Chemically-Complexing Ionic Liquids for Pre-Combustion CO$_2$ Capture

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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 CO$_2$ 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 CO$_2$ 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 identified the ideal reaction enthalpies needed for an IL that exhibits cooperative binding in order to minimize the cost needed for a pre-combustion gas separation process (previous work had focused just on energy use). Quantum chemical methods have been used to predict β-enaminoimine-based anion structures that show promise for cooperative CO2-binding. Some of these have been synthesized, along with ILs based on bispyrroles, α-N-heterocyclic β-amino alcohols, ortho-amino phenol, and N-heteroaromatic-substituted proline derivatives. Only a few of the bispyrrole ILs, which do not have attractive physical properties, show super-stoichiometric CO2 uptake. The fundamental chemistry leading to these observations have been explored both computationally and experimentally. We have successfully shown how physical cooperativity can enhance CO2 uptake, both through the effect of water and the development of a new route for CO2 capture by ILs – by reaction of CO2 with a phosphonium ylide. We have measured the solubility of other gases present in pre-combustion and post-combustion flue gas in the ionic liquids, most notably, H2S, which has high physical solubility. Finally, we have developed a new method to calculate the uptake of CO2 by reactive ionic liquids using molecular simulations and theory.

**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 finely, they do not require 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 2014 three articles have appeared reporting on efforts to increase CO2 uptake by ILs to greater than 1 mole of CO2 per mole of IL [1-3]. Luo et al. studied some hydroxypyridine-based ILs where they propose CO2 addition to the oxygen, which then facilitates addition of CO2 to the nitrogen of the pyridine ring [1]. The same group reported somewhat greater than 1/1 uptake for a carboxyl functionalized imidazolide [2]. Both of these studies use tetra-alkylphosphonium cations so CO2 reaction with the phosphonium ylide (as explained in our previous annual report and below) may be contributing to the uptake. Note that this same group reported the reaction of CO2 with phenolate anions [4].
As discussed in this report, we believe that they have misunderstood the mechanism of the CO\textsubscript{2} uptake. The third article does not suggest cooperativity, but demonstrates > 1/1 uptake for tetra-alkylammonium amino acid based ILs [3]. Recent work on H\textsubscript{2}S solubilities has attempted the molecular simulation and modeling of the limited experimental data that is available [5,6].

**Results**

In the last year, thermodynamic and process modeling has clearly identified the ideal reaction enthalpies needed for an IL that exhibits cooperative binding in order to minimize the cost needed for a pre-combustion gas separation process (previous work had focused just on energy use). Quantum chemical methods have been used to predict β-enaminoimine-based anion structures that show promise for cooperative CO\textsubscript{2}-binding. Some of these have been synthesized, along with ILs based on bispyrroles, α-N-heterocyclic β-amino alcohols, ortho-amino phenol, and N-heteroaromatic-substituted proline derivatives. Only a few of the bispyrrole ILs, which do not have attractive physical properties, show super-stoichiometric CO\textsubscript{2} uptake. The fundamental chemistry leading to these observations have been explored both computationally and experimentally. We have successfully shown how physical cooperativity can enhance CO\textsubscript{2} uptake, both through the effect of water and the development of a new route for CO\textsubscript{2} capture by ILs – by reaction of CO\textsubscript{2} with a phosphonium ylide. We have measured the solubility of other gases present in pre-combustion and post-combustion flue gas in the ionic liquids, most notably, H\textsubscript{2}S, which has high physical solubility. Finally, we have developed a new method to calculate the uptake of CO\textsubscript{2} by reactive ionic liquids using molecular simulations and theory.

**ILs Featuring Structural Cooperativity (Tasks 1-4)**

The idea of structural cooperativity is to design ILs with multiple, chemically-coupled, binding sites where the binding of CO\textsubscript{2} to the first site occurs through a relatively weak interaction and then activates other sites to facilitate stronger binding of subsequent CO\textsubscript{2} molecules. Such ILs should have increase capacities for CO\textsubscript{2} capture while avoiding an increase in the energy penalty for regeneration.

**Task 1.** Pre-combustion CO\textsubscript{2} capture system modeling to determine IL properties that minimize energy use and process cost.

**Key Findings:**

- We have used a CO\textsubscript{2} uptake isotherm model, together with a simple CO\textsubscript{2} 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 CO\textsubscript{2}, and accounts for chemical absorption of CO\textsubscript{2} at either one or two sites on the IL. Chemical absorption 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.
Some sample results are shown in Figures 1 and 2. Figure 1 is for the single-site case and shows the sensitivity of a simple processing cost function with respect to variations in $\Delta H_{\text{chem},1}$ for both temperature swing (TSA) and pressure swing (PSA) cases. Figure 2 is for the two-site case and shows the sensitivity of the cost function to $\Delta H_{\text{chem},1}$ and $\Delta H_{\text{chem},2}$ for the TSA case. In these sensitivity studies $\Delta S_{\text{chem},1}$ and $\Delta S_{\text{chem},2}$ were fixed at $-130 \text{ J/mol} \cdot \text{K}$ and other properties set to typical values for ILs. Results suggested that a TSA configuration is preferred using a relatively weak chemical binding, and that there is no significant advantage in the two-site case.

**Figure 1.** For single-site case, sensitivity of a simple processing cost function to $\Delta H_{\text{chem},1}$ for TSA and PSA configurations. $\Delta S_{\text{chem},1}$ was fixed at $-130 \text{ J/mol} \cdot \text{K}$. 
**Figure 2.** For two-site case, sensitivity of a simple processing cost function to $\Delta H_{\text{chem},1}$ and $\Delta H_{\text{chem},2}$ for the TSA case. $\Delta S_{\text{chem},1}$ and $\Delta S_{\text{chem},2}$ were fixed at $-130 \text{ J/mol-K}$.

**Outcomes:**


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. Predictions of cooperative binding candidates have focused on $\beta$-enaminoimine-based anions.

**Key findings:**

- Computation guides various $\beta$-enaminoimine-based anions for two successive CO$_2$ binding with intermediate exothermic reaction enthalpy of CO$_2$ (Figure 3).

**Figure 3:** Candidate anions for cooperative CO$_2$ binding and its reaction enthalpy of CO$_2$ based on B3LYP/6-311+G(d,p) level of theory at each binding site (kJ/mol)

**Outcomes:**

- The first CO$_2$ binding in $\beta$-enaminoimine induces second CO$_2$ binding site. A substitution for the first CO$_2$ binding site may give a tuning opportunity for successive CO$_2$ reaction in ionic liquids.
- 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. Since submission of the previous annual report, our efforts have focused on developing new synthetic strategies for the rapid construction and evaluation of IL frameworks that comprise seven distinct molecular designs. These include: 1) bis-N-heteroaromatic anions, 2) β-amino alcohols, 3) 1,2- and 1,3-diamines, 3) ortho-amino phenols, 4) proline-based N-heteroaromatic anions, 5) dihydropyrazoles, and 5) ortho-imino anilines. The following is a summary of these efforts and the new synthetic strategies that have resulted from this work.

(3a) Bispyrroles

One of our initial design concepts focused on the preparation of bis-pyrrole and polypyrrole frameworks. Carboxylation of one pyrrole anion would then lead to a hydrogen-bond activation of the second N-heteroaromatic ring down the chain leading to multiple sites for carbon capture based on a single, original anion.

**Key Findings:**

- The synthesis of phosphonium- and ammonium-based RTILs from bispyrrole proved quite challenging. Low yields of the resulting IL were observed on a consistent basis.
- The IL and immediate synthetic precursor proved prone to decomposition pathways upon exposure to heat and light. Even upon storage, these components had a very limited shelf life.
- The synthesis of bispyrrole frameworks was not readily amenable to the generation of various synthetic derivatives based on this scaffold. The functionalization of one N-heteroaromatic ring in the chain was not site selective.
- Evaluation of one bispyrrole-derived IL in which the two pyrrole rings were separated by a carbonyl functional group showed >1:1 stoichiometric CO₂ uptake, and constituted the most promising candidate from this design group.

**Outcomes/Conclusions:**

- The light and heat sensitivity of each polypyrrole-based IL that was synthesized and evaluated makes this class of compounds an unlikely target for commercial use.
- The synthetic route would need to be reevaluated in order to arrive at a general strategy that would enable access to a diverse assortment of scaffolds in high yields.
- The discovery that our bispyrrole ketone IL showed promise as a super stoichiometric carbon capture agent warrants further study. Although perhaps not cooperative in
nature, the mechanism by which this candidate reacts with CO₂ would ultimately lead to improved designs in the future based on this class of anionic IL components.

(3b) α-N-Heterocyclic β-Amino Alcohols

β-amino alcohols constituted an important class of compounds as they have been shown utilized as ligands in asymmetric catalysis and as important building blocks in the construction of more complex molecular architectures. Surprisingly, few reports exist of these ubiquitous compounds being converted into the corresponding RTILs and utility explored outside of the context of pharmaceutical drug discovery. We proposed the purposing of this amino acid derived building blocks as ILs with the potential for structural cooperativity in which the reaction of one equivalent of CO₂ would occur at the nitrogen of the α-N-heterocyclic anion initially, then thermodynamically driven to migrate down the chain to the N-alkyl-β-amine group, which would subsequently reactivate the chain through proximal hydrogen bonding with the alcohol group for additional capture of CO₂.

Key Findings:

- Although it required in an incredible synthetic effort, and many iterations and constant reevaluation of our synthetic strategy, we were able to design a universal approach toward this scaffold starting from commercially available and exceptional inexpensive glycine. This approach provided us with quantities of various N-alkyl-β-amino, α-N-heterocyclic alcohols derived from pyrroles, imidazoles, pyrazoles, 1,2,3- and 1,2,4-triazoles, and tetrazoles.
- Treatment of the IL derived from a tetrazolide aromatic ring showed ultimately showed good 1:1 uptake of CO₂, but failed to exhibit the cooperative carbon capture we were anticipating.
- Further examination with 1 equivalent of benzylchloroformate as a CO₂ surrogate resulted in selective carbamate formation at the secondary amine site.
- The addition of CO₂ followed by an activating agent, such as TMSOTf, provided the cyclic carbamate resulting from amino alcohol acylation.
- Not surprisingly, the pyrrole derived amino alcohols exhibited poor thermal and light stability under even ambient conditions.
- Although the triazole derived ILs showed weak thermodynamic binding to CO₂, the triazole derivatives, specifically 1,2,4-triazoles, exhibited a promising reaction profile with CO₂ and the potential for >1:1 stoichiometric capture.

Outcomes:

- Employing CO₂ in combination with in situ activating agents and CO₂ surrogates 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.
- Current efforts are underway that focus on developing a better understanding of the reactivity of these novel ILs with CO₂. Subsequent designs have focused on examining functional group derivatives of the heterocyclic frameworks within the amino alcohol scaffold to increase the thermodynamic profile of carbon capture and facilitate >1:1 reactivity.
• Publications: A manuscript detailing our synthetic efforts toward this novel class of compounds in currently in advanced stages of preparation.

(3c) ortho-Amino Phenolate Anions

Recently, carbon capture agents derived from phenols have become attractive candidates for IL exploration based on their ready availability, ease of synthesis, and well-established reactivity profiles with electrophilic agents, such as CO₂. As a result, we have begun to synthesize and evaluate phenol derivatives that bear an amine functionality at the 2-, 3-, and 4-positions around a benzene ring relative to the hydroxyl group on a starting phenol. Our proposed design strategy involves the initial reaction to occur at the phenolate anion that the resulting carbonate would activate the appropriately positioned amine functionality as an additional site of carbon capture.

**Key Findings:**

• After considerable experimentation, we were able to develop conditions that would enable access to orthogonally functionalized hydroxyl and amine functionalities around a core benzene ring.
• We were able to synthesize phenol derivatives that contained N-alkyl and N-acyl groups appropriately positioned relative to the hydroxyl functionality.
• Treatment of the IL derived from a 2-N-methyl amino phenolate showed good 1:1 uptake of CO₂, but the acquisition of a second equivalent proved slow and did not exhibit the thermodynamic profile we desired.
• The amino functionalities examined were either too sterically hindered (alkyl) or too deactivating (acyl) to provide adequate assembly of a polycarboxylated adduct after exposure to CO₂ at ambient or high pressures.
• Certain amino phenols had a tendency to solidify at room temperature. This was not particularly surprising given the propensity of benzene derivatives to undergo π-stacking in a macromolecular assembly. However, this does constitute an important consideration in the development of ILs based on this structural framework.

**Outcomes:**

• In general, this general architectural class of compounds are an intriguing group for future exploration as task-specific ILs. The ready availability and ease of functional group manipulation should enable optimization for a variety of applications.
• While the derivatives we have examined to date have not exhibited the reactivity profile we had anticipated, the potential exists for additional designs to operate with >1:1 stoichiometric capture of CO₂.
• The commercial availability of these starting components proved attractive from a process standpoint for future ease of scaled up synthesis.

(3d) N-Heteroaromatic-Substituted Proline Derivatives

Amino acid derivatives are a particularly attractive scaffold for materials synthesis due to their ready commercial availability, low cost, and versatile functional handles. As discussed in section II above, we were intrigued by this class of starting materials for IL design as carbon capture agents that could be acquired on large scale. As a result, we chose to focus on proline derivatives in which the carboxylic acid group is synthetically transformed into a N-heteroaromatic ring bearing the anion functionality requisite for IL assembly. We anticipated that upon exposure to carbon dioxide under pre-combustion
temperature and pressure conditions would lead to an initial thermodynamically favored carboxylation event at the proline nitrogen that would subsequently activated the heterocyclic ring for capture of a second equivalent of CO₂.

**Key Findings:**
- The synthesis of these bis-heterocyclic scaffolds proved one of our more challenging endeavors to date. Multiple protecting group strategies and revisions to the initial synthetic route were required in order to obtain sufficient quantities of the target candidate ILs. In most cases, the final deprotection and anion formation proved to be the most problematic steps in the synthesis, and required numerous iterations to establish conditions that would afford the desired IL in acceptable yield. Ultimately, the pyrrole, tetrazole, and 1,2,4-triazoles were produced and precursors to the corresponding imidazole, pyrazole, and 1,2,3-tetrazole ILs were obtained.
- The N-heteroaromatic protecting groups were quite sensitive to the conditions for IL generation. More specifically, removal of these groups provided adducts that many times were unstable to the reaction conditions required for deprotection. Examination of a diverse array of nitrogen protection groups (Boc, SiR₃, alkyl, PMB, etc.) led to the discovery that decomposition did not occur under the hydrogenation conditions required to remove a benzyl protecting group. This strategy was then employed for the assembly of the IL candidates of interest.
- Preliminary experiments with CO₂ showed excellent 1:1 uptake of CO₂, and potentially acquisition of additional equivalents. Through parallel experiments using CO₂ surrogates (i.e., chloroformates) and the addition of carboxylate trapping agents (i.e., TMSOTf) we have established that the proline nitrogen constitutes the initial site of carboxylation with the heteroaromatic nitrogen potentially positioned for a second reaction with CO₂. More details of the chemistry are given below under Task 4.
- Further analysis of these candidate ILs is necessary to establish their performance attributes and validate our initial findings into bicarboxylation of the proline-heteroaromatic scaffold. This constitutes a major area of focus moving forward on this project.

**Outcomes:**
- This class of compounds constitutes one of our most promising candidates to date, and current synthetic efforts are focused on the construction of additional molecular scaffolds for evaluation.
- Specifically, the 1,2,3-tetrazolides and imidazolides show great promise as super stoichiometric capture agents, and the designs of these compounds is readily amenable to larger molecular frameworks for extended CO₂ capture down a polyheterocyclic chain.
- Additional synthetic work is warranted in order to arrive at a synthetic scheme that would enable large-scale production of these ILs.
- Focusing on the 1,2,4-triazole substituted proline phosphonium IL as our lead candidate, we will continue to examine this general class of compounds, and remains a major focus of our study moving forward.

(3e) Diamines
Based on their commercial availability, and the extensive work that has already been performed on ethylene diamines in carbon capture, we did a perfunctory evaluation of 1,2-
and 1,3-diamines with orthogonally functionalized amine groups as ILs bearing multiple CO₂ reactive sites. We reasoned that minimal synthetic effort would be required to evaluate this class of compounds, and their potential for mass production based on readily available starting materials, made this class of candidates an logical point of interest.

Key Findings:
- We were able to establish synthetic routes toward electron deficient nitrogen-containing compounds as IL precursors using acyclic framework comprised of N-substituted aliphatic amines or ethylenediamines.
- Diamines containing orthogonal nitrogen substitution in which one nitrogen is alkylated and the other acylated, were constructed and used as starting materials for IL generation.
- In a straightforward 2 or 3 steps from inexpensive, commercially available starting materials (~$1-1.5/g) the corresponding IL precursors can be obtained.
- Interestingly, synthesis of the corresponding N-anionic ILs derived from these diamines proved less straightforward than anticipated. In general, substantial decomposition occurred upon deprotonation and cation exchange with a diverse assortment of phosphonium and ammonium cations.

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.
- Although the potential for additional work on this intriguing class of candidates will occur in the future, our difficulties in generating thermally stable ILs from the diamine precursors may ultimately limit the potential for commercial applications.

(3f) New Approaches Toward the Synthesis of Nitrones and N-Acyl Hydrazones.

A natural consequence of the intense synthetic efforts related to the construction of the RTIL candidates for this project is the design, development, and discovery of new synthetic strategies related to small molecule assembly. The development of new methods that involve the synthesis of nitrogen containing compounds, and specifically N-heterocyclic frameworks, constitutes an important area in the realm of organic synthesis. These methods are often quite valuable additions to the arsenal of synthetic strategies for the assembly of a diverse assortment of small molecule entities, whether they are in materials or pharmaceutical discovery. Our efforts have resulted in the design and development of a number of synthetic methods, of which two are particularly noteworthy. Since submission of the previous progress report, we have established viable synthetic strategies toward architecturally diverse nitrones and N-acetyl hydrazones. These two carbonyl derivatives constitutes important building blocks in heterocycle synthesis, and should find wide-ranging utility in the broadly defined area of synthesis.

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.

Hydrazones constitute one of the most ubiquitous synthetic building blocks in discovery chemistry, and their utility as starting materials in heterocycle synthesis has led to the need for the development of new methods for their construction. We have developed the first phosphine-mediated umpolung assembly of N-acyl hydrazones from 1,2-dicarboxylics and diazenes. The reaction proceeds under exceptionally mild conditions and in good to excellent yields. Our strategy toward C–N bond construction avoids the use of nucleophilic amines, which will interest chemists and engineers in the study of macromolecular functions. These findings will likely engender the development of new methods for metal-free redox condensations using readily available and inexpensive phosphine reagents.

**Key Findings:**
- We developed a highly chemoselective, umpolung approach toward nitrone and N-acyl hydrazone synthesis that constitutes a departure from conventional dehydration strategies.
- Both methods operate under exceptionally mild conditions, use inexpensive starting materials, and are readily amenable to scale up.
- These strategies enable direct access to functionalized heterocyclic frameworks that are immediate precursors to the IL counterparts described in the aforementioned sections.

**Outcomes:**
- These results open the door to previously unexplored heterocycles that can be examined as structurally cooperative CO$_2$ binding ILs.

**Task 4. Experimental testing.**

(4a) CO$_2$ Uptake Measurements for Chemical Cooperativity Candidates

The CO$_2$ uptake exhibited by several of the compounds synthesized and described in Task 3 were measured using a Hiden IGA gravimetric microbalance.

**Key Findings:**
- **$\alpha$-N-Heterocyclic $\beta$-Amino Alcohols.** Treatment of the IL derived from a tetrazolide aromatic ring showed good CO$_2$ uptake, approaching 1 mole of CO$_2$ per mole of IL at pressures of roughly 10 bar. However, it failed to exhibit the cooperative carbon capture we were anticipating.
- **ortho-Amino Phenolate Anions.** Treatment of the IL derived from a 2-N-methyl amino phenolate showed good CO$_2$ uptake, approaching 1 mole of CO$_2$ per mole of IL at
pressures of roughly 10 bar. However, the acquisition of a second equivalent proved slow and did not exhibit the desired thermodynamic profile.

- **N-Heteroaromatic-Substituted Proline Derivatives.** Preliminary experiments with CO\textsubscript{2} showed excellent 1:1 uptake of CO\textsubscript{2}, but the acquisition of additional equivalents of CO\textsubscript{2} was not observed.

**Outcomes:**
- The failure of several of the chemical cooperative binding candidates to exhibit superstoichiometric CO\textsubscript{2} uptake led us to investigate the chemistry of the N-heteroaromatic-substituted proline derivatives in more detail, as described in the next section.

(4b) **Reaction Chemistry of N-heteroaromatic-substituted proline derivatives**

The cooperative reaction we were hoping to observe with the N-heteroaromatic-substituted proline derivatives is shown below for the 1,2,4-triazolide anion (which was paired with a tetra-butylphosphonium cation ([P\textsubscript{4444}]). Unfortunately, we did not observe greater uptake than 1 mole of CO\textsubscript{2} per mole of IL. Therefore, we investigated and compared the IL with the complex anion, as well as mixtures of [P\textsubscript{66614}][1,2,4-triazolide] or [P\textsubscript{66614}][1,2,3-triazolide] with neutral molecular pyrrolidine.

**Key Findings:**
- [P\textsubscript{4444}][4-Triaz-pyrrol] was a viscous ionic liquid that solidified after reaction with CO\textsubscript{2}.
- The IL was diluted in tetraglyme to improve the mass transfer and the CO\textsubscript{2} uptake was found to be equimolar at 1 bar and 22°C. From the ATR-FTIR spectra it appears that the pyrrolidine is reacting first with CO\textsubscript{2} and then the pyrrolidine-CO\textsubscript{2} product is deprotonated. The equimolar absorption leads to the conclusion that the [4-Triaz\textsuperscript{-}] is most likely accepting the proton.
- A mixture of [P\textsubscript{66614}][4-Triaz] and pyrrolidine was prepared to compare the chemistry of the two components separated to the [P\textsubscript{4444}][4-Triaz-pyrrol] IL, where the components are connected. It was found that the separated components behaved similar to the cooperative IL. The pyrrolidine reacted with CO\textsubscript{2} first. The absorption was equimolar in amount of CO\textsubscript{2} where the [P\textsubscript{66614}][4-Triaz] accepted the proton.
- [P\textsubscript{66614}][3-Triaz] mixture with pyrrolidine led to a different reaction pathway due to the basicity of the anion. The pyrrolidine reacted with CO\textsubscript{2} in a 1 mole CO\textsubscript{2} per mole 2 moles pyrrolidine mechanism similar to reported aqueous amine chemistry. After the pyrrolidine is completely reacted, the [3-Triaz\textsuperscript{-}] anion reacts with CO\textsubscript{2} to form the carbamate product. The basicity of the anion leads to a second mole of the pyrrolidine accepting the proton instead of the IL anion.

**Outcomes:**
- Additional cooperativity motifs, as described above, are being investigated.
**ILs Featuring Physical Cooperativity (Tasks 2 and 4)**

Ionic liquids featuring physical cooperativity are designed to exhibit reactivity of one mole of CO$_2$ per mole of IL. However, it is anticipated that the CO$_2$ 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-CO$_2$ 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 CO$_2$ 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).

In the last year the team has made a number of exciting accomplishments. The work has primarily focused on understanding the effect of water on CO$_2$ uptake by AHA ILs, the relative reactivity of CO$_2$ with AHA anions versus phosphonium ylide chemistry, a new method to calculate CO$_2$ uptake by reactive ILs, and the prediction of physical gas solubilities and diffusion coefficients in ILs in situations that would be relevant if the IL were confined in a solid adsorbent or membrane.

(2a) Physical cooperation mechanism of water to azolide-CO$_2$ binding

*Key findings:*
- The MP2/aug-cc-pvtz level of studies reveals that water can competitively bind to the azolide in the range of reversible $\Delta H_{CO2}$ (Figure 4). The addition or contamination by water may impact the reactivity of CO$_2$ in azolide based ionic liquids.

![Figure 4.](image-url) The CO$_2$ binding enthalpies and Water binding enthalpies at 298K ($\Delta H_{CO2}$, kJ/mol) from MP2/aug-cc-pvtz computation
• Water breaks strong interionic interaction between tetraalkylphosphonium cation and 1,2,3-triazolide anions and modulates the ability of anions to combine with CO$_2$. (Figure 5).

![Image of spatial distribution function](image1)

**Figure 5.** Spatial distribution function for 1,2,3-triazolide, and 1,2,3-triazolide with equimolecular water additive coupled from classical molecular dynamics simulation for 200 ion pairs of [P$_{2228}$][1,2,3-triazolide] model system. Red is cation density while blue is water density.

• The “Metadynamics” simulation reveals that the free energy of barrier to form bicarbonate in ILs is higher than the barrier in aqueous condition and lower than gaseous condition. (Figure 6). The activation free energy barrier is -13 kcal/mol while the formation and decomposition of bicarbonate is almost thermo-neutral.

![Image of CO$_2$ binding free energy profile](image2)

**Figure 6.** CO$_2$ binding free energy profile by metadynamics at 300K based on [P$_{2228}$][azolide] one ion pair in 15 Å cubic box model systems.
**Outcomes:**

- The amount of bicarbonate in experiments is usually less than 10%, which implies the appropriate selection of ILs can avoid the formation of undesirable bicarbonate byproduct in the presence of water.
- Lee and Schneider, manuscript in preparation

**(2b) Competing cation and anion reactions with CO₂**

**Key findings:**

- The proton transfer from phosphonium \([\text{P}2222]\) to phenolates at ambient condition induces formation of stable ylide and CO₂ can bind carboanion rather than phenolates (Figure 7).

**Figure 7.** B3LYP/6-311+G(d,p) comparison of anion- and ylide-mediated reactions of CO₂ with \([\text{P}2222]\)[ phenolate](black), \([\text{P}2222]\)[ phenolate](red), and \([\text{P}2222]\)[ phenolate](blue). Energies in kJ/mol.

- When acidic proton is available in cation counterpart, the CO₂ reaction chemistry of oxy-anion is not parallel to the CO₂ reaction chemistry of azolide.
- The CO₂ reactivity of phenolate-based ILs in literature needs careful re-examination.

**Outcomes:**

- Lee and Schneider, manuscript in preparation

**(2c) Coupled quantum-classical models for predicting reactive isotherms**

**Key findings:**

- Development of thermodynamic cycle for the Gibb’s free energy of reaction combining QM and MM calculations to predict absorption isotherms. (Figure 8).
Figure 8: Thermodynamic free energy cycle for the reaction of CO$_2$ in IL. Free energies are determined based upon the following steps: (1) vaporization of the IL at constant temperature and pressure; (2) reaction of the IL with CO$_2$ in the gas phase; (3) condensation of the reacted and unreacted IL gas individually; (4) mixing of the unreacted IL liquid with the reacted IL liquid; Steps 3 and 4 combined represent the free energy to solvate a reacted IL:CO$_2$ complex in unreacted IL.

- Combining all steps from the thermodynamic cycle, the free energy of reaction can be calculated using the following expression

$$\Delta G_{\text{rxn}}(\xi, P, T) = \xi (\Delta G_H) - RT \ln \left( \frac{P}{P_0} \right) - T \Delta S_{\text{mix}}$$

where $\Delta G_H$ is the standard state free energy of the gas phase reaction plus the difference in the enthalpy of vaporization of the reacted IL and the unreacted IL.

Figure 9: Isotherm sensitivity to $\Delta G_H$ parameter. Lines are labeled with the value of $\Delta G_H$ in kJ/mol. All isotherms are at a temperature of 300 K with a reference pressure of 1 bar.
Outcomes:
- The expression for the free energy of reaction can be used to predict absorption isotherms. However, isotherms are sensitive to the \( \Delta G_H \) parameter for quantitative solubility prediction.
- Application of this thermodynamic cycle to predict reactive isotherm at different temperature condition.
- Quintin and Schneider, manuscript in preparation

(2d) Calculation of pure gas absorption isotherms and self-diffusion coefficients in IL confined in graphite slit-pores

Key findings:
- Computed CO\(_2\) and H\(_2\) absorption isotherms in IL confined in graphite slit-pores of width 2 nm and 5 nm. IL in 5 nm graphite slit-pore showed larger CO\(_2\) and H\(_2\) solubilities. Gas solubilities in confined systems were larger than in bulk systems. 
- Self-diffusion coefficients of CO\(_2\), H\(_2\) and IL were reduced by an order of magnitude in 2 nm pores when compared to the bulk system. Self-diffusion coefficients of IL in 5 nm pores were similar to bulk. However, CO\(_2\) and H\(_2\) self-diffusion coefficients were reduced by about 20%.
- Surface interactions and presence of bulk region of IL in 5 nm slit-pore had a synergistic effect that contributed to larger gas solubilities as opposed to 2 nm pore where IL bulk region is absent.

(2e) Calculation of mixed gas solubility, self-diffusion coefficients and perm-selectivities

Key findings:
- Computed CO\(_2\)/H\(_2\) mixed gas solubilities in IL confined in 2 nm and 5 nm graphite slit-pores at 30 bar and 333 K. Similar to the pure gas solubilities, IL in 5 nm slit-pore had larger mixed gas solubilities.
- Self-diffusion coefficients for mixed gas-IL systems showed trends similar to pure gas-IL mixtures. H\(_2\) self-diffusion coefficients were larger than CO\(_2\) self-diffusion coefficients. Gas self-diffusion coefficients were an order of magnitude greater than those of IL.
- CO\(_2\) perm-selectivities were computed from the solubility and self-diffusion results. IL in bulk phase had larger CO\(_2\) perm-selectivities than confined IL systems. (Table 1)

Table 1: CO\(_2\) perm-selectivities (\( \beta_{CO_2/H_2}^P \)) in bulk [C\(_4\)mim][Tf\(_2\)N] and [C\(_4\)mim][Tf\(_2\)N] confined in graphite slit-pores.

<table>
<thead>
<tr>
<th>System</th>
<th>( \beta_{CO_2/H_2}^P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL+CO(_2)+H(_2)</td>
<td>10.6(_1)</td>
</tr>
<tr>
<td>IL+CO(_2)+H(_2)+2 nm slit-pore</td>
<td>7.71(_6)</td>
</tr>
<tr>
<td>IL+CO(_2)+H(_2)+5 nm slit-pore</td>
<td>10.1(_1)</td>
</tr>
</tbody>
</table>
Task 4. Experimental testing.

(4a) Solubility of H₂S in ILs

Sulfur in 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, last year we reported H₂S solubilities in four different ILs. Ultimately, we measured H₂S solubilities in ten different ILs. **Key Findings:**

- The physical solubility of H₂S in ILs is very high, with Henry’s law constants ranging from 4.3 to 11.2 bar at 30 °C.
- Measurements of H₂S solubilities at temperatures between 30 °C and 70 °C resulted in partial molar enthalpies of absorption between -17 and -23 kJ/mol. An example is shown in the Figure 10.
- H₂S reacts irreversibly with ILs containing aprotic heterocyclic anions.

![Figure 10. H₂S solubility in a typical IL as a function of temperature.](image)

**Outcomes:**

- Bennett and Brennecke, manuscript in preparation

(4b) Quantifying Ylide Formation

Previously, we have shown that some of the CO₂ uptake with tetra-alkylphosphonium AHA ILs is due to the formation of a phosphonium ylide that can react with CO₂. In the past year we have quantified the reaction of the phosphonium cation with CO₂ for various different AHA ILs, using a combination of NMR and IR spectroscopies. **Key Findings:**

- Less reaction of CO₂ with the phosphonium cation is observed for AHA ILs with anions that bind more strongly with CO₂.
- Cation-CO₂ complex forms much more slowly compared to anion-CO₂ complex.
The system can be modeled as two independent parallel reactions. The first is the reaction of CO\(_2\) with the anion of the IL. The second reaction forms the cation-CO\(_2\) product and the reprotonated anion.

**Outcomes:**
- Thomas R. Gohndrone and Joan F. Brennecke, manuscript in preparation.

(4c) Phenolate ILs for CO\(_2\) Capture

As mentioned above, there has been increasing interest in the literature on the use of phenolate ILs for CO\(_2\) capture. As a result, we synthesized and tested several phenolate ILs.

**Key findings:**
- The cation of \([P_{66614}][\text{Phenolate}]\) reacts with CO\(_2\) at 22°C and 60°C, where no noticeable amount of the anion is reacted with CO\(_2\) at equilibrium. This contradicts the reaction presented in literature. The total uptake is about 0.4 mole of CO\(_2\) per mole of IL at 1 bar and 22°C.
- The reaction products change with time. Initially, from the in-situ ATR-FTIR, it appears the anion is reacting with CO\(_2\); however at equilibrium the cation-CO\(_2\) product is the only product formed.
- The uptake can be varied by adding electron withdrawing groups to the para position of the phenol ring. \([4-\text{NO}_2-\text{phenol}]^-\) does not react with CO\(_2\) and only physical absorption is seen. The CO\(_2\) solubility is increased for the \([4-\text{MeO-phenol}]^-\) relative to \([\text{phenol}]^-\).
- CO\(_2\) reacted with the anion of \([N_{2227}][\text{Phenol}]\), however the IL is not stable and decomposed. Results do point to the opportunity to use nucleophilic oxygen in a cooperative environment.

**Outcomes:**
- The reactivity of CO\(_2\) with various phenolate ILs is being investigated in more detail.
- A manuscript on the phosphonium phenolate chemistry is in progress.

**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 CO\(_2\) 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 CO\(_2\) 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 cost requirement for the CO$_2$ 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 CO$_2$. 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 CO$_2$ uptake with physical cooperativity. We can provide near quantitative predictions of the physical solubility of many gases. For ones that are less quantitative, like H$_2$S, we have measured the solubilities experimentally. Our understanding is that modeling of the various CO$_2$ capture technologies supported by GCEP by the group of Ed Rubin gives very favorable results for the IL technology that we have developed.

**Future Plans**

This project will conclude on 7/16/15. Therefore, the plans for the remainder of the project continue to be aligned with the project proposal and focus on concluding work and publishing the results.

1. Pre-combustion CO$_2$ capture system modeling to determine IL properties that minimize energy use and process cost.
   a. Complete sensitivity analysis and submit publications
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. Submit publications
3. Synthesis of the new ILs identified by QM and classical molecular simulation.
   a. Synthesis of several new ILs with β-enaminoimine-based anions are still in progress.
   b. Submit publications
4. Experimental testing.
   a. Submit publications

**Publications and Patents**

4. Samuel Seo, M. Aruni DeSilva and Joan F. Brennecke, “Physical Properties and CO$_2$ Reaction Pathway

Presentations
19. Joan F. Brennecke, Samuel Parr Lecture, Carbon Capture with Ionic Liquids, Department of Chemical Engineering, University of Illinois at Urbana-Champaign, May 7, 2015.


References

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