

Chemically-Complexing Ionic Liquids for Pre-Combustion CO₂ Capture

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Progress Report
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All researchers are at the University of Notre Dame. Please note that the post-doctoral and graduate student researchers hold anywhere from 0-100% appointments on the GCEP project. Everyone is listed who has contributed anything to the project in the last year.

Abstract

In this project we are using a systematic approach to the design and development of novel, chemically-complexing ionic liquids (ILs) for the separation of CO₂ from pre-combustion gases, as occur for example, in an integrated gasification combined cycle (IGCC) process for power generation. We aim to investigate three new types of ILs for pre-combustion CO₂ capture: 1. Weak specific binding aprotic heterocyclic anionic (AHA) ILs; 2. ILs featuring structural cooperative complexation; and 3. ILs featuring physical cooperative complexation.

In the last year, thermodynamic and process modeling has clearly identifies the ideal reaction enthalpies needed for an IL that exhibits cooperative binding in order to minimize the energy needed for a pre-combustion gas separation process. In addition, numerous

compounds have been synthesized, which were designed, based on quantum mechanics and molecular simulations, to exhibit structural cooperative CO₂ complexation for superstoichiometric carbon capture. To date one of those compounds has shown CO₂ uptake significantly greater than 1 mole of CO₂ per mole of IL. Significant progress has been made in developing computational methods needed to explain physical cooperativity and we have clearly demonstrated that water can be used to control CO₂ uptake through physical cooperativity. We have experimentally measured both H₂S and N₂ solubilities in ILs and we have developed a method to rapidly predict physically dissolved mixed gas solubilities. We have fully characterized a new route for CO₂ capture – by reaction of CO₂ with a phosphonium ylide.

Introduction

ILs are salts with low melting points, wide liquid phase operating ranges, and endless tunability. They are attractive for CO₂ capture because they can be used in conventional absorber/stripper equipment, their interactions with CO₂ and selectivity for absorption of CO₂ over other gases can be tuned exquisitely, they require no added water to serve as a diluent or carrier (which adds an energy penalty during regeneration for alkanolamine-based CO₂ capture), and they have the potential to operate at higher temperatures than traditional CO₂ absorption media.

Over the last twelve years, the IL research team at Notre Dame has made both fundamental scientific and technological advancements in the development of ILs for post-combustion CO₂ capture. We were the first to report high physical CO₂ solubility in ILs and have subsequently used a combination of theory, molecular simulation, and synthesis and testing of new materials, to develop ILs with even higher physical dissolution of CO₂ and high selectivity for CO₂ over O₂, N₂, H₂, CH₄, H₂S and other gases. Our funding from DOE NETL (since 2004) for post-combustion flue gas separations has led us to incorporate opportunities for chemical complexation with CO₂ in the ILs. Major advances have included doubling the capacity to 1 mole of CO₂ per mole of IL by incorporating the amine functionality on the anion, developing aprotic heterocyclic anions that completely eliminate the horrendous (i.e., orders of magnitude) increase in viscosity experienced by other ILs when they react with CO₂, and the ability to tune the reaction enthalpy.

Background

In the last year there have been numerous publications on the solubility of CO₂ in conventional ILs, as well as in variations of the ILs with aprotic heterocyclic anions (AHAs) that we have developed. We are not aware of any publications that demonstrate cooperative binding of CO₂ by ILs. There have been some measurements published of H₂S solubilities in conventional ILs, primarily by researchers in Iran.¹⁻³ There have also been MD calculations of gas solubilities, including those of CO₂, H₂S and H₂, primarily in conventional ILs.^{4,5}

Results

In the last year, thermodynamic and process modeling has been done which clearly identifies the ideal reaction enthalpies needed for an IL that exhibits cooperative binding in order to minimize the energy needed for a pre-combustion gas separation process. In addition, numerous compounds have been synthesized, which were designed, based on quantum mechanics and molecular simulations, to exhibit structural cooperative CO₂

complexation for super-stoichiometric carbon capture. To date one of those compounds has shown CO₂ uptake significantly greater than 1 mole of CO₂ per mole of IL. Significant work has been done on computational method development needed to explain physical cooperativity (especially the effect of the cation and surrounding ILs). We have clearly demonstrated that water can be used to control CO₂ uptake through physical cooperativity. We have experimentally measured both H₂S and N₂ solubilities in ILs and we have developed a method to rapidly predict physically dissolved mixed gas solubilities. We have fully characterized the reaction of CO₂ with the phosphonium cation (i.e. ylide formation) and begun quantification of this phenomenon for a wide range of ILs with aprotic heterocyclic anions.

ILs Featuring Structural Cooperativity.

The idea of structural cooperativity is to design ILs with multiple, chemically-coupled, binding sites where the binding of CO₂ to the first site occurs through a relatively weak interaction and then activates other sites to facilitate stronger binding of subsequent CO₂ molecules. Such ILs should have increase capacities for CO₂ capture while avoiding an increase in the energy penalty for regeneration.

Task 1. Pre-combustion CO₂ capture system modeling to determine IL properties that minimize energy use and process cost.

Key Findings:

- We can use a CO₂ uptake isotherm model, together with a simple CO₂ capture process model, to determine target IL physical property values that will minimize specified objective functions (energy usage, processing cost, etc.) and to do related sensitivity studies. The uptake isotherm model accounts for physical absorption of CO₂, which is characterized by the parameters ΔH_p and ΔS_p , the enthalpy and entropy of absorption, and accounts for chemical absorption of CO₂ at either one or two sites on the IL, which is characterized by the parameters $\Delta H_{\text{chem},1}$ and $\Delta S_{\text{chem},1}$, the enthalpy and entropy of reaction, and (for the two-site case) the additional parameters $\Delta H_{\text{chem},2}$ and $\Delta S_{\text{chem},2}$. For the two-site case, the second site is treated as activated by absorption at the first site. The process model can be configured to include temperature and/or pressure swings, and includes energy integration.
- An example of the type of results that can be obtained is shown by the contour plot in Figure 1. This shows the sensitivity of a simple processing cost function with respect to variations in $\Delta H_{\text{chem},1}$ and $\Delta H_{\text{chem},2}$, and is for the case of a pressure-swing process configuration with $\Delta S_{\text{chem},1}$ and $\Delta S_{\text{chem},2}$ fixed at $-130 \text{ J/mol}\cdot\text{K}$ and other properties set to typical values for ILs. This particular study indicates the presence of a region of $(\Delta H_{\text{chem},1}, \Delta H_{\text{chem},2})$ pairs that perform well for the specified objective function.

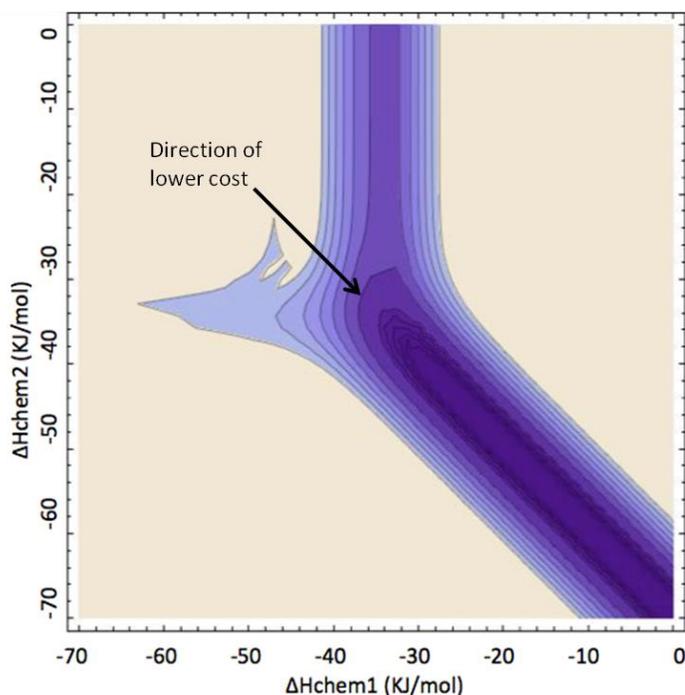


Figure 1. Contour plot showing sensitivity of a simple processing cost function to ΔH_1 and ΔH_2 for the case of $\Delta S_1 = \Delta S_2 = -130 \text{ J/mol}\cdot\text{K}$ and a pressure-swing process configuration. Lowest costs are in a region running diagonally from about $(-30, -40)$ towards the lower right.

Outcomes

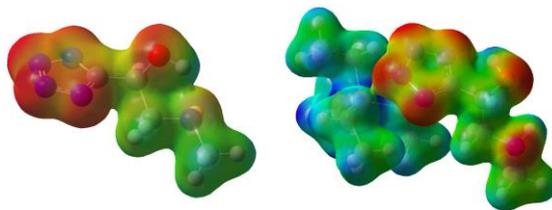
- Presentation (Hong, Brennecke and Stadtherr) to be submitted for AIChE Annual Meeting, November 2014

Task 2. Quantum mechanical and classical molecular simulation to design new IL materials that satisfy the criteria developed by the process modeling.

First-principles and classical molecular simulations are an integral element of our GCEP efforts. Continual feedback between the two, through our regular all-hands meetings and close interactions between graduate students from all groups, helps assure maximum impact. These models contribute in two essential ways: (1) by guiding the innovation and discovery process through predictions of structure-activity relationships, and (2) by providing quantitatively reliable predictions of physical and chemical properties. Specifically, we have been able to make predictions of “cooperative” CO_2 binding candidates.

Key findings:

- Computation guides various azolide-based anions for two successive CO_2 binding with intermediate exothermic reaction enthalpy of CO_2 .
- Electrostatic potential map reveals presence of cation can alter the binding order of CO_2 in cooperative process. Effective charge for first CO_2 binding on anion with cation counterpart can be different from anion only model:



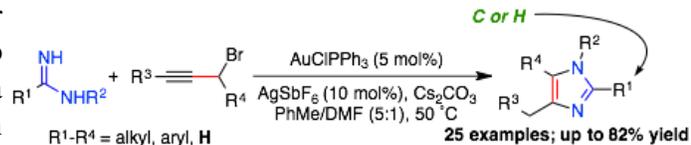
Electrostatic potential map of [anion(C)] and [P₂₂₂₂][anion(C)] model based on B3LYP/6-31G(d,p) level of theory

Outcomes:

- Not only the exothermic CO₂ reaction enthalpy but also reactivity of second CO₂ binding site is critical to realize cooperative CO₂ binding on anion.
- Reactivity prediction for allosteric interaction contribute to design cooperative CO₂ binding ionic liquid system

Task 3. Synthesis of the new ILs identified by QM and classical molecular simulation.

In contrast to current strategies aimed at maximizing CO₂ capture, our efforts have focused on the design and synthesis of new *N*-heterocyclic materials with multiple, chemically-coupled, binding sites. Our hypothesis is that the binding of CO₂ to the an initial site occurs through a relatively weak interaction and then activates other sites within the framework to facilitate stronger binding of subsequent CO₂ molecules while avoiding an increase in the energy penalty for regeneration. Inspired by the allosteric regulation of enzymes, material regeneration and loss of CO₂ is then achieved by disruption of this new electrostatic environment through the use of a catalytic chemical release mechanism. The implementation of this structural cooperativity design concept should lead to ILs with increased capacities for CO₂ capture.



(1) New Synthetic Approaches Towards Amidine and Imidazole Construction

The imidazole ring constitutes one of the most versatile *N*-heteroaromatics in organic synthesis. Imidazolium salts are frequently employed as either the cationic or anionic component of task specific room temperature ionic liquids (RTILs) as well as immediate precursors to *N*-heterocyclic carbenes (NHCs). To rapidly identify new *N*-heterocyclic materials for the gas phase separation of CO₂, we sought a flexible approach toward imidazole construction that would enable a high degree of structural diversity at C4 and C5 in a highly convergent fashion. Given that site specific functionalization of heterocycles is challenging due to issues of poor regioselectivity and low functional group compatibility, our alternative strategy was to incorporate the desired functionality prior to heterocycle fabrication. Over the course of this study it became clear that a new method for the multicomponent assembly of amidines was necessary to access a structurally diverse array of starting materials for an efficient imidazole synthesis. In recent years

amidines have become a common synthetic building block in heterocycle construction and the synthesis of heterocycle-based materials. Our approach was to develop a mild and diversifiable route that avoids the direct use of amines and expensive transition metal catalysts while providing the corresponding *N*-sulfonyl amidines without the need for chromatographic purification.

Key Findings:

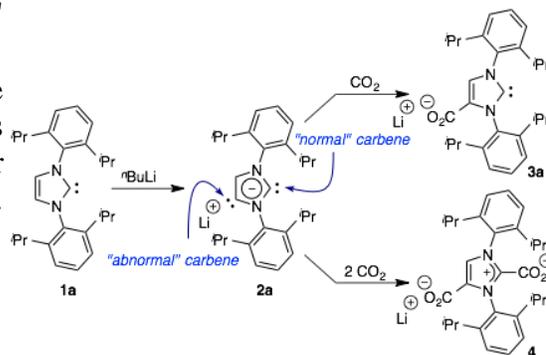
- Developed an amidine alkylation-propargyl halide coupling event that set the stage for an *in situ* Au(I)/Ag(I)-catalyzed 5-endo-dig cyclization and C–C double bond isomerization to directly assemble the functionalized imidazole framework.⁶
- The method provides direct access to C2-unsubstituted imidazoles, a benefit that has yet to be reported by other cycloaddition strategies.
- Developed a method that involves the coupling of an oxime and TsN₃ to yield the target amidine *via* an unprecedented iminophosphorane. The strong driving force of P=O bond formation and preorganization of each component results in a mild, chemoselective Beckmann-like ligation event.⁷

Outcomes:

- Established a streamlined approach toward imidazole construction from readily available starting materials.
- **Publication:** Meyer, C. J.; Vogt, M.; Ashfeld, B. L. "Direct Access to Functionalized Imidazoles Employing a Au(I)/Ag(I)-Catalyzed Formal [3+2] Cycloaddition of Amidines and Propargyl Bromides." *Manuscript submitted for publication.*

- Designed an amine-free approach for amidine synthesis that exploits the reactivity of azides and is readily scalable without the need for chromatographic purification of the products.

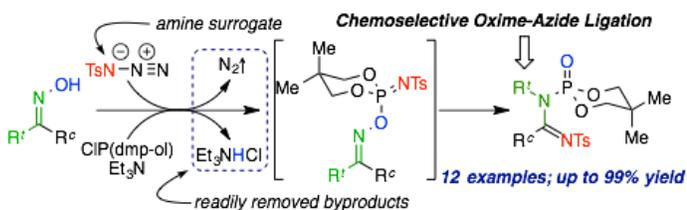
- **Publication:** Fleury, L. M.; Wilson, E. E.; Vogt, M.; Fan, T. J.; Oliver, A. G.; Ashfeld, B. L. "An Amine-Free Approach Toward *N*-Toluenesulfonyl Amidine Construction: A Phosphite-Mediated Beckmann-Like Ligation of Oximes and Azides." *Angew. Chem. Int. Ed.* **2013**, 52 (44), 11589-11593.



(2) Abnormal *N*-Heterocyclic Carbenes

With routes established to the starting components we turned our attention toward our initial heterocyclic targets. "Abnormal" *N*-heterocyclic carbenes (*a*NHCs), in which the carbene center is no longer positioned between two stabilizing nitrogen atoms within the ring, have only recently drawn the attention of the synthetic community.⁸

Based on recent reports by our group⁹ and others that demonstrate the versatility of NHCs and *a*NHCs as carbon capture materials,^{10,11} we speculated that by virtue of the more



electron rich heterocycle and presumptive greater nucleophilicity, anionic NHDCs were candidates to bind CO₂ both at C5 and C2 to generate the dicarboxylate adduct.

Key Findings:

- We discovered that *in situ* generation of anionic dicarbene **2a** by treatment of carbene **1a** with ⁿBuLi followed by prolonged exposure to a stream of dry CO₂ at -78 °C provided the imidazolylidene C5-carboxylate **3a** as the sole product in 90% yield.
- The absence of the C2/C5-dicarboxylated adduct **4** was particularly surprising considering our previous findings where we demonstrated that even solid NHCs react rapidly at C2 under an atmosphere of CO₂.

Outcomes:

- **Publication:** Vogt, M.; Wu, C.; Oliver, A. G.; Schneider, W. F.; Ashfeld, B. L. "Site Specific Carboxylation of Abnormal Anionic N-Heterocyclic Dicarbenes with CO₂." *Chem. Commun.* **2013**, 49 (98), 11527-11529.
- This result provided us with insight into the exceptional positional selectivity for carboxylation at the less stabilized abnormal carbene center at C5 rather than the normal mode of reactivity resulting in C-C bond formation at C2 observed with NHCs, and inspired us to examine alternative heterocyclic frameworks.

(3) *N*-Heterocyclic Amino Alcohols as Reactive ILs

Our next materials design with the potential for structural cooperativity was to target β-amino alcohols bearing an IL component. Binding of CO₂ to one nitrogen anion would activate a subsequent amine through proximal hydrogen bonding with the alcohol.

Key Findings:

- Treatment of a tetrazolide IL with 1 equivalent of benzylchloroformate as a CO₂ surrogate resulted in carbamate formation at the secondary amine site.
- Exposure to an excess of benzylchloroformate led to the anticipated polycarboxylated adduct.

Outcomes:

- Employing a CO₂ surrogate in a reaction with the tetrazolide IL establish the point of initial CO₂ binding.
- The absorption of two equivalents of chloroformate solidified the potential of these designs to be effective in superstoichiometric CO₂ capture.
- While current efforts are focusing on understanding the reactivity of these novel ILs, during the course these efforts we identified a 3rd generation design based on a monoacylanionic diamine substructure and a revolutionary new approach to nitrones that allows direct access to oxazolidines, a potentially new class of heterocyclic ILs.

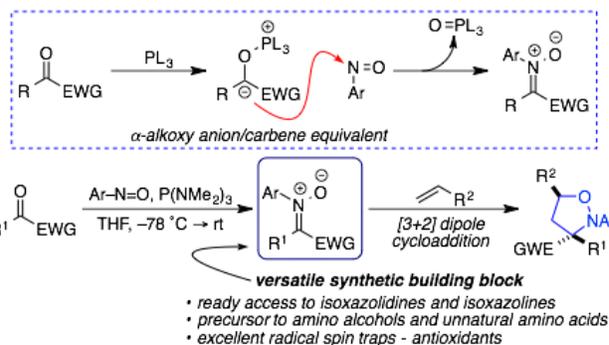
(4) New Approaches Toward the Synthesis of Nitrones

Nitrones, which exhibit the reactivity of extended carbonyls characterized by an anionic oxygen and electrophilic carbon separated by a cationic nitrogen, are mainly exploited as 1,3-dipoles in [3+2] cycloadditions to assemble heterocyclic isoxazolidines and isoxazolines. Conventional methods used in the construction of nitrones typically involve the addition of a nucleophilic amine to an electrophilic carbon. As a result, issues of chemoselectivity can arise when multiple electrophilic sites are present. To address these challenges, we sought a method that would directly and chemoselectively provide ketonitrones, even in the presence of more electrophilic groups such as aldehydes. Our

strategy relied on an umpolung retrosynthetic C–N bond disconnect to avoid the use of nucleophilic amines, an important consideration in reaction development.

Key Findings:

- We developed a highly chemoselective, umpolung approach toward nitron synthesis that constitutes a departure from conventional dehydration strategies.
- The reaction works under very mild conditions, uses inexpensive starting materials, and is readily amenable to scale up.
- Allows direct access to functionalized heterocyclic frameworks that are immediate precursors to their IL counterparts.



Outcomes:

- **Publication:** Chavannavar, A. P.; Oliver, A. G.; Ashfeld, B. L. “An Umpolung Approach toward *N*-Aryl Nitron Construction: Phosphine-Mediated Addition of 1,2-Dicarbonyls to Nitroso Electrophiles.” *Manuscript submitted for publication.*
- These results open the door to previously unexplored heterocycles that can be examined as structurally cooperative CO₂ binding ILs.

(5) Diamine ILs

Key Findings:

- Synthetic routes toward electron deficient nitrogen-containing ILs using acyclic framework comprised of *N*-substituted aliphatic amines or ethylenediamines have been established.
- In a straightforward 2 or 3 steps from inexpensive, commercially available starting materials (~\$1-1.5/g) the corresponding IL precursors can be obtained.

Outcomes:

- This class of ILs are more amenable to large scale production and have the potential for being less viscous, by virtue of among other properties a lower molecular weight, than the heterocyclic compounds we have examined to date.
- At this stage in the project, 6 amines and diamine derivatives have been constructed and will soon be evaluated for their stability and efficacy toward cooperative CO₂ capture.

Task 4. Experimental testing.

In the past year, five of the candidate ILs that should exhibit structural cooperativity were tested.

Key findings:

- All five structural cooperativity ILs were viscous liquids with glass transition temperatures well below room temperature. All except SCIL4 had decomposition temperatures, as measured by TGA, greater than 250 °C.

- The CO₂ uptake of all five ILs, shown in Figure 2, is lower than expected, with only one (SCIL2) reaching capacities well over 1 mole CO₂/mole IL.
- The temperature dependence of the CO₂ uptake is shown for one of the ILs (SCIL1) in Figure 3. The small changes in solubility with temperature indicate a small reaction enthalpy between CO₂ and the IL.

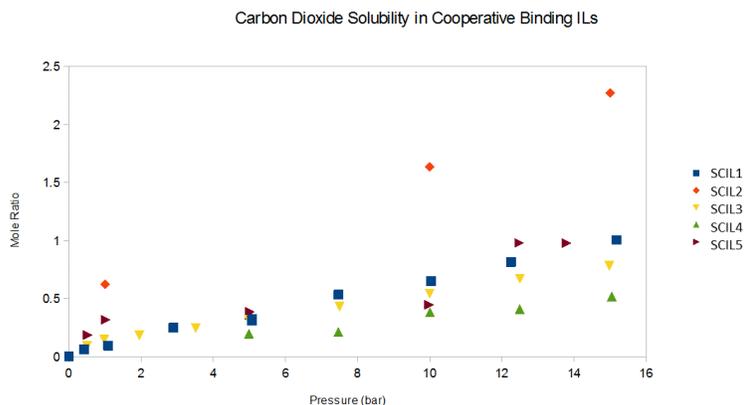


Figure 2. CO₂ uptake (moles CO₂/mole IL) as a function of pressure at 22 °C for five different ILs that should exhibit structural cooperativity.

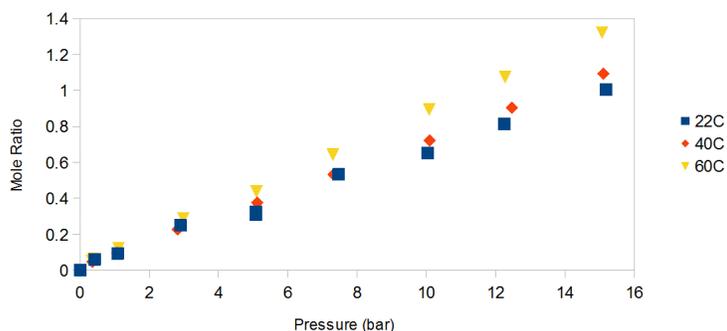


Figure 3. CO₂ uptake as a function of temperature for one of the structural cooperativity ILs.

Outcomes:

- Additional characterization of the SCIL/CO₂ complexes will be carried out to determine if anticipated chemistry is occurring.

ILs Featuring Physical Cooperativity

Ionic liquids featuring physical cooperativity are designed to exhibit reactivity of one mole of CO₂ per mole of IL. However, it is anticipated that the CO₂ uptake can be controlled with additives and the nature of the cation. Understanding the physical cooperativity effect requires both quantum mechanical and classical molecular simulation

to go beyond anion-CO₂ binding to include the cation, clusters of anions and cations and full liquid phase modeling. In addition, we need to measure and model the solubility of non-reactive gases that is needed to determine the selectivity of the IL for removing CO₂ from pre-combustion gases. Advances in the last year are described below.

Task 2. Quantum mechanical and classical molecular simulation to design new IL materials that satisfy the criteria developed by the process modeling (physical cooperativity).

Several computational advances have been made in the last year that related to AHA ILs (without structural cooperativity) for use in pre-combustion CO₂ capture.

(1) Benchmarking and application of first-principles models to azolide-CO₂ binding

Key findings:

- Affordable DFT methods nicely reproduce more computationally expensive and accurate *ab initio* calculations of azolide-CO₂ binding. The results of the PW91 and PBE/PBE functional recover high quality CCSD(T)//MP2 results.
- Anion-only models reproduce experimentally observed trends in CO₂ uptake in corresponding ILs, but exhibit absolute deviations related to the anion-cation interactions

Outcomes:

- Contribution to Seo et al., *J. Phys. Chem B*, in revision
- Lee and Schneider, manuscript in preparation

(2) Development and application of *ab initio* molecular dynamics models for CO₂ reaction with cation/anion clusters

Key findings:

- Cations modulate the ability of anions to combine with CO₂ and can “guide” CO₂ to intrinsically less reactive sites.
- “Potential of mean force” (PMF) methods quantitatively capture these interactions and greatly improve agreement between theory and experiment. [P₂₂₂₈][2-cyanopyrrolide]-CO₂ binding enthalpy inferred by PMF calculations agree well with experiment.
- *ab initio* molecular dynamics simulation correctly predict large differences in CO₂ binding between ammonium and phosphonium-based ILs with same azolide anion.

Outcomes:

- Lee and Schneider, manuscript in preparation

(3) Coupled quantum-classical models for predicting reactive isotherms

Key findings:

- Developed thermodynamic cycle that couples *ab initio* PMFs and classical molecular dynamics simulation to predict full isotherms over range of conditions.
- Thermodynamic cycle nearly quantitatively recovers isotherm of [P₂₂₂₈][2-cyanopyrrolide] at ambient condition. [P₂₂₂₈][2-cyanopyrrolide] ionic liquid forms nearly ideal mixtures when reacted with CO₂ because a solution consisting of reacted and unreacted IL has nearly zero enthalpy of mixing.

Outcomes:

- Extensions to other anions, especially ionic liquid system with strong cation/anion interaction.
- Application of this thermodynamic cycle to predict reactive isotherm at different temperature condition.

(4) Calculation of pure and mixed gas isotherms

Key findings:

- Computed absorption isotherms for pure CO₂, H₂ and SO₂ are in excellent agreement with available experimental results, and predictions were made for extreme conditions where experimental data are not available. The predicted solubility of H₂S is roughly twice that of the available experimental results *but* due to the lack of enough experimental data, it is hard to estimate the uncertainties in the experimental result.
- Mixed gas isotherms for CO₂/SO₂ and CO₂/H₂S mixtures were computed at a range of temperatures and pressures.
- SO₂ and H₂S work as a co-solvent and enhance the solubility of CO₂ such that selectivities are predicted to be non-ideal. The simulations reveal that non-ideal selectivity is mainly due to increasing van der Waals interaction between the gases.

Outcomes:

- Singh and Maginn, manuscript in preparation

Task 4. Experimental testing.

(1) Physical cooperativity with addition of water

Key Findings:

- [P₆₆₆₁₄][2-CNPy] does not undergo reprotonation in the presence of water and CO₂ over the timescale of our CO₂ absorption experiments.
- CO₂ uptake by [P₆₆₆₁₄][2-CNPy] varies substantially with the addition of water (which would be present in pre-combustion gases), as shown in Figure 4. This is an excellent example of the physical cooperativity that we proposed and that we can use to control CO₂ uptake by ILs.

Outcomes:

- Samuel Seo, Mauricio Quiroz-Guzman, M. Aruni DeSilva, Tae Bum Lee, Yong Huang, Brett F. Goodrich, William F. Schneider and Joan F. Brennecke, "Chemically Tunable Ionic Liquids with Aprotic Heterocyclic Anion (AHA) for CO₂ Capture," *J. Phys. Chem. B*, under revision.

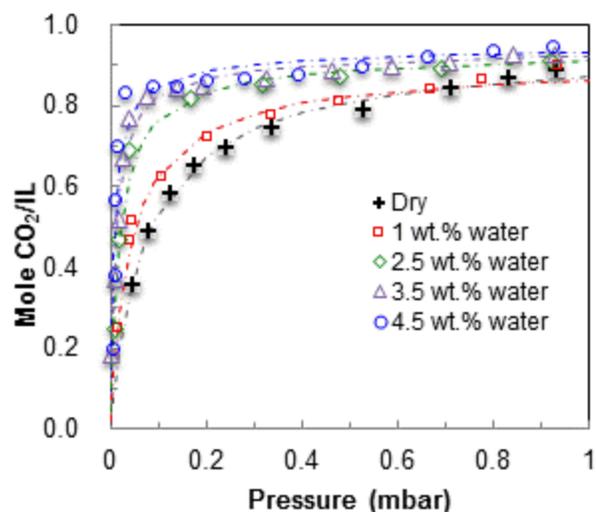


Figure 4. CO₂ capacity in CO₂:IL molar ratio of [P₆₆₆₁₄][2-CNPy] at room temperature (22 °C): pure (squares), with 1 wt% water (pluses), with 2.4 wt% water (diamonds), with 3.5 wt% water (triangles) and with 4.5 wt% water (circles).

(2) Solubility of H₂S in ILs

Sulfur is present in pre-combustion flue gas as H₂S. There are very few measurements of H₂S in ILs, undoubtedly due to the significant safety concerns associated with its use. After much planning and numerous safety reviews, we have successfully measured H₂S solubilities in four different ILs.

Key Findings:

- H₂S solubility in ILs can be safely and accurately be measured using a Rubotherm gravimetric microbalance, generally operated at sub-atmospheric pressure, with the entire equipment in a floor length ventilation hood.
- The solubility of H₂S in ILs is very high, as shown for the four ILs in Figure 5.
- H₂S solubility is completely reversible.

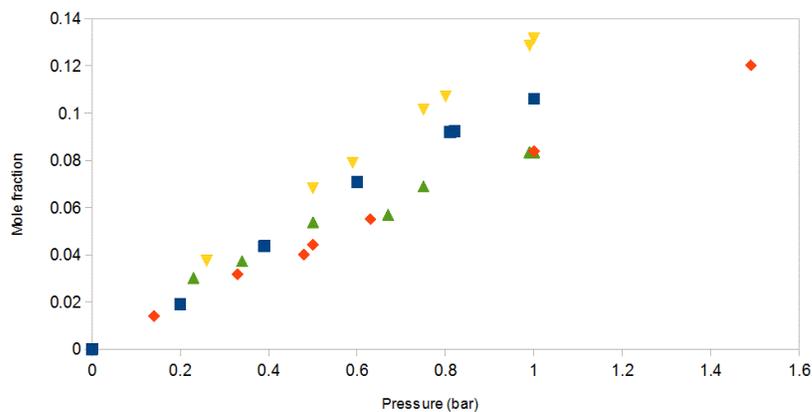


Figure 5. Solubility of H₂S in four different ILs at 30 °C.

Outcomes:

- Bennett and Brennecke, manuscript in preparation

(3) Solubility of N₂ in ILs

The solubility of N₂ and H₂ (which is important for pre-combustion flue gas) in ILs is very low. Therefore, the measurement of the solubility of these gases is relatively difficult and accounts for the low number of experimental results in the literature. We have measured the solubility of N₂ in fifteen different ILs at 60 °C, as shown in Figure 6.

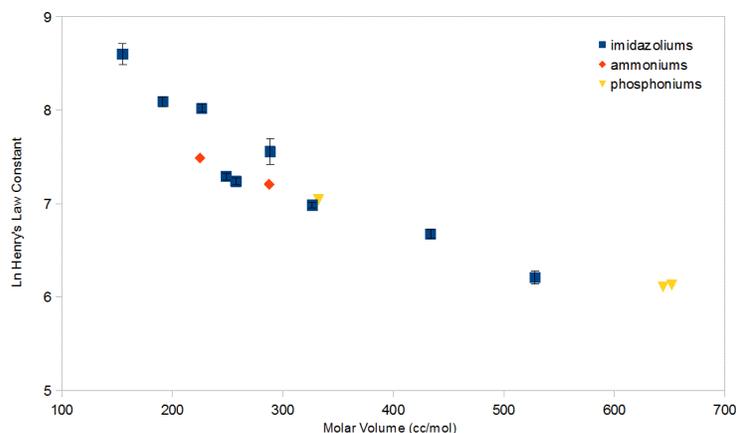


Figure 6. Solubility of N₂ in imidazolium, phosphonium and ammonium ILs at 60 °C.

Key Findings:

- The solubility of N₂ in ILs roughly correlates with the molar volume of the IL.
- There is very little temperature dependence to the solubility of N₂ in ILs, indicating that the enthalpy of absorption is almost zero.

Outcomes:

- Bennett and Brennecke, manuscript in preparation

Ylide Chemistry

In the first seven months of the project, we discovered that a parallel reaction of CO₂ can occur with phosphonium ILs. In the past year significant additional computational and experimental work has been done to understand this phenomenon.

Key Findings:

- The phosphonium reaction with CO₂ occurs via the in situ generation of a carbon ylide by α -deprotonation of the phosphonium cation by the strongly basic heterocyclic anionic component of the IL. It has been fully characterized experimentally by FTIR, ¹H, ¹³C, ³¹P, and 2D HMBC NMR, and MS.
- Computation predicts proton transfer from phosphonium [P₂₂₂₂] to azolides above room temperature inducing formation of ylide carboanion that becomes new site for CO₂ reaction.

- Ylide reaction channel is both predicted and observed to be suppressed with ammonium [N₂₂₂₂] cations.

Outcomes:

- Thomas R. Gohndrone, Tae Bum Lee, M. Aruni DeSilva, Mauricio Quiroz-Guzman, William F. Schneider, Joan F. Brennecke, "Competing Cation- and Anion-CO₂ Reactions in Azolide Ionic Liquids," *ChemSusChem*, in press

Additional Information

We have provided full chemical and physical property characterization for both a non-reactive and a reactive (AHA) ionic liquid to the group of Professor Ed Rubin at Carnegie-Mellon University for their work in systems modeling of the technologies developed/being developed by other GCEP-funded projects.

Progress

The goal for the three-year project is to have an optimal IL that meets all physical and chemical property criteria determined by process modeling to achieve 90% pre-combustion capture of CO₂ for no more than a 10% energy penalty and a 15% increased cost. The ILs developed here will increase the molar capture ratio and be able to capture and release CO₂ using very small temperature or pressure swings. As ILs do not require water as a diluent or carrier, a large energy benefit is already gained over aqueous amine technologies. Any IL capture process with similar capacity will give an energy benefit over aqueous amines. However, the proposed ILs designed with optimized absorption enthalpies will further minimize energy use. Beyond that, cooperativity effects are targeted at achieving the final decrease in energy requirements to meet the <10% penalty target. Because conventional absorber/stripper technology can be used, equipment costs can be minimized. Also, absorbent costs are expected to be low due to the long lifetime of the materials and the large number of cycles it can complete without the need for purging/disposal.

Towards this goal we have developed a thermodynamic and process model that identifies appropriate enthalpies of reaction for two-site cooperative binding ILs to minimize the energy requirement for the CO₂ separation process. Based on quantum mechanics and molecular simulation we have designed compounds to meet these requirements. Some of these ILs have been synthesized but the correspondence between predicted and experimental properties of the cooperative binding ILs is not yet quantitative. As a result, we have been developing more sophisticated modeling tools and working to more carefully probe the chemistry of the synthesized ILs with CO₂. Results with single site binding ILs are superb. Not only can we predict properties from modeling, we have shown that we can further fine-tune the control of the CO₂ uptake with physical cooperativity. We can provide near quantitative predictions of the physical solubility of many gases. For ones that are less quantitative, like H₂S, we have measured the solubilities experimentally. Thus, we have made great strides in the design of ILs for optimized separation of CO₂ from pre-combustion flue gas.

Future Plans

The plans for this project continue to be aligned with the project proposal. This includes:

1. Pre-combustion CO₂ capture system modeling to determine IL properties that minimize energy use and process cost.
 - a. Refine objective functions used and perform multiobjective analysis (Pareto analysis)
 - b. Perform additional sensitivity studies for other IL and process parameters and for additional process configurations
 - c. Perform multivariable optimization studies
2. Quantum mechanical and classical molecular simulation to design new IL materials that satisfy the criteria developed by the process modeling for weak specific binding, structural cooperativity and physical cooperativity.
 - a. Refinement of force fields
 - b. Extensions of quantum/classical hybrid models
 - c. Predictions of CO₂/H₂O mixed gas uptake
 - d. Guide synthesis towards application-optimal IL discovery
 - e. Development of simulations methods that enable direct calculation of chemical absorption of gases
3. Synthesis of the new ILs identified by QM and classical molecular simulation.
4. Experimental testing.
 - a. Measurements of CO₂ uptake by ILs showing structural cooperativity
 - b. Measurements of physical cooperativity using multiple AHA ILs and additives besides water
 - c. Solubility of H₂ in ILs
 - d. Quantification of phosphonium ylide reaction with CO₂
5. LCA Modeling.
 - a. Begin work using commercially available package

Publications and Patents

- L. M. Fleury, E. E. Wilson, M. Vogt, T. J. Fan, A. G. Oliver, B. L. Ashfeld, "An Amine-Free Approach Toward N-Toluenesulfonyl Amidine Construction: A Phosphite-Mediated Beckmann-Like Ligation of Oximes and Azides." *Angew. Chem. Int. Ed.* **2013**, 52 (44), 11589-11593.
- M. Vogt, C. Wu, A. G. Oliver, W. F. Schneider, B. L. Ashfeld, "Site Specific Carboxylation of Abnormal Anionic N-Heterocyclic Dicarbenes with CO₂." *Chem. Commun.* **2013**, 49 (98), 11527-11529.
- T. R. Gohndrone, T. B. Lee, M. A. DeSilva, M. Quiroz-Guzman, W. F. Schneider, J. F. Brennecke, "Competing Cation- and Anion-CO₂ Reactions in Azolide Ionic Liquids," *ChemSusChem*, in press

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