Design and Evaluation of Ionic Liquids as Novel CO_2 Absorbents

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Abstract

Progress from the fourth quarter 2005 activity on the project "Design and Evaluation of Ionic Liquids as Novel CO_2 Absorbents" is provided. Major activities in three areas are reported: compound *synthesis*, *property measurement* and *molecular modeling*.

Last quarter we reported the first ever experimental measurement of SO_2 solubility in an ionic liquid. We showed that SO_2 was very soluble in the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([hmim][Tf_2N]). This quarter, we have measured SO_2 solubility in two more ionic liquids: 1-hexyl-3-methylpyridinium bis(trifluoromethanesulfonyl)imide ([hmpy][Tf_2N]) and 1-hexyl-3-methylimidazolium lactate ([hmim][lactate]). As with [hmim][Tf_2N], we find very high solubility of SO_2 in these ionic liquids, but the lactate compounds shows the highest affinity for SO_2 at low pressure. CO_2 solubility was measured in three new compounds: [boronium][Tf_2N], 1-hexyl-3-methylimidazolium acesulfumate ([hmim][ace]), and 1-hexyl-3-methylimidazolium saccharinate ([hmim][sac]). We find relatively poor solubility of CO_2 in the latter two compounds, and solubility comparable to [hmim][Tf_2N] in the boronium compound. We also synthesized four new ionic liquids this quarter and continued refinement of our molecular simulation technique for measuring gas solubility.

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Introduction

Ionic liquids are a new and exciting class of compound that have the potential to overcome many of the problems associated with current CO_2-capture techniques. Ionic liquids (ILs) are organic salts that are liquid in their pure state near ambient conditions. ILs are regarded as potentially environmentally-benign solvents due to their immeasurably low vapor pressure, which essentially eliminates the opportunity for solvent release to the atmosphere.

The goal of this project is to obtain a fundamental understanding of the solubility of CO_2 and other components present in flue gas in ILs, with the practical objective of tailoring the properties of the liquid to maximize the engineering properties for this process. Our plan is to do this through a combination of *synthesis and experimental measurements*, *molecular simulation* and *applications development.* This sixth quarterly technical report (Q1 2006) describes the results of our work on this project from 10/01/2005 through 12/31/05).

Executive Summary

Ionic liquids (ILs) are organic salts that are liquid in their pure state near ambient conditions. They are a new and exciting class of compound that have the potential to overcome many of the problems associated with current CO_2-capture techniques. This project is concerned with developing a fundamental understanding of the solubility of flue gas species (mainly CO_2) in ionic liquids. Using this knowledge, we hope to develop new IL compounds that can be used in a cost effective manner for CO_2 capture. During Q1 2006, we have focused on three major activities: *synthesis*, *physical property measurement* and *molecular modeling*.

Compound Synthesis

Four new ionic liquids have been synthesized and characterized. Three of these contain amine groups on the cation, which we anticipate may lead to chemical complexation with CO_2 and thus yield very high CO_2 carrying capacity. The other ionic liquid contains five acetate groups on the anion, which we believe may lead to weak complexation with CO_2.

Physical Property Measurement

CO_2 isotherms have been measured for three new ionic liquids, while SO_2 isotherms have been measured for two compounds. CO_2 capacity is lower than what we obtain with a benchmark compound for two of the three ionic liquids, and no better than the benchmark for the third compound. Thus we have not been able to increase CO_2 solubility this quarter. We do see, however, very high SO_2 solubility in both compounds tested. One compound shows the highest SO_2 solubility yet witnessed. This opens up the intriguing possibility of using a single solvent to remove both CO_2 and SO_2 from a flue gas stream.

Molecular Modeling

We have performed simulations of CO2 solubility in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate. Results at low pressure agree reasonably well with experimental capacities, but liquid densities appear to be too low. We are investigating the source of this discrepancy.

Experimental

Gas absorption was measured using a gravimetric microbalance, as described in our previous reports.

Results and Discussion

Synthesis

The four new ionic liquids shown in Figure 1 were synthesized in our labs this quarter.

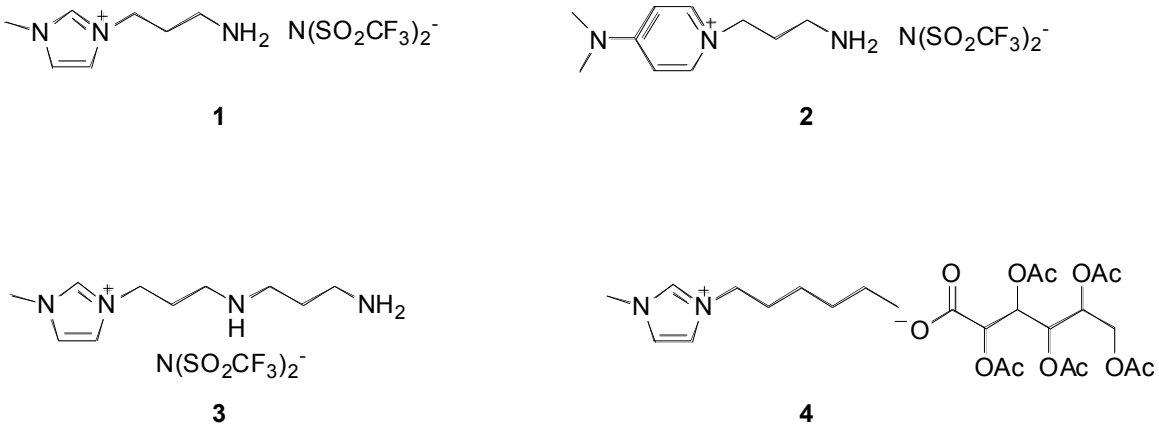


Figure 1: Four new compounds made in our lab this quarter.

Compounds 1-3 contain amine functionality on the cation. The idea behind making these compounds is that the amine group may weakly complex CO_2, thereby enhancing low-pressure solubility as well as capacity. Compound 4 has five acetate groups on the anion, which we suspect may also complex with CO_2. These compounds still must be purified and characterized.

Property Measurement

Last quarter we reported the first ever SO_2 solubility measurement in an ionic liquid. We found that SO2 was very soluble in the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([hmim][Tf_2N]). This quarter, we have measured SO_2 solubility in two more ionic liquids: 1-hexyl-3-methylpyridinium bis(trifluoromethanesulfonyl)imide ([hmpy][Tf_2N]) and 1-hexyl-3-methylimidazolium lactate ([hmim][lactate]). We find that SO_2 is about as soluble in [hmpy][Tf2N] as in [hmim][Tf2N], but it is much more soluble in [hmim][lactate] that either ionic liquid, as can be seen from Figure 2.

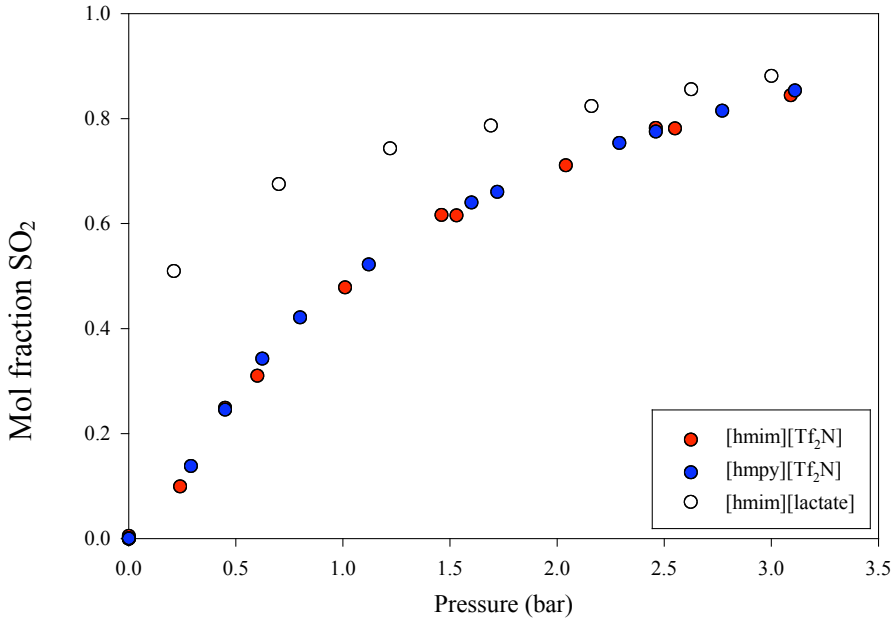
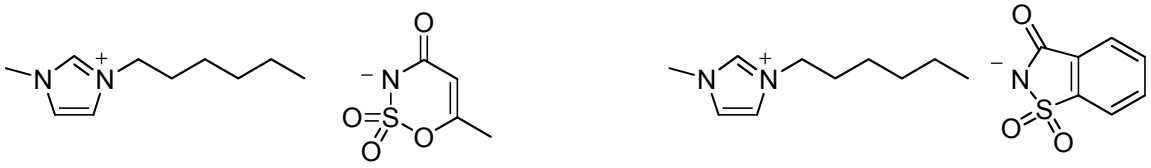


Figure 2: SO_2 isotherms at 25 ^oC for three ionic liquids. Notice the rapid uptake at low pressure for the lactate species.

This result suggests that it may be possible to use ionic liquids to simultaneously remove both CO_2 and SO_2 from flue gas in a one-step operation.

The [hmim][lactate] shows a fundamentally different behavior than the other two species. This is consistent with our earlier findings, where we saw that ionic liquids made with the lactate anion has much higher CO_2 solubility than ionic liquids with other anions. This suggests that the lactate anion is assisting in the weak complexation of CO_2 and SO_2 in the liquid. We will be attempting to confirm this and deduce the mechanism through H^1 NMR experiments. We also plan to make additional compounds with the lactate anion to see if we can improve upon the stability of the systems. Recall from earlier reports that the thermal stability of the lactate-based ionic liquids is not as good as for other systems.

We also measured CO_2 solubility in three new ionic liquids. Two of those compounds are shown in Figure 3. The third compound is a boronium [Tf2N] species. Figure 4 shows a comparison of the CO_2 isotherms for the boronium compound compared against our standard [hmim][Tf2N] ionic liquid. Note that [hmim][Tf2N] has one of the highest CO_2 solubilities of any ionic liquid, although preliminary indications are that its capacity is still too low to be economically attractive. Figure 4 shows that the boronium-based ionic liquid has about the same affinity for CO_2 and the [hmim][Tf2N]. It had been suggested by Prof. Jim Davis that the boronium ionic liquid had much higher CO_2 solubility, but our experiments do not show this.



[hmim][acesulfumate] [hmim][saccharinate]

Figure 3: Two new compounds made recently in which CO_2 solubility has been measured.

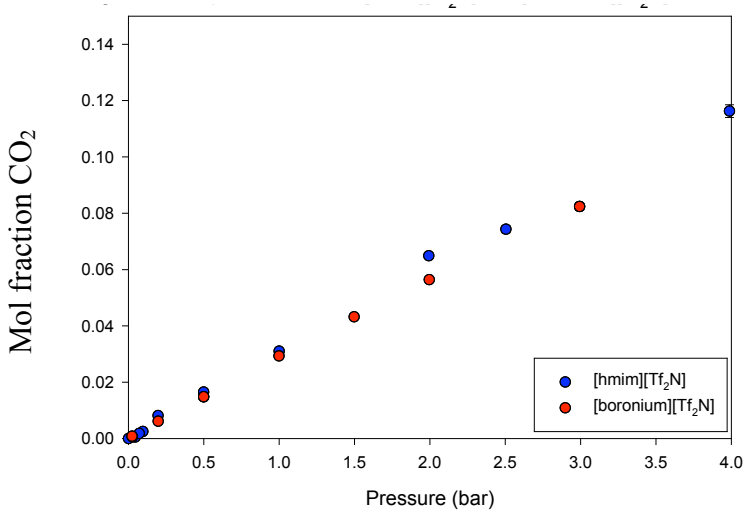


Figure 4: CO_2 isotherms for [boronium][Tf2N] and the standard [hmim][Tf2N]. We see little difference in solubility between the two liquids.

In Figure 5 we show how the CO_2 solubility of the two compounds in Figure 3 compare with [hmim][Tf2N]. The two new anions (acesulfumate and saccharinate) were expected to provide binding opportunities for CO_2 and thus enhance solubility by weak complexation. As the results in Figure 5 show, this is not the case. Both ionic liquids showed lower CO_2 solubility than the standard.

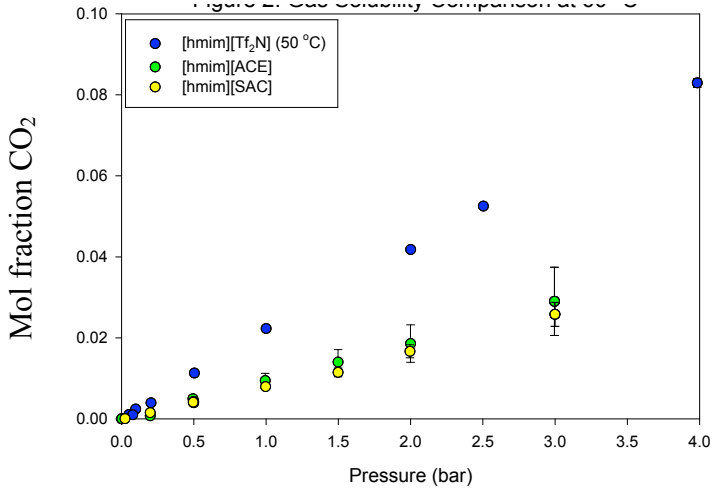


Figure 5: CO_2 isotherms for the compounds in Fig 3. Note that neither ionic liquid shows better performance than the standard.

Equipment

We had mechanical problems with all three of our absorption balance systems. Our Cahn balance (low pressure) system has had a failed pressure transducer and also is experiencinig stability problems. The mid-level pressure system (IGA) needs to have the roughing vacuum pump repaired. The high pressure and corrosive gas system (Rubotherm) is also experiencing some mechanical problems. All of these problems are normal "wear and tear" issues, but they may slow down the isotherm measurements in the coming quarter and we work to bring the balances back into good working condition.

Simulations

To simulate gas solubility in ionic liquids, we have been developing a new simulation method that incorporates variable solute concentrations coupled with appropriate simulation of the condensed phase. The statistical mechanical ensemble consistent with this formulation is the N_1f_2PT ensemble, in which there are a constant number of ionic liquid molecules (N_1), a constant gas phase fugacity of the solute (f_2), constant total pressure and constant temperature. To perform these simulations, we have to develop and test new software that can perform these calculations. Since the last quarterly report, we have begun computing isotherms and generalized the code for multi—component systems. Unfortunately, our results yield liquid densities that are too low compared to experiment. We are working right now to determine the source of this problem.

Other Activities

We presented two papers at the American Institute of Chemical Engineers conference in Cincinnati this quarter. We are also working with researchers at NETL on a CRADA involving the use of ionic liquids in supported liquid membranes for gas separation.

Conclusion

We continue to synthesize new ionic liquids, characterize them and test their solubility at a good pace. Our work on the simulation part of the project has suffered some setbacks, but is still within bounds of the schedule. Overall,we have completed all the project milestones to date, and are on track to meet the Q2 2006 milestones.

References

None.