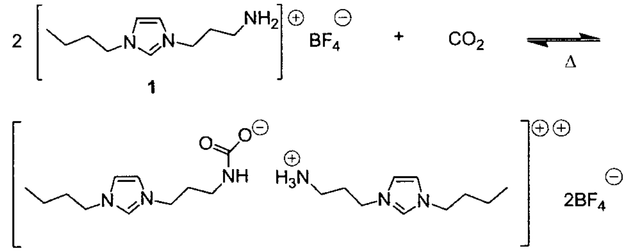
The most attractive approach for the separation of a target compound from a mixture of gases in a gas stream is selective absorption into a liquid.[3] Such interactions between gases and pure liquids or solutions are the bases for numerous gas separation technologies, including commercial systems for the removal of CO$_2$ from natural gas. These scrubbing processes include ones in which the simple, differential dissolution of the target gas into the liquid phase is of principal importance. More common are processes in which a chemical reaction of the target gas with a solute in the liquid phase is the main mode of sequestration.

With either mode of gas removal, the vapor pressure of the solvent itself plays a significant role in gas−liquid processes, usually to their detriment. In the case of large-scale CO$_2$ capture, aqueous amines are used to chemically trap the CO$_2$ by way of ammonium carbamate formation. In these systems, the uptake of water into the gas stream is particularly problematic. Compounding the water uptake difficulty is the loss into the gas stream of the volatile amine sequestering agent.

A liquid that could facilitate the sequestration of gases without concurrent loss of the capture agent or solvent into the gas stream should prove to be a superior material in such applications. To this end, ionic liquids (low-temperature molten salts) have been proposed as solvent reagents for gas separations.[4] Due to the Coulombic attraction between the ions of these liquids, they exhibit no measurable vapor pressure up to their thermal decomposition point, generally >300 °C. This lack of vapor pressure makes these materials highly attractive for gas processing. Indeed, for these purposes they may be thought of as "liquid solids", incorporating some of the most useful physical properties of both phases.

Despite the general promise of ionic liquids (IL) in gas treatment, the molten salts used so far for CO$_2$ separation are generally "off the shelf" materials such as $(CH_3)_4NF\cdot 4H_2O$ that are not optimized for this purpose, frequently depending upon another volatile reagent—water— to function.[4−6] For instance, the latter salt uses the very weakly basic bifluoride ion to drive the net generation of bicarbonate from CO$_2$ and water. In this light, the development of new ionic liquids designed for CO$_2$ capture is clearly desirable.

Scheme 1. Proposed Reaction between TSIL **1** and CO$_2$



Recent work suggests that the chances for preparing a broad array of ionic liquids with ions incorporating functional groups are rather good.[7] Moreover, certain of these new "task-specific" ionic liquids have proven useful in both synthetic and separations applications.[8−12] Here, we report our first IL designed for CO$_2$ capture.

The cation of this new task-specific ionic liquid consists of an imidazolium ion to which a primary amine moiety is covalently tethered. This novel salt readily and reversibly sequesters CO$_2$. To our knowledge, no molten salts have been previously reported that use the cation as the agent of fixation, and only one type of salt has been reported to fix the CO$_2$ as a carbamate, in a fashion similar to that of standard amine scrubbing agents.

The new ionic liquid is prepared from commercially available starting materials. The cation core is assembled by the reaction of 1-butylimidazole with 2-bromopropylamine hydrobromide in ethanol. After 24 h under reflux, the ethanol is removed in vacuo and the solid residue dissolved in a minimal quantity of water that is brought to ∼pH 8 by the addition, in small portions, of solid KOH. The product imidazolium bromide is then separated from the KBr byproduct by evaporation of the water, followed by extraction of the residue with ethanol−THF, in which the imidazolium salt is soluble. Subsequent ion exchange with NaBF$_4$ in ethanol/water gives the product salt **1** in 58% overall yield. NMR and FAB-MS verify the structure and composition of the new IL.[13] After drying under vacuum at 80 °C, the product is a relatively viscous, water free (down to NMR detection limits) liquid that may be used directly for CO$_2$ sequestration [Scheme 1].

Consistent with observations by Brennecke and co-workers, CO$_2$ at 1 atm exhibits intrinsic solubility in the "conventional" ionic liquid phase 1-hexyl-3-methyl imidazolium hexafluorophosphate, [6-mim]PF$_6$.[14,15] This is manifested by a 0.0881% increase in mass of the IL upon exposure to CO$_2$, and also by the FT-IR spectrum of the gas-treated IL, which has peaks characteristic of dissolved CO$_2$ at 2380 and 2400 cm.$^{-1}$ In a similar fashion, **1** also exhibits a mass increase when exposed to CO$_2$, but one that considerably exceeds that observed with [6-mim]PF$_6$. When 1.2896 g of pure **1** is exposed to a stream of bone dry CO$_2$ for 3 h at 1 atm at room temperature (∼295 K), a total mass gain of 0.0948 g (7.4%) is

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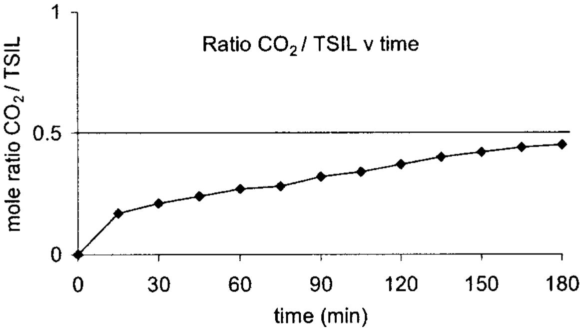

Figure 1. CO_2/TSIL molar ratio as a function of time.

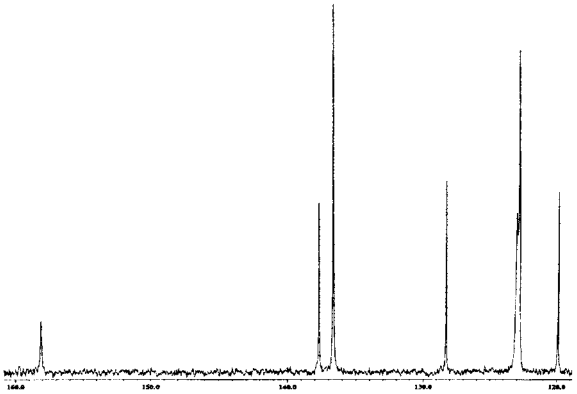

Figure 2. ^{13}C NMR spectrum of the low-field region of **1** after treatment with CO_2.

observed, a vastly greater increase than that observed for [6-mim]-PF_6. This manifest superiority of **1** for CO_2 capture over [6-mim]-PF_6 prompts our assignment of the term “task-specific” to describe this IL.

The molar uptake of CO_2 per mole of TSIL during the 3 h exposure period approaches 0.5, the theoretical maximum for CO_2 sequestration as an ammonium carbamate salt [Figure 1]. This per mole uptake of CO_2 by the amine-appended TSIL is comparable to those of standard sequestering amines such as monoethanolamine (MEA), β,β'-hydroxyaminoethyl ether (DGA), and diisopropanolamine (DIPA). The process of CO_2 uptake is reversible, CO_2 being extruded from the IL upon heating (80−100 °C) for several hours under vacuum. The recovered ionic liquid has been repeatedly recycled for CO_2 uptake (five cycles) with no observed loss of efficiency.

Significantly, the sequestration of CO_2 by the TSIL via its fixation as an ammonium carbamate is borne out by comparison of both the FT-IR and NMR spectra of the gas-untreated and gas-treated materials. In the FT-IR, the spectrum of the CO_2 treated material manifests a new absorption at 1666 cm^{-1}, consistent with a carbamate C=O stretch. Among the other prominent IR changes are those associated with N−H resonances. Centered at 3238 cm^{-1}, a broad amide N−H band with considerable fine structure is now present. Another broad but similarly notable new band is centered around 3623 cm^{-1}, and is assigned as an ammonium N−H stretch. Perhaps equally noteworthy is the virtual absence of bands associated with dissolved CO_2. When subjected to heating under vacuum, the FT-IR spectrum of the sample returns to a pre-CO_2 exposure appearance.

The ^{13}C NMR spectrum [Figure 2] of the CO_2 treated product similarly substantiates TSIL-ammonium carbamate formation.[16] Most notably, a new resonance is observed at δ 158.11, attributable to a carbamate carbonyl carbon. Also new is a peak at 56.52 ppm, consistent with a methylene carbon attached to the carbamate nitrogen atom. The other features of the spectrum generally consist of peaks near those of the starting free-amine TSIL. However, the new resonances are “doubled” due to one-half of the amine TSIL becoming a carbamate- and the other an ammonium-appended species.

While molten salts have been used in CO_2 separation, they are few in number and are unoptimized for the application. Within this context, we believe our results are of particular significance in establishing that ionic liquids can be designed for the processing of gases, in this case CO_2.

While the relatively high viscosity of **1** might limit its eventual use in large-scale gas scrubbing applications, ample opportunities exist for designing variants with improved physical and chemical properties. We anticipate that such new compounds will prove useful in further studies centering upon the selective sequestration and transport of CO_2 and other gases by TSIL.

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(13) NMR (300 mHz, ^1H, CD_3CN): δ 9.13 (s, 1H, ring C(2)H); 7.58 (dd, 1H, ring H); 7.49 (dd, 1H, ring H); 4.32 (t, 2H, CH_2-N_{ring}); 4.17 (t, 2H, CH_2-N_{ring}); 2.70 (m, 2H, CH_2-N_{amine}); 2.04 (m, 2H, CH_2); 1.84 (m, 2H, CH_2); 1.31 (m, 2H, CH_2); 0.86 (t, 3H, CH_3). NMR (75.57 mHz, ^{13}C, CD_3CN): δ 135.94 (ring C(2)); 122.64 (ring C); 122.43 (ring C); 49.65 (CH_2-N_{ring}); 47.26 (CH_2-N_{ring}); 44.21 (CH_2-NH_2); 29.35 (CH_2); 27.91 (CH_2); 21.82 (CH_2); 13.02 (CH_3). FAB-MS (*p*-nitrobenzyl alcohol matrix): *m/z* 182.
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(16) NMR (75.57 mHz, ^{13}C, DMSO-d_6): δ 158.12 (carbamate C); 137.71 (ring C(2)); 136.68 (ring C(2)); 128.34 (ring C); 123.06 (ring C); 122.86 (ring C); 119.93 (ring C); 56.52 (br, $CH_2-N_{carbamate}$); 49.16 (CH_2-N_{ring}); 46.24 (CH_2-N_{ring}); 33.10 (CH_2); 31.78 (br, CH_2); 19.58 (CH_2); 19.29 (br, CH_2); 18.99 (CH_2); 13.86 (CH_3); 13.78 (CH_3) [peaks described as “broad” consist of what appear to be overlapped, unresolved resonances]. NMR (300 mHz, ^1H, DMSO-d_6): δ 9.41 (s, 1H, ring C(2)H); 9.38 (s, 1H, ring C(2)H); 7.89 (br, 2H, overlapped carbamate N−H, ring H); 7.69 (s, 1H, ring H); 7.16 (s, 1H, ring H); 7.85 (s, 1H, ring H); 6.76 (br, 3H, $-NH_3^+$); 4.36 (br m, 2H, CH_2); 4.18 (br m, 4H, CH_2); 2.90 (br m, 2H, CH_2); 2.82 (br m, 2H, CH_2); 2.16 (br m, 2H, CH_2); 1.91 (br m, 2H, CH_2); 1.75 (m, 4H, CH_2); 1.19 (overlapping m, 6H, CH_2); 0.82 (overlapping t, 6H, CH_3).

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