Design and Evaluation of Ionic Liquids as Novel CO_2 Absorbents

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Abstract

Progress from the second quarter 2005 activity on the project "Design and Evaluation of Ionic Liquids as Novel CO_2 Absorbents" is provided. Major activities in two areas are reported: *property measurement* and *molecular modeling*. We also began work on a collaboration with other researchers at NETL on the use of ionic liquids in supported liquid membranes.

Gas solubilities have been measured for several of the ionic liquids synthesized during Q4 (2004) and Q1 (2005). A new class of anion has been discovered which has resulted in the highest CO_2 solubility yet reported for a physical ionic liquid absorbent. Continued progress on computational modeling of the ionic liquids has been made.

Table of Contents

List of Graphical Materials

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 third quarterly technical report (Q2 2005) describes the results of our work on this project from 01/01/2005 through the end of the third quarter (03/31/05).

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 the third quarter of the project, we have focused on two major activities: *physical property measurement* and *molecular modeling*.

Physical Property Measurement

CO_2 solubility has been measured in two new ionic liquids, while O_2 solubility has been measured in five ionic liquids. A new fluorinated anion class has been discovered which gives the highest CO2 solubility yet recorded for a physical ionic liquid absorbent. We found that CO_2 solubility in 1-n-butyl-3-methylimidazolium acetate was extraordinarily high. Through a combination of NMR and gas solubility measurements, have determined that a chemical complex is formed with this compound. We have completed the installation of a new absorption measurement apparatus that will enable us to examine SO_x compounds as well as go to pressures beyond 20 bar.

Molecular Modeling

We have made great progress in completing and validating a new type of simulation method called semi-grand ensemble hybrid Monte Carlo. This technique enables gas absorption isotherms to be simulated directly. We have completed portions of the code that require creation and destruction of gas solute molecules and are working on methods to control the pressure through volume fluctuation moves.

Experimental

Gas absorption was measured using a gravimetric microbalance, as described in our previous publications (Anthony et al., 2001; Macedonia et al., 2000).

Results and Discussion

Property Measurement

Henry constants were measured for CO_2 and O_2 in 1-propyl-3-methylimidazolium tris(heptafluoropropyl)trifluorophposphate ([pmim][bFAP]) and 1-butyl-3-methylimidazolium acetate ([bmim][acetate]). The structures of these cations and anions is shown in Figs. 1-3. Gas solubility results are in Table 1. Based on our calculations, we suspected that the highly fluorinated "FAP" anions would increase CO_2 solubility to a large extent, and the present results confirm this.

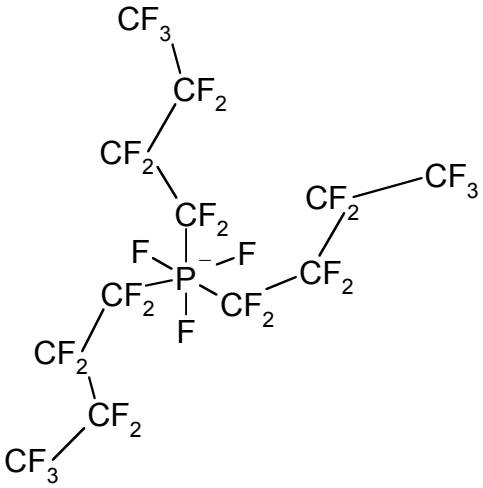
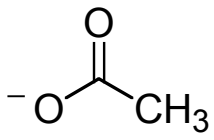
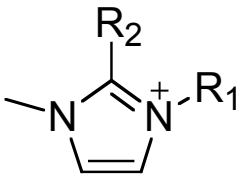


Fig. 1: The tris(heptafluoropropyl)trifluorophosphate (bFAP) anion.



[acetate

Fig. 2: The acetate anion.



[bmim]: $R_1 = C_4H_9$, $R_2 = H$

Fig 3: The [bmim] cation. For [pmim], R1 is replaced with a propyl group.

CO_2 solubility in this compound is the highest for any physical absorbent yet reported (i.e. the Henry constant is very low). The acetate anion has an even lower Henry constant, but we now believe this is due to chemical complexation. NMR results suggest that the acetate anion extracts a proton from the C2 position of the imidazolium ring, forming acetic acid in the process. Fig. 4 shows the mechanism we believe is operative.

Ionic Liquid	H (bar)	
	25oC	60oC
Carbon Dioxide		
[pmim][bFAP]	20.2 ± 0.6	32.9 ± 0.7
[bmim][acetate]	3.0 ± 0.01	5.9 ± 0.02
Oxygen		
[pmim][bFAP]	282.9 ± 12.9	389.5 ± 217.4

Table 1: Henry constants for CO2 and O2 in two different imidazolium-based ionic liquids.

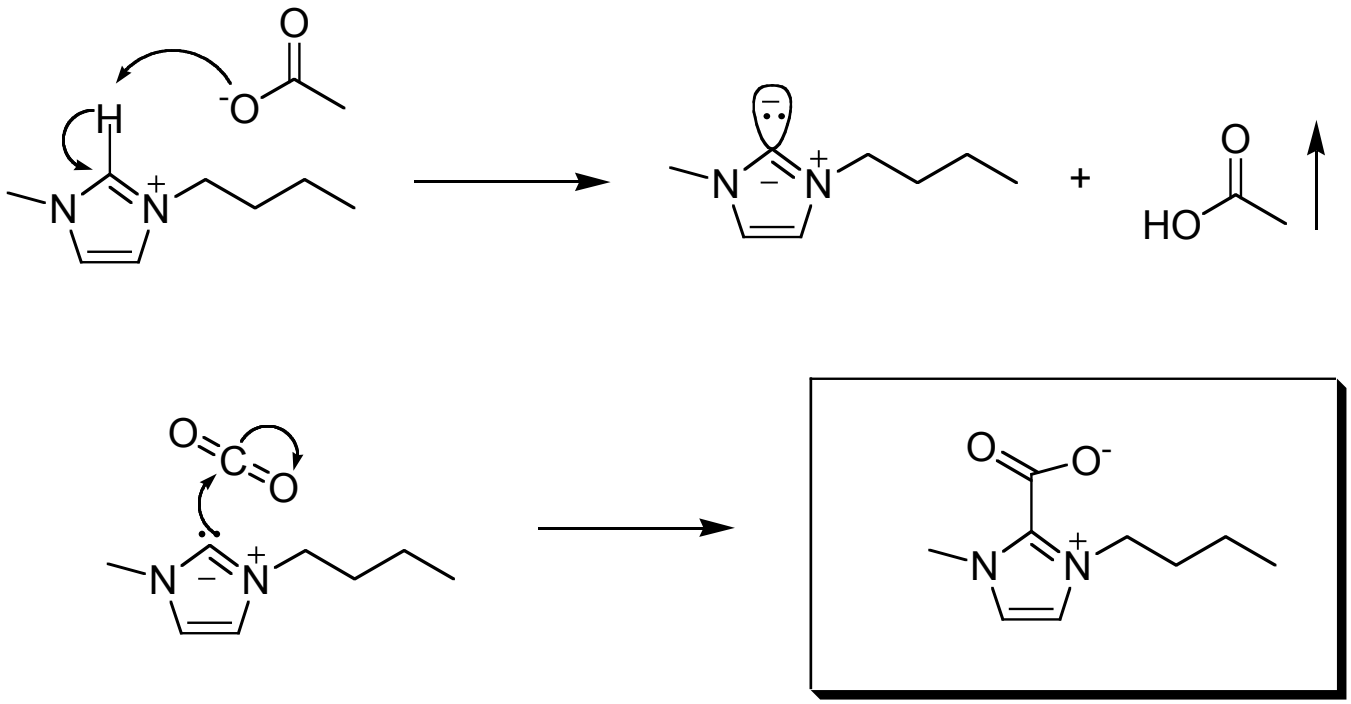


Fig. 4: Proposed mechanism for enhanced CO2 solubility in imidazolium acetate ionic liquids.

We measured O_2 solubility in various FAP-based ionic liquids, and found that the FAP anion also increased the solubility of this gas. Fig. 5 shows the results of these experiments, and compares FAP-based solubilities to those obtained with the bis(trifluoromethanesulfonyl))amide ([Tf2N]) anion. The current results show that the FAP anion yields a higher O_2 solubility than Tf2N. We plan to measure N_2 solubility in these compounds as well, since this gas is more relevant for flue gas applications.

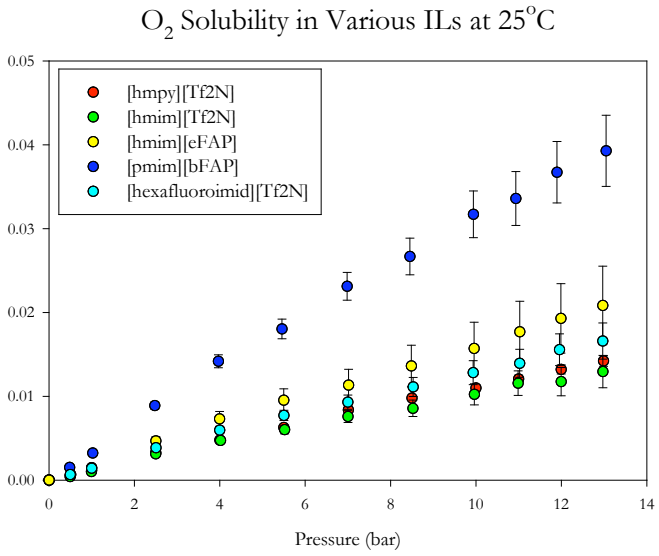


Fig. 5: O_2 solubility in different FAP and Tf2N-based ionic liquids.

Equipment

We have completed the installation of a new gravimetric balance system (Rubotherm), which will provide us with the capability of measuring isotherms of SO_x gases. We have begun testing the apparatus, and hope to have it validated by Q3 2005.

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. We continue to work on the algorithm and write the software. Since the last quarterly report, we have successfully implemented the grand canonical ensemble method and tested our software against established benchmarks. We are now working on removing the constant volume constraint that will enable variable pressures to be simulated.

Other Activities

We hosted the Council for Chemical Research's NICHE conference on ionic liquids at Notre Dame in February. This conference brought together researchers from dozens of academic and industrial groups in the US and Europe to review the state-of-the-art in ionic liquids. At the meetings, Prof. Maginn met with David Luebke from NETL and

discussed a joint collaboration in which ionic liquids would be tested in supported liquid membranes. A CRADA is now being drafted for this project.

Conclusion

We continue to make good progress on our project in developing an understanding of the link between chemical structure and CO_2 solubility in ionic liquids. In the last quarter, we have measured additional gas solubility data, and continue to make progress toward the development of a robust molecular modeling method for the direct calculation of gas solubility. We have discovered a new class of fluorinated anions that have the highest CO_2 solubility yet recorded for a physical absorbent. We have completed all the project milestones to date, and are on track to meet the Q3 2005 milestones by June 30, 2005.

References

Anthony, J. L., E. J. Maginn, et al. (2001). "Solution thermodynamics of imidazolium-based ionic Liquids and Water." *J. Phys. Chem. B* **105**: 10942-10949.

Macedonia, M. D.; Moore, D. D.; Maginn, E. J.; Olken, M. M. *Langmuir* **2000**, *16*, 3823-3834.