

Design and Evaluation of Ionic Liquids as Novel CO₂ Absorbents

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Abstract

This is the final report for project DE-FG26-04NT42122 “Design and Evaluation of Ionic Liquids as Novel CO₂ Absorbents”. The objective of this “breakthrough concepts” project was to investigate the feasibility of using ionic liquids for post-combustion CO₂ capture and obtain a fundamental understanding of the solubility of CO₂ and other components present in flue gas in ionic liquids. Our plan was to obtain information on how composition and structure of ionic liquid molecules affected solubility and other important physical properties via two major efforts: *synthesis and experimental measurements* and *molecular simulation*. We also planned to perform preliminary systems modeling study to assess the economic viability of a process based on ionic liquids.

We accomplished all the milestones and tasks specified in the original proposal. Specifically, we carried out extensive quantum and classical atomistic-level simulations of a range of ionic liquids. These calculations provided detailed information on how the chemical composition of ionic liquids affects physical properties. We also learned important factors that govern CO₂ solubility. Using this information, we synthesized or acquired 33 new ionic liquids. Many of these had never been made before. We carried out preliminary tests on all of these compounds, and more extensive tests on those that looked most promising for CO₂ capture. We measured CO₂ solubility in ten of these ionic liquids. Through our efforts, we developed an ionic liquid that has a CO₂ solubility 2.6 times greater than the “best” ionic liquid available to us at the start of the project. Moreover, we demonstrated that SO₂ is also extremely soluble in ionic liquids, opening up the possibility of using ionic liquids to remove both SO₂ and CO₂ from flue gas. In collaboration with Trimeric Inc., a preliminary systems analysis was conducted and the results used to help identify key physical properties that must be optimized to enable ionic liquids to be cost-competitive for CO₂ capture. It was found that increasing the capacity of the ionic liquids for CO₂ would be important, and that doing so could potentially make ionic liquids more effective than conventional amine solvents.

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List of Graphical Materials

Figure 1: Isotherm of CO₂, N₂ and O₂ in a pyridinium-based ionic liquid at ambient temperatures.

Figure 2: Isotherms for SO₂, CO₂, O₂, and N₂ in the same pyridinium-based ionic liquid as shown in Figure 1. Note the difference in pressure scale. This result shows that it could be possible to use ionic liquids to remove SO₂ and CO₂ from flue gas.

Figure 3: Comparison of low pressure solubility of CO₂ in ionic liquids and other solvents. Values are higher for ionic liquids.

Figure 4: Simulated and experimental isotherms for CO₂ in [hmim][Tf₂N] at 333 K.

Introduction

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. Prior to the start of this project, we showed that some ionic liquids can absorb large quantities of CO₂ while only absorbing negligible amounts of nitrogen. Due to this finding, we undertook a study to see if we could determine what the underlying physical factors were for high CO₂ solubility, and if the properties of ionic liquids could be tuned to optimize this solubility. When we began this project, no previous work had been done to investigate ionic liquids for CO₂ capture. The goal was to tune the properties of the ionic liquid in such a way so as to optimize the performance of these materials for CO₂ capture.

Rather than take a purely “Edisonian” approach in which many compounds were synthesized and tested, we coupled the experimental synthesis and testing work to atomistic level simulations. These simulations were designed to provide fundamental, atomic-level information on the factors responsible for high (or low) solubility and other properties. Armed with this information, we conducted targeted experiments and testing, as reported on below.

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 CO₂-capture techniques. This project was concerned with developing a fundamental understanding of the solubility of flue gas species (mainly CO₂) in ionic liquids. Using this knowledge, we hoped to develop new IL compounds that can be used in a cost effective manner for CO₂ capture. As a result of this project, we synthesized or acquired 33 new ionic liquids and measured CO₂ solubility in 10 of these. We also developed and applied advanced atomistic simulation methods to provide insight into what structural and chemical factors affect the performance and properties of ionic liquids. As a result of these efforts, we increased the physical solubility of ionic liquids by a factor of 2.6 times versus the “best” ionic liquid known at the start of the project. We also demonstrated that chemical functionality can be added to ionic liquids, which increases the solubility of CO₂ by a factor of 40 or more. Through a preliminary systems analysis, it was found that solubilities in this range, coupled with the other known properties of ionic liquids, should make ionic liquid solvents at least as economically attractive as amine-based solvents. These results, obtained over the three years of the project, suggest that further study is warranted to investigate if ionic liquids really can be designed to possess superior performance characteristics. We can conclude that the project, which set out to determine if this potential “breakthrough concept” was viable, has been successful in establishing that indeed ionic liquids may provide a new and better way of performing post-combustion CO₂ capture.

Summary of Results

New Ionic Liquids and Testing

Table 1 shows a list of all the ionic liquids we evaluated as part of this project, along

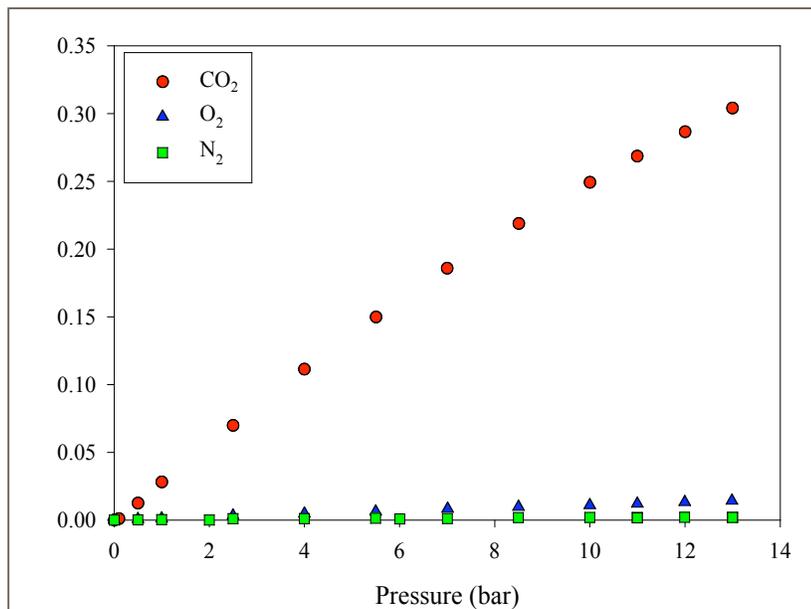


Figure 1: Isotherm of CO₂, N₂ and O₂ in a pyridinium-based ionic liquid at ambient temperatures.

with the measurements that have been made. Most of these compounds dissolve CO₂ via a physical solubility mechanism. From the results of the systems analysis, however, we learned that greater capacities would be needed. In response to this, new ionic liquids were made and evaluated which were capable of forming chemical

complexes with CO₂. These materials did in fact increase CO₂ solubility. Adding such functionality will be the focus of additional ongoing investigations. A typical isotherm is shown in Figure 1.

From results such as those shown in Fig. 1, we determined that ionic liquids had very high selectivity for CO₂ versus other species present in flue gas. We also learned that SO₂ is extremely soluble in ionic liquids. Fig. 2 shows the SO₂ isotherm in the same ionic liquid as that shown in Fig. 1. Notice the different pressure scale, and how much more soluble SO₂ is than CO₂. The ionic liquid is also stable in the presence of SO₂, something not observed with amines.

It is important to understand how the solubility of CO₂ compares between conventional solvents and ionic liquids. Figure 3 shows such a comparison on a volumetric basis, and we can see that there is a significant enhancement in solubility when compared to

conventional solvents.

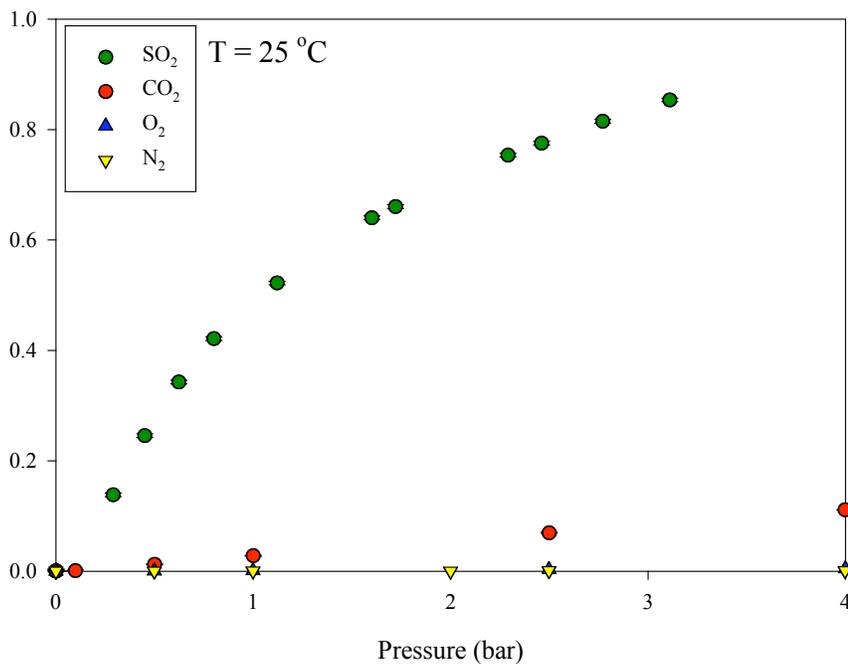


Figure 2: Isotherms for SO₂, CO₂, O₂, and N₂ in the same pyridinium-based ionic liquid as shown in Figure 1. Note the difference in pressure scale. This result shows that it may be possible to use ionic liquids to remove both SO₂ and CO₂ from flue gas.

In support of the systems analysis study, we measured many other properties, such as viscosities, heat capacities, and thermal decomposition. Table 2 shows the result of a series of thermal decomposition measurements. Note that

internal code names are used for the ionic liquids. In general, we can see that these liquids (all of which dissolve CO₂ physically) have very high thermal stability.

Abbreviation	Density	Viscosity	Cp	Thermal Decomp	Freezing	Solubility Data
[hmim][Tf ₂ N]	X	X	X	X	X	X
[hmmim][Tf ₂ N]	X	X	X	X	X	X
[bmim][TFA]						
[bmim][C ₇ F ₁₅ CO ₂]						
[b ₂ -Nic][Tf ₂ N]		X	X	X	X	
[hmpy][Tf ₂ N]	X	X	X	X	X	X
[hmim][eFAP]						X
[hmim][pFAP]	X					X
[pmim][bFAP]						X
[N ₄₄₄₄][doc]		X		X		
[C ₆ H ₄ F ₉ mim][Tf ₂ N]						X
[C ₈ H ₄ F ₁₃ mim][Tf ₂ N]						X
Ecoeng 500		X	X	X		
Ecoeng 41 M		X	X	X	X	
[hmim][SAC]	X				X	X
[hmim][ACE]						X
[Et ₃ NBH ₂ mim][Tf ₂ N]						
[choline][Tf ₂ N]						
[N ₃₁₁₁][Tf ₂ N]						
[hmim][PF ₆]						
[bmim][Tf ₂ N]		X				
[bmim][methide]						
[bmim][acetate]						
[hmim][lactate]	X					
[TMG][Tf ₂ N]						
[TMG][NO ₃]						
[H ₂ NC ₃ H ₆ mmim][Tf ₂ N]						
[H ₂ NC ₃ H ₆ mim][Tf ₂ N]						
[H ₂ NC ₃ H ₆ mpy][Tf ₂ N]						
[bmim][PF ₆]						
[N ₇₇₇₇][lactate]	X					
[hmim][Glu-OAc]	X					
[H ₂ NC ₃ H ₆ NHC ₃ H ₆ mmim][Tf ₂ N]						

Table 1: A list of all the ionic liquids tested as part of this project. The headings show which tests were performed. Cp refers to the constant pressure heat capacity.

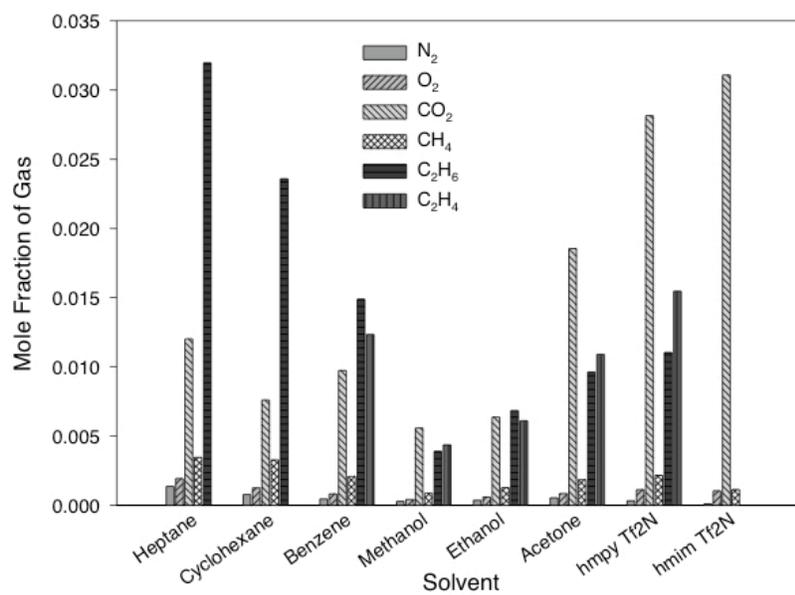


Figure 3: Comparison of low pressure solubility of CO₂ in ionic liquids and other solvents. Values are higher for ionic liquids.

Physically absorbing ILs	Onset Temperature (°C)
CV0001	435
CV0002	423
NDIL0001	427 *
NDIL0003	437 *
NDIL0006	399 *
NDIL0007	419
NDIL0010	393 *
SI0001	281 *
SI0002	215 *
NDIL0005	319 *
NDIL0008	292
NDIL0009	277

Table 2: Thermal decomposition data for various ionic liquids. Results with an asterisk appeared in *J. Chem. Thermodynamics*, **2005**, 37, 559-568.

Molecular Simulations

In support of this project, we developed and tested a new simulation algorithm specifically designed to overcome many of the problems associated with gas solubility calculations in ionic liquids. We call the method “continuous fractional component Monte Carlo” or CFC MC. This method relies on gradual biased insertions on the gas molecule in the condensed liquid phase to overcome sampling problems found with

Table 3: Simulation results for CO₂ absorption in [hmim][Tf₂N]. Fugacity was determined using the Peng-Robinson equation of state. Uncertainties in mole fraction and volume are given in parentheses.

Temperature (K)	Pressure (bar)	Fugacity (bar)	X_{CO_2}	V (cm ³ /mol)
333.2	4	3.9384	0.071 (0.006)	311.3 (2.2)
333.2	8	7.7552	0.131 (0.003)	293.7 (1.0)
333.2	17.15	16.04	0.239 (0.004)	262.5 (1.5)
333.2	48.0	39.6144	0.520 (0.002)	182.1 (0.5)
333.2	83.6	59.22	0.627 (0.001)	149.5 (0.2)
333.2	200.0	90.04	0.689 (0.001)	131.0 (0.5)
423.2	8	7.8936	0.059 (0.004)	337.7 (1.2)
423.2	17.15	16.66637	0.108 (0.005)	321.0 (1.0)
423.2	83.60	73.09148	0.343 (0.005)	251.6 (1.0)
423.2	200.0	149.82	0.562 (0.003)	180.4 (1.0)

conventional methods. We have used the CFC MC method to compute the isotherm for CO₂ in the ionic liquid [hmim][Tf₂N]. The results are shown in Table 3 and Figure 4. As can be seen, the simulations capture the experimental solubility quantitatively.

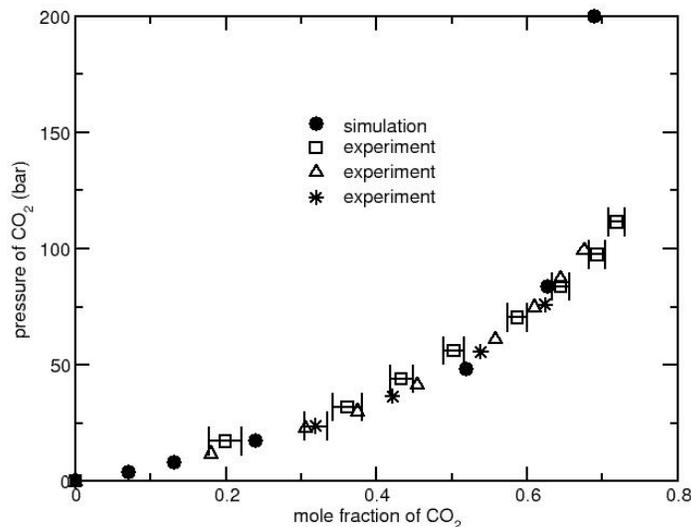


Fig. 4. Simulated and experimental isotherms for CO₂ in [hmim][Tf₂N] at 333 K. The triangles are the data from [1], the squares are from [2] and the stars are from [3]. The experimental Henry's law constants range from 42.8 to 52.3 bar [4], while the simulations predict a value of 49.4 bar.

We now have a robust and general simulation method that can enable us to predict how CO₂ and other gas solubility varies with molecular structure. We can also compute other vital properties, such as viscosity, density, and heat capacity. Given this capability, the simulations and experiments can “feed off” each other in a synergistic manner, helping develop new materials with desired properties.

Systems Analysis

Trimeric Inc. carried out a preliminary systems analysis study to determine if it was at all feasible to use ionic liquids for post combustion CO₂ capture. Because we still have little

data on the properties of these materials and no detailed work on optimizing a process design, the study was necessarily approximate. The intention, however, was to help identify those areas where properties should be tuned and to see if ionic liquids are at least competitive with other technologies. Assuming or extrapolating various properties, the Trimeric report found that, indeed, if these materials could be optimized further, they could become more cost effective than the base amine-based solvent systems. Table 4 shows some of the preliminary results from this study using a “100 X” case that assumes a physical solvent with 100 times the capacity of a base ionic liquid. Because there are so many assumptions that had to go into these calculations, it is not clear that ionic liquids can be made to have these economic numbers. However, the study does suggest that ionic liquid solvents have the potential to be effective, which justifies additional study.

Description	Units	MEA Base Case	100X Ionic Liquid
Circulation rate	gpm	46,400	82,000
Derated capacity	MWe	281	327
CO ₂ capture purchased equipment costs	MM\$	56.5	40.4
Compression purchased equipment costs	MM\$	17.9	30.0
Total purchased equipment costs	MM\$	74.4	70.4

Table 4: Summary of results from a tentative systems analysis study for a hypothetical ionic liquid solvent.

Publications and Conferences

Refereed Journal Articles

“Measurement of SO₂ Solubility in Ionic Liquids”, Jessica L. Anderson, JaNeille K. Dixon, Edward J. Maginn, Joan F. Brennecke, *Journal of Physical Chemistry B*, 110, 15059-15062 (2006).

“Continuous Fractional Component Monte Carlo: An Adaptive Biasing Method for Open System Atomistic Simulations”, Wei Shi and Edward J. Maginn, *Journal of Chemical Theory and Computation*, 3, 1451-1463 (2007).

Presentations

“Tuning Ionic Liquids for CO₂ Gas Absorption”, JaNeille K. Dixon, Mark Muldoon, Sudhir N.V.K. Aki, Jessica Anderson, Joan F. Brennecke, and Edward J. Maginn, AIChE Annual Meeting, Cincinnati, OH, November, 2005.

“Gas Solubilities in Tunable Ionic Liquids”, Jessica Anderson, JaNeille K. Dixon, Mark Muldoon, Edward J. Maginn, and Joan F. Brennecke, AIChE Annual Meeting, Cincinnati, OH, November, 2005.

“Ionic Liquids As CO₂ Capture Media”, J.K. Dixon, M.J. Muldoon, J.L. Anderson, S.N.V.K. Aki, J.F. Brennecke and E.J. Maginn, Thermo International 2006, Boulder, CO, August, 2005.

“Pure and Mixed Gas Solubilities in Tunable Ionic Liquids”, J.L. Anderson, D.J. Couling, D.G. Hert, S.N.V.K. Aki, J.K. Dixon, M.J. Muldoon and J.F. Brennecke, Thermo International 2006, Boulder, CO, August, 2005.

“Ionic Liquids as Absorption Media for CO₂ Capture”, Jessica L. Anderson, JaNeille K. Dixon, Edward J. Maginn, Joan F. Brennecke, AIChE Annual Meeting, San Francisco, CA, November, 2006.

“Designing Ionic Liquids for CO₂ Capture”, JaNeille K. Dixon Mark Muldoon, Sudhir N.V.K. Aki, J. L. Anderson, J. F. Brennecke and E. J. Maginn , American Chemical Society, MAR 26 2006.

“Ionic Liquids for Post-Combustion CO₂ Capture”, Joan Brennecke, Jessica L. Anderson, JaNeille K. Dixon, and Edward J. Maginn, AIChE Spring meeting, Houston, TX, April 2007.

Conclusions

We set out to determine if it was at all feasible to use ionic liquids in post-combustion CO₂ capture. At the time, no other groups had investigated this as a possibility. We have showed that one can tune ionic liquids to increase CO₂ solubility, and that SO₂ is also highly soluble. Without any process optimization and assuming realistic properties of the liquid, a tentative systems analysis indicated that ionic liquids have the potential to be more economically attractive than amine-based systems. Based on this work, we have met all the objectives we set out to accomplish at the start of the project. We have indeed shown that ionic liquids may be a viable technical option for post-combustion capture, and additional work is called for. Our work has caught the attention of several other groups; we are aware of at least two other research initiatives looking at CO₂ capture with ionic liquids. These efforts are based in Europe and China, and we are in touch with both groups to track our progress against theirs.

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2. S. N. V. K. Aki, B. R. Mellein, E. M. Saurer, and J. F. Brennecke, *J. Phys. Chem. B* 108, (2004) 20355.
3. A. Scurto, personal communication.
4. J. F. Brennecke, personal communication.