

Chemically-Complexing Ionic Liquids for Pre-Combustion CO₂ Capture

Activity Number 73
Progress Report (7 month period)
9/1/12-3/31/13

Investigators

Joan F. Brennecke, Keating-Crawford Professor, Chemical and Biomolecular Engineering
Brandon Ashfeld, Assistant Professor, Chemistry and Biochemistry
Edward J. Maginn, Professor, Chemical and Biomolecular Engineering
William F. Schneider, Professor, Chemical and Biomolecular Engineering, and Chemistry and Biochemistry
Mark A. Stadtherr, Keating-Crawford Professor, Chemical and Biomolecular Engineering
J. Edward Bennett, Graduate Student, Chemical and Biomolecular Engineering
Murukkuwadura DeSilva, Post-doctoral Research Associate, Chemical and Biomolecular Engineering
Thomas J. Gohndrone, Graduate Student, Chemical and Biomolecular Engineering
Bo Hong, Graduate Student, Chemical and Biomolecular Engineering
Doyun Lee, Post-doctoral Research Associate, Chemistry and Biochemistry
Tae Bum Lee, Post-doctoral Research Associate, Chemical and Biomolecular Engineering
Samuel Seo, Graduate Student, Chemical and Biomolecular Engineering
Ramesh Singh, Post-doctoral Research Associate, Chemical and Biomolecular Engineering
Monika Vogt, Post-doctoral Research Associate, Chemistry and Biochemistry
Han Xia, Graduate Student, Chemical and Biomolecular Engineering

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 first (7 month) reporting period.

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 first seven months of the project we have made the significant progress on the second class of compounds – ILs featuring structural cooperativity. This includes quantum calculations of binding energies of candidate materials, synthesis of three specific ILs designed for structural cooperativity in the complexation of CO₂,

characterization of and measurement of the CO₂ capacity of these materials, and the development of a thermodynamic model for multi-site cooperative binding. In addition, we have developed a method to predict the physical solubility of CO₂ and H₂ in ionic liquids, which is applicable for the use of all three types of IL materials in the separation of CO₂ from pre-combustion gases. Finally, we have discovered and fully characterized additional chemistry that is occurring when sufficiently basic anions are paired with phosphonium cations, leading to cation CO₂ complexation.

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

The primary information that has appeared in the literature in the last seven months that is relevant to this project are measurements of physical H₂ solubility in various ILs. Due to the inherent difficulties associated with obtaining accurate solubility measurements of low molecular weight, sparingly soluble gases, a high degree of variability exists in published values of H₂ solubility in ILs. However, these recent reports provide additional data points for comparison of our molecular simulations of H₂ solubility (see below). We are aware of no publications on cooperative CO₂ binding with ILs or publications focused on pre-combustion CO₂ separations with chemically-reactive ILs.

Results

Since project initiation, significant progress has been made toward the design and synthesis of new ILs which feature structural cooperative CO₂ complexation for super-stoichiometric carbon capture. We have succeeded in establishing a method to allow rapid prediction of CO₂ and H₂ physical solubility in ionic liquids using advanced molecular simulations. Finally, through a systematic evaluation of anion-cation IL

combinations we discovered the facile *in situ* generation of versatile phosphorus-based carbon ylides in the presence of basic heterocyclic anions. Our observation of the resulting carboxylation of the cation under an atmosphere of CO₂ may lead to a paradigm shift in materials design for chemical complexation. Results for each of these three areas are organized by Task number in the discussion below.

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. The first step of systems modeling for ILs featuring structural cooperativity is the development of an appropriate thermodynamic model. Thus, we have established a CO₂ uptake isotherm model for an activated CO₂ absorption mechanism. It is assumed that the IL in its original form has a single CO₂ reaction site: IL + CO₂ → IL-CO₂. This first reaction activates a new CO₂ reaction site on the IL-CO₂ complex molecule: IL-CO₂ + CO₂ → IL-(CO₂)₂. The uptake isotherm developed is:

$$Y = \frac{K_1 P_{CO_2} + 2K_1 K_2 P_{CO_2}^2}{1 + K_1 P_{CO_2} + K_1 K_2 P_{CO_2}^2}.$$

Here Y is the CO₂ uptake (moles CO₂ per mole of IL), P_{CO_2} is the partial pressure of CO₂, and K_1 and K_2 are the equilibrium constants corresponding to the first and second reactions, respectively. The equilibrium constants are functions of temperature given by:

$$K_i = \exp \frac{(-\Delta H_i + T\Delta S_i)}{RT}, \quad i = 1, 2.$$

The ΔH_i and ΔS_i , $i = 1, 2$, represent the standard enthalpy and entropy of reaction, respectively, for reactions 1 and 2. This uptake model can be regarded as an extension of the well-known Langmuir isotherm. Figure 1 shows a few uptake isotherms for the case of $\Delta S_1 = \Delta S_2 = -130$ J/mol·K, $\Delta H_1 = -20$ kJ/mol and $\Delta H_2 = -85$ kJ/mol. The increasingly sigmoidal shape of the uptake isotherm as temperature is decreased indicates the potential to achieve large differences in uptake with relatively small differences in pressure. We plan to combine this isotherm model with a simple CO₂ capture process model and use this approach to determine target IL physical property values (e.g., ΔH 's and ΔS 's).

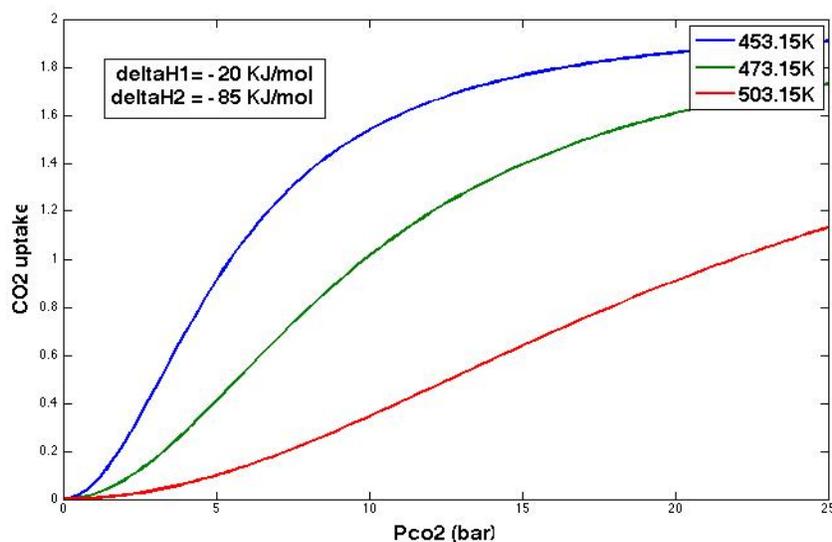


Figure 1: Model uptake isotherms for an activated CO₂ absorption mechanism for the case of $\Delta S_1 = \Delta S_2 = -130 \text{ J/mol}\cdot\text{K}$, $\Delta H_1 = -20 \text{ kJ/mol}$ and $\Delta H_2 = -85 \text{ kJ/mol}$.

Task 2. Quantum mechanical and classical molecular simulation to design new IL materials that satisfy the criteria developed by the process modeling. Inspired by the cooperative binding of O₂ by hemoglobin and the allosteric regulation of enzymes, we have used quantum calculations to design ILs with aprotic heterocyclic anions (AHA) to sequentially capture additional CO₂. The mechanism of CO₂ binding originates from the charge transfer from the AHA to CO₂, which can compensate for the disfavored bent geometry of the CO₂. The great diversity of heterocyclic anions that one can envision that might have structural cooperativity features is large so we have applied *ab initio* computation to determine the intermediate first CO₂ binding ($\Delta H_{\text{CO}_2(1)}$), followed by a stronger second CO₂ binding ($\Delta H_{\text{CO}_2(2)}$) at 298K (Eq 1 and 2).

$$\Delta H_{\text{CO}_2(1)} = H_{\text{AHA-CO}_2} - (H_{\text{AHA}} + H_{\text{CO}_2}) \quad (1)$$

$$\Delta H_{\text{CO}_2(2)} = H_{\text{AHA-2CO}_2} - (H_{\text{AHA-CO}_2} + H_{\text{CO}_2}) \quad (2)$$

The B3LYP/6-31G(d,p) level of theory, which is an entry level of *ab initio* computation, was used to rapidly filter candidates for sequential CO₂ binding AHA ILs. In our initial efforts, the first binding of CO₂ ($\Delta H_{\text{CO}_2(1)}$) was very exothermic while the second CO₂ ($\Delta H_{\text{CO}_2(2)}$) binding was slightly exothermic or endothermic, which would not favor the sequential binding of CO₂ (Table I). We introduced electron-withdrawing groups to reduce the binding enthalpy of the first CO₂ and incorporated a linker group to release steric hindrance induced by the formation of two carbamates. The enhanced second CO₂ binding was facilitated by the strong hydrogen bond formation between the bound CO₂'s. With adequate arrangement of functional groups and tuning of anion basicity, we have designed four AHA structures which should show sequential binding of additional CO₂ with meaningful exothermic reaction enthalpies (AHA15, AHA16,

AHA17, and AHA18 in Table I). Efforts are currently underway in to synthesize these lead candidate AHA ILs.

Table I: First and second CO₂ binding enthalpies ($\Delta H_{\text{CO}_2(1)}$ and $\Delta H_{\text{CO}_2(2)}$) at 298K for various AHAs based on B3LYP/6-31G(d,p) level of theory

AHAs	$\Delta H_{\text{CO}_2(1)}$ (kJ/mol)	$\Delta H_{\text{CO}_2(2)}$ (kJ/mol)	AHAs	$\Delta H_{\text{CO}_2(1)}$ (kJ/mol)	$\Delta H_{\text{CO}_2(2)}$ (kJ/mol)
[AHA1]	-104.8	-5.1	[AHA11]	-16.1	13.4
[AHA2]	-97.7	-0.6	[AHA12]	-71.2	7.9
[AHA3]	-56.3	7.7	[AHA13]	-66.9	-11.9
[AHA4]	-65.1	8.9	[AHA14]	-73.1	-27.2
[AHA5]	-99.1	4.1	[AHA15]	-88.9	-39.6
[AHA6]	-88.3	-6.7	[AHA16]	-47.6	-51.2
[AHA7]	-24.3	-15.0	[AHA17]	-52.8	-39.3
[AHA8]	-73.7	17.5	[AHA18]	-39.3	-84.3
[AHA9]	-69.3	14.8			
[AHA10]	-87.9	-8.7			

Task 3. Synthesis of the new ILs identified by QM and classical molecular simulation. Our efforts have focused on the development of novel *N*-heterocyclic ionic liquids (ILs) featuring cooperative CO₂ absorption for increased CO₂ capacity. Initial efforts have focused on the design and synthesis of two heterocyclic core frameworks that incorporate multiple, chemically coupled CO₂ binding sites. To date, three different ILs have been synthesized and successfully reacted with CO₂. Preliminary evidence suggests that at least one of these ILs reversibly reacts with more than one molecule of CO₂ per molecule of IL providing a proof of concept for our approach. Current and future efforts are focused on evaluating our second generation designs to optimize cooperative binding features. Additional molecular designs include amino acid derivatives of which the synthesis of four different ILs are underway.

Task 4. Experimental testing. The CO₂ capacity of one of the AHA ILs designed to exhibit structural cooperativity has been measured at 22, 40 and 60 °C, using a Hiden Gravimetric microbalance (Figure 2). While, the capacity reaches more than one mole of CO₂ per mole of IL at 15 bar of CO₂ pressure, it is important to bear in mind that this observation alone is not evidence of structural cooperativity. We have many AHA ILs that achieve 1 mole CO₂ per mole of IL capacity at 15 bar CO₂ pressure. However, all single-binding ILs that reach high CO₂ capacities show sharp uptakes at very low pressures (less than 1 bar), which is indicative of a large negative value of the heat of reaction. The IL shown in Figure 2 does not exhibit this sharp uptake at low pressures. Taken together, these results indicate that the high capacity is a result of cooperative binding (a lower magnitude of the enthalpy of reaction of the first CO₂, which activates the stronger binding of the second CO₂). We anticipate that the cooperative binding ILs suggested by the quantum calculations should be even more effective than this initial success.

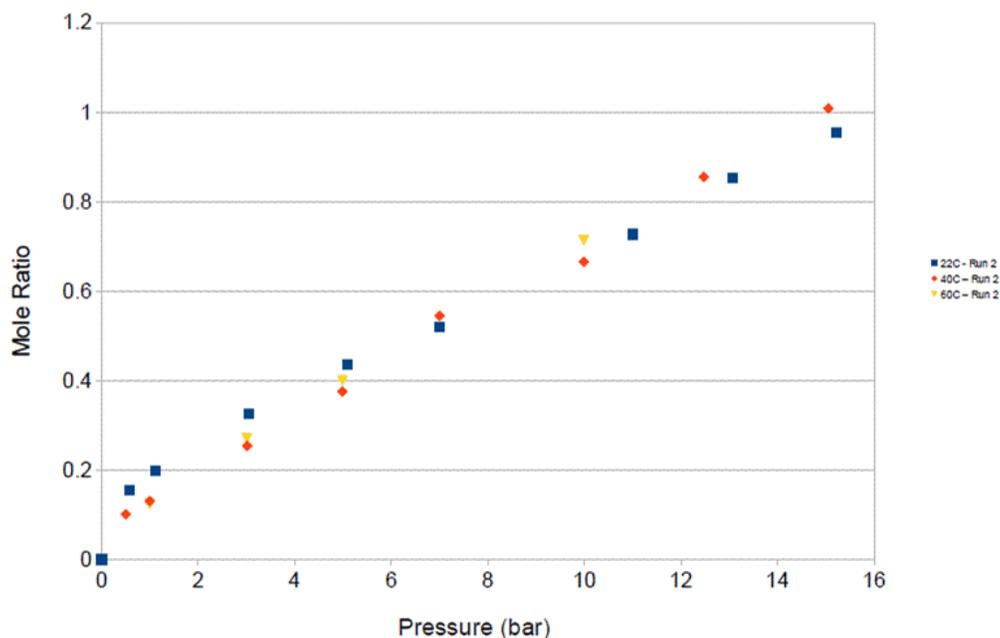


Figure 2: CO₂ uptake of AHA IL with structural cooperative binding.

Prediction of Physical Solubility of Gases

Task 2. Quantum mechanical and classical molecular simulation to design new IL materials that satisfy the criteria developed by the process modeling. Our objective is to develop and apply molecular modeling methods to predict the pure and mixed gas solubility of H₂ and CO₂ in ionic liquids under gasification conditions. We began by first developing methods and validating calculations against published experimental and computational results.

Isothermal-isobaric Gibbs ensemble Monte Carlo (NPT-GEMC) simulations were used to compute the absorption isotherms of CO₂ and H₂ in the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([HMIM⁺][TF₂N⁻]). Temperatures ranged from 313 to 573 K and pressures up to 100 bar in the case of CO₂ and 500 bar in the case of H₂. The TraPPE three-site model [1] was selected to describe the intermolecular potential between CO₂ molecules and the intermolecular potential between H₂ molecules was represented by two-site model of Cracknell [2]. The force field parameters for IL [HMIM⁺][TF₂N⁻] were taken from Shi and Maginn [3].

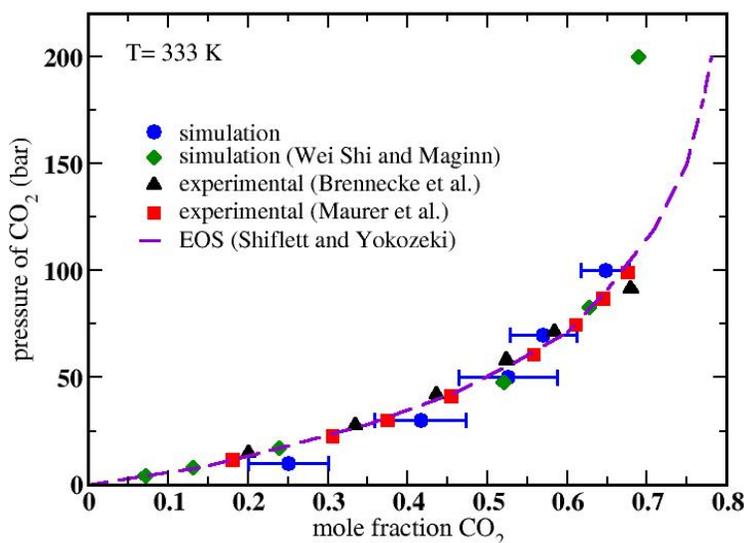


Figure 3: The computed isotherms for CO₂ in [HMIM⁺][TF₂N⁻] at 333 K by different research groups. The simulation results from this work, results from Shi and Maginn [3], Brennecke *et al.* [4] and Maurer *et al.* [5] are shown using circle (blue), diamond (green), triangle (black), and square (red) respectively. The dashed purple line shows an equation of state prediction by Shiflett and Yokozeki [6].

Figure 3 shows a comparison of CO₂ isotherms in [HMIM⁺][TF₂N⁻] at 333 K, reported by different research groups. At pressures up to 50 bar, the predicted solubility is slightly higher than the experimental data, whereas at pressures above 50 bar the results are in excellent agreement. Note that the simulation results of Shi and Maginn [3] were carried out with a different method that did not explicitly account for the gas phase; such an approach is questionable for mixtures at the conditions relevant for this project, hence the need to develop the NPT-GEMC approach. A comparison of H₂ isotherms at 333K is reported in Figure 2. The computed absorption isotherms and Henry's law constant agree well with the experimental results of Maurer *et al.* [7], Peters *et al.* [8], and Costa Gomes [9]. However, the simulation results do not agree with those reported by Noble *et al.* [10]. The partial molar enthalpy was calculated for H₂ using the van't Hoff relationship and a value of 1.49 kJ/mole was determined. The value is in reasonable agreement with the experiment value of 4.09 kJ/mole reported by Maurer *et al.* [7]. Unlike CO₂ that has a negative enthalpy of absorption (and thus the solubility increases with decreasing temperature), the simulations correctly predict that the solubility of H₂ increases with increasing temperature.

Given that the simulations accurately model pure gas isotherms, the next step is to compute selectivity for CO₂/H₂ mixtures. While ultimately more challenging to conduct than pure gas simulations, the modeling approach developed here is amenable to this task.

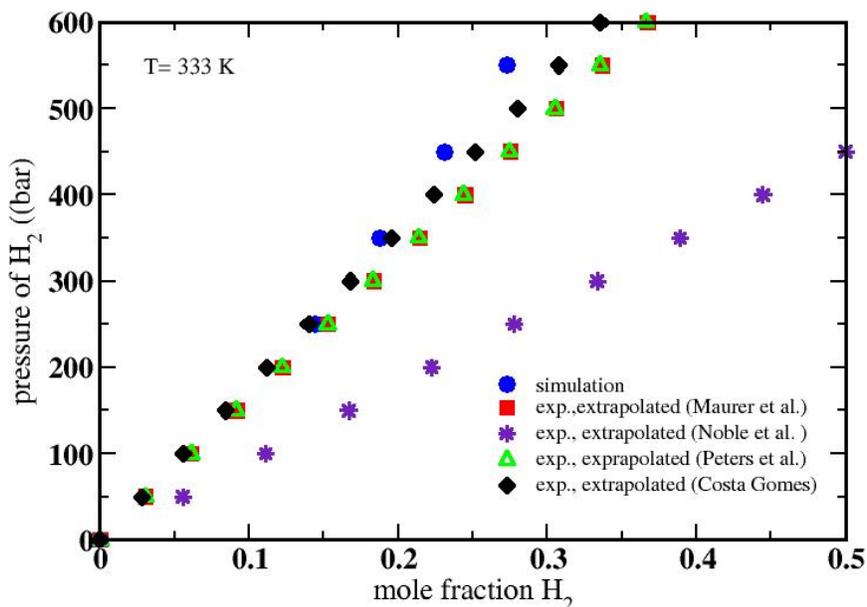


Figure 4: The computed isotherms for H₂ gas in [HMIM⁺][TF₂N⁻] at 333 K by different research groups. The simulation results from this work, results from Maurer *et al.* [7], Noble *et al.* [10], Peters *et al.* [8], and Costa Gomes [9] are shown using circle (blue), square (red), star (purple), triangle (green) and diamond (black) respectively.

Ylide Chemistry

Phosphonium cations are highly desirable counterions for aprotic heterocyclic anions (AHAs) due to the excellent thermal stability of the resulting phosphonium-based ILs, a necessity for pre-combustion flue gas separations. As part of this project (with additional funding from a DOE ARPAe grant), we have shown that at high temperatures (≥ 60 °C), an additional reaction beyond the already known anion-CO₂ interaction occurs between phosphonium-based ionic liquids (ILs) and CO₂. Presumably, 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 (Figure 5). Using ATR-FTIR spectroscopy, ¹H NMR spectroscopy, ³¹P NMR spectroscopy, 2D NMR spectroscopy and quantum calculations, we have conclusively shown that AHAs like 2-cyanopyrrolide can abstract the α -proton from the tetra-alkylphosphonium cation leading to the observed carboxylation event. Furthermore, we have shown that the reaction is reversible. This side reaction is eliminated when tetra-alkylammonium cations are employed. Despite the observation that ammonium-based ILs are less thermally stable than the corresponding phosphonium salts, these results provide an exciting new mechanism to be exploited in chemically complexing materials design. An abstract of these results was selected for an oral presentation at the fifth Congress on Ionic Liquids

which took place in Vilamoura, Portugal, April 21-25, 2013. Graduate student Thomas Gohndrone presented the results to an assembly of >500 conference attendees.

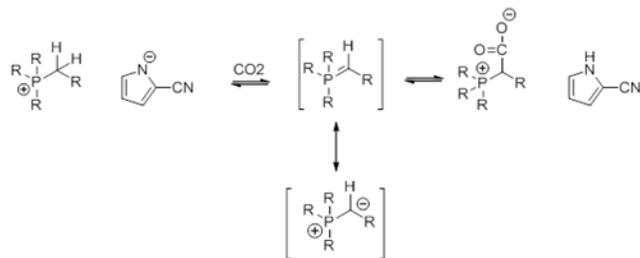


Figure 5: Proposed reaction of phosphonium cation with a AHA, using [2-cyanopyrrolide] as an example.

Additional Information

Professor Ed Rubin at Carnegie-Mellon University was very recently awarded a grant from GCEP to perform systems modeling of the technologies developed/being developed by other GCEP-funded projects. We met with Professor Rubin in November, 2012 at the AIChE meeting in Pittsburgh, PA, and have subsequently hosted Professor Rubin for a joint Department of Chemical and Biomolecular Engineering and Center for Sustainable Energy at Notre Dame seminar on April 2, 2013. We are currently executing a non-disclosure agreement with Professor Rubin so that we can supply him with current information for him to use in his systems modeling of ILs for CO₂ capture.

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.

Clearly, in just 7 months we have made progress towards this goal. We have successfully designed, synthesized and tested new materials that demonstrate the cooperativity effects proposed, and developed a model that shows that cooperativity can be used to advantage in a CO₂ capture process. We can now predict solubilities of H₂ (and, therefore, CO₂/H₂ selectivities) in ILs from molecular simulation, which greatly

reduces the need for difficult H₂ solubility experiments. Finally, we have identified and characterized unanticipated chemistry by which the CO₂ reacts with the cation when tetra-alkylphosphonium cations are used.

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.
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.
3. Synthesis of the new ILs identified by QM and classical molecular simulation.
4. Experimental testing.
5. LCA Modeling.

Publications and Patents

No publications or patents have resulted in the first 7 months of this project.

References

- [1] B. Chen, J.I. Siepmann, M.L. Klein, *The Journal of Physical Chemistry B*, 105 (2001) 9840-9848.
- [2] R.F. Cracknell, *Physical Chemistry Chemical Physics*, 3 (2001) 2091-2097.
- [3] W. Shi, E.J. Maginn, *The Journal of Physical Chemistry B*, 112 (2008) 2045-2055.
- [4] S.N.V.K. Aki, B.R. Mellein, E.M. Saurer, J.F. Brennecke, *The Journal of Physical Chemistry B*, 108 (2004) 20355-20365.
- [5] J. Kumelan, Á. Pérez-Salado Kamps, D. Tuma, G. Maurer, *The Journal of Chemical Thermodynamics*, 38 (2006) 1396-1401.
- [6] M.B. Shiflett, A. Yokozeki, *The Journal of Physical Chemistry B*, 111 (2007) 2070-2074.
- [7] J. Kumelan, Á. Pérez-Salado Kamps, D. Tuma, G. Maurer, *Journal of Chemical & Engineering Data*, 51 (2006) 1364-1367.
- [8] S. Raeissi, L.J. Florusse, C.J. Peters, *Journal of Chemical & Engineering Data*, 56 (2011) 1105-1107.
- [9] M.F. Costa Gomes, *Journal of Chemical & Engineering Data*, 52 (2007) 472-475.
- [10] A. Finotello, J.E. Bara, D. Camper, R.D. Noble, *Industrial & Engineering Chemistry Research*, 47 (2007) 3453-3459.

Contacts

Joan F. Brennecke: jfb@nd.edu

Brandon Ashfeld: bashfeld@nd.edu

Edward J. Maginn: ed@nd.edu

William F. Schneider: wschneider@nd.edu

Mark A. Stadtherr: markst@nd.edu

J. Edward Bennett: jbenet4@nd.edu

Murukkuwadura DeSilva: MurukkuwaduraAruni.DeSilva.1@nd.edu

Thomas J. Gohndrone: Thomas.Gohndrone.1@nd.edu

Bo Hong: bhong@nd.edu
Doyun Lee: Doyun.Lee.394@nd.edu
Tae Bum Lee: Tae.B.Lee.391@nd.edu
Samuel Seo: Samuel.Seo.11@nd.edu
Ramesh Singh: Ramesh.Singh.33@nd.edu
Monika Vogt: Monika.Vogt.15@nd.edu
Han Xia: Han.Xia.12@nd.edu