

PROGRESS REPORT (Quarterly)

1. DOE Award Number and Name of Recipient

Award number: DE-NT0005287
Name of recipients: Georgia Tech Research Corporation

2. Project Title and Name of Project Director/PI

Title: Reversible Ionic Liquids as Double-Action Solvents for Efficient CO₂ Capture
PI: Dr Charles. A. Eckert
Co-PI: Dr. Charles L. Liotta

3. Date of Report and Period Covered

Date of report: January 31, 2010
Period covered: October 1, 2009 – December 31, 2009 (Budget Period 2 – Q1)

4. Executive Summary

The objective of this project is to develop reversible ionic liquids as solvents for post-combustion recovery of CO₂ from fossil fuel-fired power plants. These novel solvents are neutral molecules which react with CO₂ to form an ionic liquid, which then dissolves additional CO₂ by a physi-sorption mechanism. Subsequently modest elevations in temperature reverse the reaction and yield pure CO₂ for disposal. Because of this dual mode, capacity can be large, and we are modifying the precursor structure using structure-property relationships to optimize both physical properties and thermodynamic properties. By incorporating silanes in the molecules we reduce viscosity substantially to augment mass transfer.

We are creating, testing, and optimizing reversible ionic liquids for applications in CO₂ capture, and we shall do the process design and cost analysis for their implementation. In addition we shall develop a process for commodity-scale production of our solvents.

We continue to make substantial progress through the fifth quarter of this project, meeting or exceeding projected achievements. Our major contributions for the fifth quarter include:

- We continue to collect data for the absorption of CO₂ and conversion of molecular liquid to ionic liquid for the 4 silyl-amine based reversible ionic liquids: (3-aminopropyl)trimethoxysilane, (3-aminopropyl)triethoxysilane, (3-aminopropyl)triethylsilane, and (3-aminopropyl)tripropylsilane. Both pieces of information are measured using attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy and our Generation 3 custom made high pressure reaction vessel. To date, all experiments have been completed for the pressure range of 0-70 bar at temperatures of 35°C, 50°C, and 75°C. Experiments have been initiated at 100°C over the aforementioned pressure range for the four compounds. **(TASK 4)**
- We have successfully synthesized and characterized two additional reversible ionic liquids: (3-aminopropyl)diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane, and (3-aminopropyl)trihexylsilane. **(TASK 2)**
- We have identified a model to allow for the determination of the equilibrium constants as a function of the experimental data collected with FTIR. **(TASK 4)**

Our goal remains to minimize the cost and energy requirements of CO₂ capture to help DOE meet its goal – 90% CO₂ capture with no more than a 30% increase in cost by 2020.

5. Results of Work

a. Approach

1- Synthesis and Characterization of Custom Reversible ILs

We proposed to investigate the use of a variety of amine and guanidine based materials for the capture and subsequent controlled release of CO₂. We have currently synthesized and fully characterized four candidates: (3-aminopropyl)trimethoxysilane, (3-aminopropyl) triethoxysilane, (3-aminopropyl)triethylsilane, and (3-aminopropyl) tripropylsilane, as previously reported. We have successfully synthesized and isolated three more candidates to be tested as CO₂ capture agents (Figure 1): (3-aminopropyl) ethyldimethylsilane, (3-aminopropyl)trihexylsilane, and (3-aminopropyl)diisopropyl (1H,1H,2H,2H-perfluoropentyl)silane.

The candidates in Figure 1 were chosen to increase CO₂ capacity of the solvents and, in the case of (3-aminopropyl)diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane, to apprehend structure/property relationship (via the fluorinated side chain electronic effect) on the capture and release of CO₂. (**TASK 5**) The results from the ATR FT-IR measurements (to be discussed in more detail later in this report) indicate that swelling of the ionic liquids and subsequently the amount of CO₂ absorbed increases as the side chains attached to the Si- group become bulkier. We believe this is due to a decrease in packing efficiency of the ions which will likely be further decreased due to the asymmetry of (3-aminopropyl)ethyldimethylsilane and increased bulkiness of (3-aminopropyl)trihexylsilane. And in an attempt to understand how strong of an influence

the side chains on the Si- group have on the thermodynamics of CO₂ capture and release we will examine (3-aminopropyl)diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane.

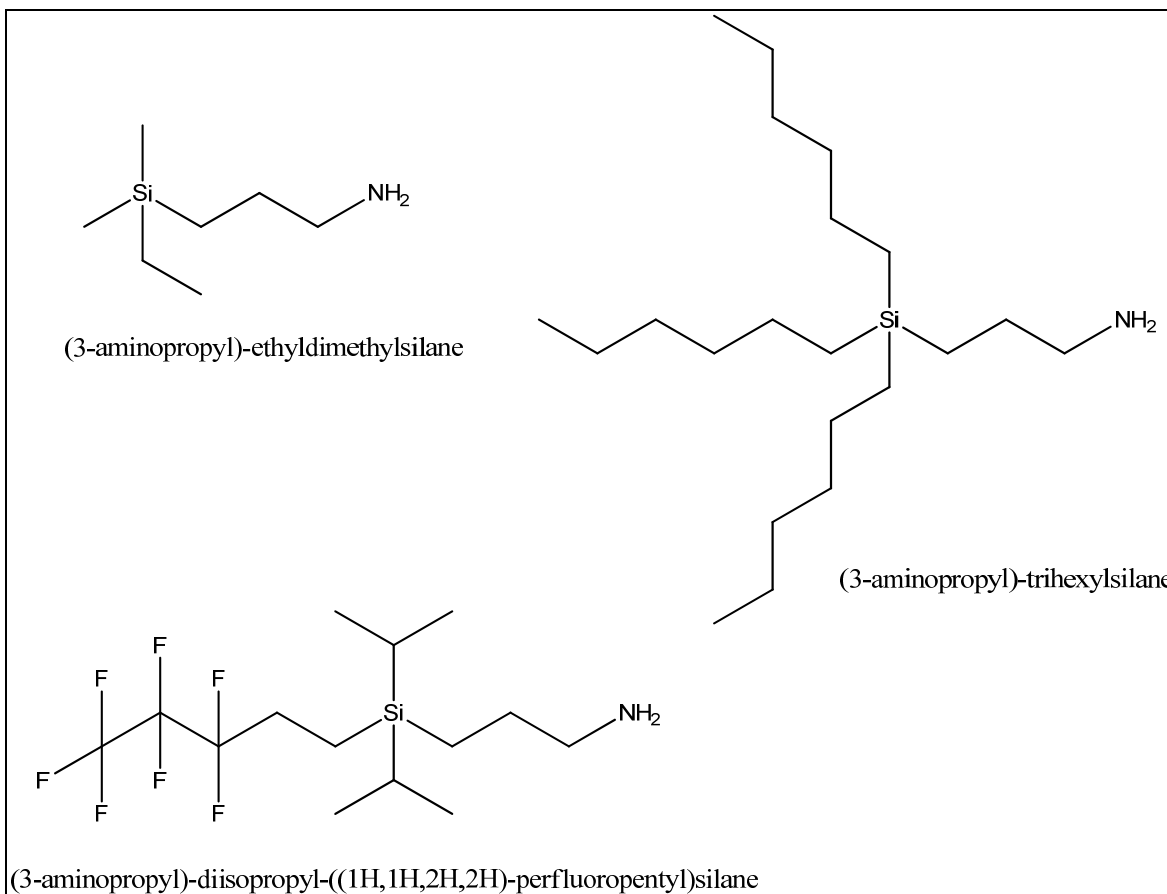


Figure 1. Structures of third generation silyl-amine based reversible ionic liquids.

As synthesized, each of these candidates will be tested for CO₂ capture as illustrated by the general reaction scheme in Figure 2. The resulting reversible ionic liquids will be fully characterized (NMR, elemental analysis, FT-IR, mass spectroscopy (MS), and solvatochromic polarity measurements). The solvatochromic polarity measurements will be performed using an HP 8453 UV-Vis Spectrophotometer and the polarity probe Nile

Red. The wavelength of maximum absorption (λ_{max}) for the probe in a given solvent is relative to the polarity of the solvent. The λ_{max} of Nile Red has been found and reported for hundreds of solvents, making this an efficient approach for determination of solvent polarity.

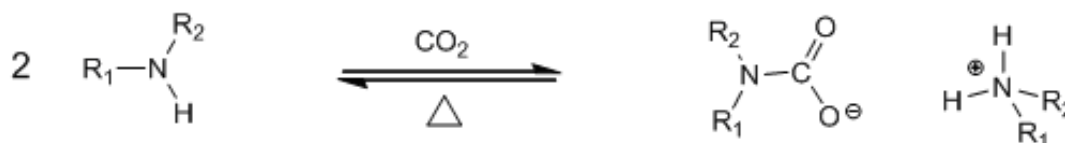


Figure 2. Reaction of custom-made amine with CO_2 to form reversible ionic liquids.

The loss of CO_2 upon heating will be explored using NMR and differential scanning calorimetry (DSC). The DSC experiments are performed on a Q20 TA Instruments machine, with a temperature profile of $20^\circ C/min$ or $30^\circ C/min$ ramp rates from $20^\circ C$ initial temperature to $300^\circ C$ or $400^\circ C$ final temperature. The first endotherm was taken to represent the loss of CO_2 with the second endotherm representing the decomposition of the molecular liquid.

Although the stability tests confirmed that the trialkyl-substituted precursors were stable over a period of two months in both water- and oxygen-containing environments, we shall still perform the experiment on the precursors that show promising thermodynamic properties or absorption capacities to ensure industrial viability of our new solvents.

Additionally, we will look to capture ^{13}C labeled CO_2 to differentiate and quantify the chemisorbed (single or multiple reactions) and physisorbed CO_2 present in the reversible ionic liquid. We anticipate capacities to exceed the 1:2 CO_2 to solvent ratio achieved by single reaction stoichiometry. Quantitative ^{13}C NMR will be used to perform the analysis and the results will be compared with FT-IR data. Candidates that exhibit

favorable properties for use as CO₂ capture agents (such as usable liquid range, stability, capability to release CO₂, etc.) will then be tested for determination of thermodynamic properties, viscosity, and capacity.

2- Thermodynamics of CO₂ Capture

We proposed to exploit our knowledge of molecular design to understand and optimize the chemistry – for example using linear free energy relationships to account for electron donation or withdrawal and related effects (such as neighboring group effects) to increase capacity and modify the thermodynamics. Once promising candidates are identified after undergoing the characterization experiments (as describing in the previous section) we will then start to look at their thermodynamic properties and CO₂ capture capacities. The equilibrium constant K representative of the capture (and release) of CO₂ can be found by measuring the conversion of the precursor molecule to ionic liquid at a given temperature and CO₂ concentration, and compensation for the non-ideal behavior of the ionic species.

We are using attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectroscopy to determine the conversion under a broad range of conditions. ***This measurement technique allows for the simultaneous measurement of conversion and CO₂ capacity.*** The ATR FT-IR optics bench used for data collection will be the Heated Golden Gate ATR sample accessory supplied by Specac, with a working temperature range up to 300°C and pressure rating for the tungsten carbide embedded diamond being 15,000psi.

Equilibrium measurements are currently being performed by using a custom designed and built ATR FT-IR high pressure reactor. Although the scrubbing will be carried out at our near atmospheric pressure, the pressure range of the instrument permits us to ascertain better the effect of CO₂ concentration on both equilibria and rates. Consultation for the design was offered by Dr. Sergei Kazarian of Imperial College London. *We are now using the Generation 3 stainless steel reactor, which has been successfully tested at temperatures to 150°C and pressures to 1500psi.* We are currently studying the reaction of the (3-aminopropyl)trimethoxysilane, (3-aminopropyl)triethoxysilane, (3-aminopropyl)triethylsilane, and (3-aminopropyl)tripropylsilane with CO₂ using simultaneous ¹H, ¹³C NMR and IR spectra being collected on the same sample. The ¹H, ¹³C NMR used is a Bruker AMX 400 located in the School of Chemistry and Biochemistry at Georgia Tech. The purpose of collecting simultaneous spectra on both the NMR and IR will be to correct for changes in molar absorptivity of our samples as they are converted from the molecular liquid form to the ionic liquid form. We will first analyze five different conversions for the same sample to verify that the carbonyl peak intensity is linearly proportional to the conversion determined by ¹H NMR. Previous experiments performed on the reversible ionic liquid N-butyl-N,N,N,N-tetramethylguanidinium methylcarbonate indicated that linearity between conversion and carbonyl intensity holds true.

In addition, we can gather information on the approximate amount of CO₂ that is physically absorbed into the ionic liquids using the FT-IR data that is collected for the equilibrium measurements. The CO₂ that is in solution and not chemically bound to the amine (referred to as “free CO₂”) has a very distinct absorption band in the mid-infrared

region (the ν_3 band of CO_2 at *ca.* 2335 cm^{-1}). Following the Beer-Lambert Law, the absorbance of this band is directly proportional to the concentration of this “free CO_2 ” absorbed in solution. A calibration curve relating the absorbance of CO_2 and the concentration was obtained for a methanol/ CO_2 system using VLE data found in literature to calculate the concentration of CO_2 at various temperatures and pressures. For the analysis, density of the ionic liquid is required. This information will be measured using a 2.0 mL pycnometer. Additional information to be collected will be the refractive index values for each of the tested compounds at the temperature of data collection. This information will be used to determine the penetration depth of the reflectance signal, as it is a function of the difference in refractive indices of the sample and the diamond crystal.

Experimentation has been started for the following custom-made candidates: (3-aminopropyl)triethylsilane and (3-aminopropyl)tripropylsilane using pure CO_2 feed streams. As we determine the equilibrium constants at multiple temperatures, we will be able to determine the heat of reaction for the specific molecular structures. The molecular structures will be systematically altered to allow for the use of structure-property relationships where we can determine the optimal molecular configuration to give us desired capacities and enthalpies for reversing our solvents and expelling the CO_2 . For example, the compound (3-aminopropyl)diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane will allow for us to determine the effect of fluorinated side chains on the enthalpic properties of the CO_2 capture candidates. The custom reversible ionic liquids that show promising pure CO_2 capacities and reaction enthalpies will be investigated with altered feed streams to examine the effects of mixed N_2/CO_2 streams, water, SO_x , NO_x , and carryover from the scrubbers. This will give us insight into how the solvents behave under

“real world” operating conditions. We can then further modify the structures to overcome any problems that arise.

For the evaluation of the equilibrium constants, we are looking at examining the non-ideal behaviors (activity and fugacity coefficients) of our one component ionic liquids. We have started looking at an equation-of-state (EOS) model to account for the non-ideal behavior of the ionic species in the solution. This information will be useful to develop accurate expression for the equilibrium constants and offer insight into how specific molecular structures can advantageously deviate from ideality for the purpose of CO₂ capture and, more importantly, release.

3- Viscosity Studies as a Function of CO₂ capture

The change in viscosity as a function of CO₂ capture will be investigated. As will be discussed later in this report, viscosity measurements have been conducted for the four candidates that have been successfully synthesized and characterized ((3-aminopropyl)trimethoxysilane (3-aminopropyl)triethoxysilane, (3-aminopropyl)triethylsilane, and (3-aminopropyl)tripropylsilane). The rheological results indicate that there is a three order of magnitude change in viscosity as they are completely converted from the molecular liquid to the ionic form. Laboratory observations indicate that the change in viscosity is non-linear, with viscosity increasing sharply at high conversions. The viscosity as a function of conversion for each candidate is being measured using a MCR300 controlled stress rheometer supplied by Anton Paar, located in the Complex Fluids Group Laboratory at Georgia Tech. *We are currently examining the effect of conversion to ionic form on the viscosity of (3-aminopropyl)tripropylsilane, as well as mixtures of ionic liquids.*

4- Scrubber Process Design

An ASPEN simulation to treat a *model coal-fired power plant flue gas stream has been developed and validation with existing literature data is underway*. Initially, the model will be used to evaluate targets for our CO₂ capture agents to meet the goal of 90% CO₂ capture with no more than a 35% increase in cost. We are using the monoethanolamine (MEA) process as a basis for comparison, and are altering the operating conditions to give us targets for the development of one component reversible ionic liquids. The parameters we look to optimize are the enthalpy of capture and release, the capture and release temperatures, CO₂ capacities of the solvent, and viscosity of the solvent. The data acquired in the laboratory for the custom-made reversible ionic liquids will be put into the model and evaluated as it is collected, giving us real-time analysis of the economic viability and performance of our solvents. This information will be used to direct the modifications to molecular structure in order for us to meet the goals set forth by DOE and our previous models.

Additional design issues that we plan to consider in the future are the effects of the presence of SO₂, NO₂, and carryover gypsum particles from the scrubber in the gas. We do know that our reversible ionic liquids will also absorb SO₂, but the thermodynamics and kinetics have not yet been investigated. We suspect that the NO₂ will not affect the process as proposed, but need to verify this. The surface of gypsum particles is ionic, so these will probably adsorb small amounts of the ionic liquid, but it is likely that this is

reversible with temperature. All these issues will be considered and verified by experiment as we move forward.

b. Results and Discussion

***I-* Synthesis and Characterization of Custom Reversible ILs**

As reported in Quarter 4, three additional silyl-amine based reversible ionic liquids have been successfully synthesized and isolated, as evidenced by ^1H NMR. The characterization has been completed for the (3-aminopropyl)trihexylsilane and (3-aminopropyl)diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane, and includes: confirmation of liquid salt formation via visual inspection with ^{13}C and ^1H NMR, confirmation of reversal and determination of reversal temperature with DSC, FT-IR of both the molecular and ionic liquids, and solvatochromic polarity measurements using Nile Red and UV-Vis spectroscopy (**TASK 2**).

The characterization of (3-aminopropyl)ethyltrimethylsilane was halted after the initial inspection of salt formation. The asymmetric compound does react readily with CO_2 to form an ionic pair. However, the compound is a solid with a melting point of 57°C - 63°C , and upon melting it releases CO_2 . In order to continue the examination of the affect of ionic liquid asymmetry on the solvent properties, we will start to look at mixtures of the six reversible ionic liquid candidates that have all been successfully characterized. This work has been initiated.

The synthesis and characterization of the one component guanidine based reversible ionic liquids have shown to be challenging. The synthesis of

tetramethylbutylguanidine (TMBG, Figure 3) was optimized providing consistently isolated yields of 70-80 %.

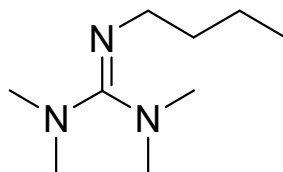


Figure 3. Tetramethylbutylguanidine, benchmark compound for synthesis of one component guanidine based reversible ionic liquids.

Our group demonstrated that equimolar mixtures of TMBG with alcohols react *reversibly* with CO₂ to form ionic liquids (guanidinium alkylcarbonates). By analogy, we shown that TMBG:water (1:1) mixture forms an ionic guanidinium bicarbonate upon reaction with CO₂. Unlike the alcohol analogues, however, the guanidinium bicarbonate requires more energy to be reversed to its molecular liquid form—either higher reversal temperature or longer time (12 hrs) at 80°C. Furthermore, dealing with two-component reversible ionic liquids can be challenging from a processing stand-point. As a consequence, we proposed to synthesize a one-component guanidine system by replacing the butyl group with an alkyl-alcohol (N''-(2-hydroxy-ethyl)-N,N,N',N'-tetramethyl-guanidine) and alkyl-amine (N''-(2-amino-ethyl)-N,N,N',N'-tetramethyl-guanidine), shown in Figure 4 (**TASK 3**).

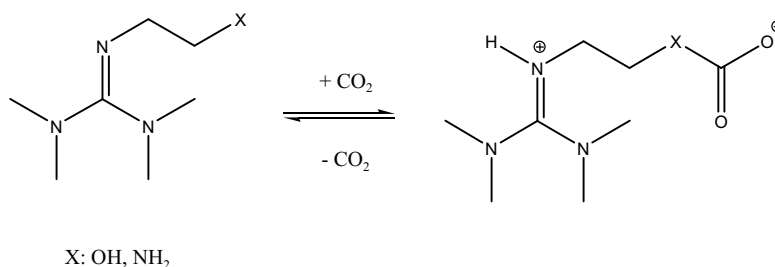


Figure 4: General structure of one component guanidine reversible ionic liquids.

We previously attempted the synthesis of *N''*-(2-hydroxyethyl)-*N,N,N',N'*-tetramethylguanidine starting from *N,N,N',N'*-tetramethylurea. However, due to the large number of byproducts formed during the reaction, we were unable to isolate the desired product in considerable quantities. An alternative approach to the synthesis of alcohol-containing guanidines has been published recently in the literature.^a This approach uses a simple one-step procedure starting from *N,N,N',N'*-tetramethylguanidine and propylene oxide. The two compounds are stirred together in toluene for 48 hours and the product is isolated by removal of the solvent. We are currently attempting to synthesize *N''*-(2-hydroxypropyl)-*N,N,N',N'*-tetramethylguanidine using this method, seen in Figure 5. Once this product has been isolated, we will investigate the formation of the corresponding one-component ionic liquid and follow with the complete characterization of both molecular and ionic liquids.

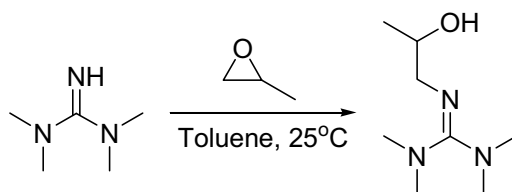


Figure 5: Proposed synthesis of *N''*-(2-hydroxypropyl)-*N,N,N',N'*-tetramethylguanidine.

2- Thermodynamics of CO₂ Capture

Data is currently being collected to determine the conversion and concentrations of CO₂ in the reversible ionic liquids at temperatures up to 150°C and pressure up to 70 bar

^a Jun Huang, Anders Riisager, Rolf W. Berg, Rasmus Fehrmann, "Tuning Ionic Liquids for High Gas Solubility and Reversible Gas Sorption," *Journal of Molecular Catalysis A: Chemical*, 170-176 (2008).

for the 4 silyl-amine based compounds: (3-aminopropyl)trimethoxysilane, (3-aminopropyl)triethoxysilane, (3-aminopropyl)triethylsilane, and (3-aminopropyl)tripropylsilane. This information will be used with the appropriate model to determine the thermodynamic properties of CO₂ capture. To date, the experiments have been successfully performed for the pressure range of 0-70 bar at 35°C, 50°C, and 75°C for all 4 compounds. During Quarter 5, two reactors were damaged due to routine use. Both were repaired, but the result was a delay in data collection of 6 weeks. Nevertheless, we continue to stay ahead of track with the data collection and will finish all FT-IR experimentation by Quarter 6. We will then move on to testing the (3-aminopropyl)trihexylsilane and (3-aminopropyl)diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane, along with mixtures of the reversible ionic liquid capture agents.

Due to the shouldering that was observed in the DSC thermograms of the reversal of the ionic liquid species, we had hypothesized that there may be multiple ionic species being formed in solution as the silyl-amines react with CO₂, in addition to the carbamate. We reacted the (3-aminopropyl)tripropylsilane with ¹³CO₂ to form a carbamate with the carbonyl species “labeled” as ¹³C in order to examine the sample with ¹³C NMR. The resulting NMR is shown in Figure 6, zoomed in from 157ppm to 165ppm, where the carbonyl carbon of the carbamate is seen. There is evidence for another carbonyl containing species in the reaction of (3-aminopropyl)tripropylsilane with CO₂, but the integrated area of the small peak is <0.1% of the area of the larger carbamate peak. Although this was not a quantified ¹³C NMR, it does indicate that any species being formed is in a negligible concentration. We will further investigate the method for which the DSC data is collected to determine the cause of the shouldering in the thermogram.

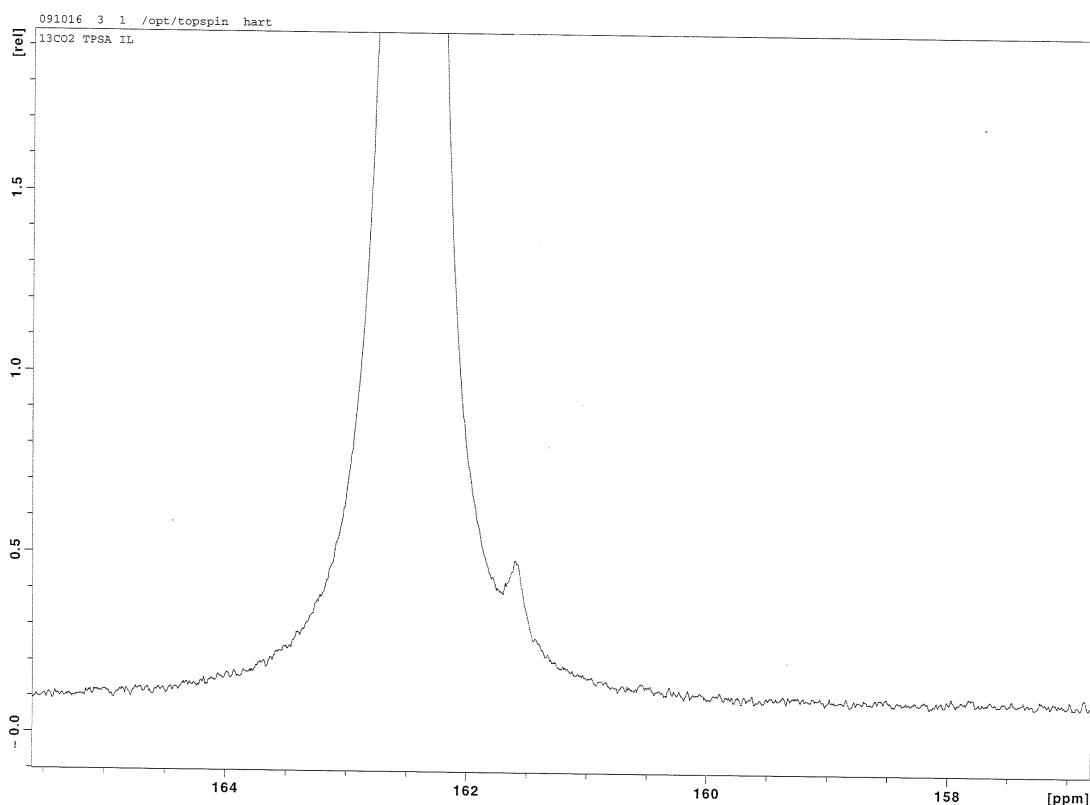


Figure 6: ^{13}C NMR spectra of reaction product from (3-aminopropyl)tripropylsilane with $^{13}\text{CO}_2$.

In evaluating the equilibrium constant (K), we are going to use the conversion of the molecular liquid to ionic liquid as well as the dissolved CO_2 concentration as measured by the FT-IR. We will evaluate the equilibrium constant with an activity based approach to account for the non-ideality of the mixture. We expect the system to exhibit a non-ideal behavior because of the highly polar nature of the liquid and the dissimilarity of the molecules in the system (CO_2 , the amine precursor, and the highly polar ionic liquid).

The evaluation of the equilibrium constant involves the estimation of the activity coefficient (γ) with excess Gibbs energy models. Conventionally, these models contain one or more adjustable parameters that are optimized to best fit the experimental data. In ternary systems, the binary interaction parameters are first obtained from experimental

VLE data for each pair of system components and are used to estimate the γ for ternary systems. However, since our reversible ionic liquids are synthesized in house (no previous experimental data available) and due to the nature of the system (the reversible ionic liquid is only formed in the presence of the molecular liquid and CO₂), we are developing a unique approach to estimate the ternary system activity coefficients for the experimental data directly. We are going to combine different adjustable parameters into a one-term adjustable parameter. We are examining different thermodynamic models that are reported to represent mixtures containing polar and non-polar components such as the Universal Quasichemical (UNIQUAC), Universal Functional Activity Coefficient (UNIFAC), and Wilson. We plan to correlate the equilibrium data at the experimental conditions and adjust the activity coefficients to best-fit the P-x experimental data.

The evaluation of the activity coefficients will lead to constructing the structure-property relationships. We will examine the behavior of the different reversible ionic liquids – in terms of CO₂ capture and release - and how it relates to physical properties such as polarity or molecular volume/surface area. This analysis will provide insight into the molecular behavior of these liquids and allows for the design of an optimum method for CO₂ capture.

3- Viscosity Studies

We are currently in the process of measuring the change in viscosity versus conversion of the molecular liquid to the ionic liquid for the compound (3-aminopropyl)tripropylsilane, as well as the viscosities of the two newly synthesized and characterized reversible ionic liquids. Upon completion, we will move onto the mixture of

molecular liquids and corresponding ionic liquid mixtures. Additionally, we will examine the viscosities of the newly synthesized and characterized (3-aminopropyl)trihexylsilane and (3-aminopropyl)diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane. We hypothesize that the mixtures could afford lower viscosities of either the pure species, resulting in tunability of the solvent properties with respect to the composition of the mixture. This information will give us much insight into when the solution takes on the high viscosity that is characteristic of ionic liquids. At lower conversions, it is hypothesized that the ionic species are fully solvated by the molecular liquid. Thus, the viscosity stays fairly low until a “critical” conversion. Knowledge of this “critical” conversion is crucial for the design and optimization of a process utilizing reversible ionic liquids for carbon capture.

c. Conclusion

We continue to make substantial progress towards helping the DOE achieve the goal of 90% CO₂ capture with no more than a 30% increase in cost by 2020. The recent advancements in the project have resulted in a submittal and acceptance for a publication in the journal *Fluid Phase Equilibria*.

Significant accomplishments were made during the 5th Quarter of the project by successfully characterizing 3 new silyl amine-based reversible ionic liquids. We continue to stay ahead of schedule on the thermodynamic analysis (**TASK 4**), and have used the measurement technique to simultaneously investigate conversion of the molecular liquids and absorption capacity in the ionic liquids for four CO₂ capture solvent candidates. Viscosity measurements are being completed; combined with the characterization data (**TASK 2**), we are getting the required information for the structure-property relationship

analysis (**TASK 5**). And importantly, the information being collected is giving insight into compounds with enhanced properties for the application to CO₂ capture from fossil fuel-fired power plants. The information gathered thus far leads us to hypothesize that the silyl-amine reversible ionic liquid candidates are far superior to the one component guanidine reversible ionic liquids, but we are continuing with the synthesis and characterization of the guanidine compounds for verification (**TASK 3**).

6. Cost Status

This information is being provided independently by the Grants and Contracts department of Georgia Tech Research Corporation.

7. Milestone Status

The two milestones listed in the Project Management Plan for Year Two are as follows:

ID	Milestone Description	Planned Completion	Verification Method
D	Complete laboratory synthesis and characterization of 2nd new single-component silyl amine-based reversible ionic liquid and 2nd new single-component silyl guanidine-based reversible ionic liquid.	3/30/10:	Progress Report describing synthesis and characterization of 2nd new silyl amine-based and guanidine-based reversible ionic liquids

E	Complete synthesis and characterization of single-component Silyl Amine-Based ILs	6/30/2010	Synthesis and Characterization results for Silyl Amine-Based ILs documented in Progress Report
F	Complete laboratory measurement of the thermodynamics of formation of one new single-component silyl amine-based reversible ionic liquid and one new single-component silyl guanidine-based reversible ionic liquid.	9/30/2010	Progress Report describing thermodynamics of formation of new single-component silyl amine-based and single-component silyl guanidine-based reversible ionic liquids

At this time, Milestone D has been completed with respect to the silyl-amine based ionic liquids, and we have developed a new strategy for the synthesis of the silyl-guanidine based reversible ionic liquids.

Work on Milestones E and F are underway and moving along well and should be finished ahead of schedule.

8. Summary of Significant Accomplishments

The significant accomplishments are:

- Prepare, isolate, purify and *fully characterize* six total amine-based reversible ionic liquids for CO₂ capture
- Commence ATR FT-IR studies on the four candidates to get information for thermodynamics and directly measure the absorption capacities
- Successfully measure viscosities for molecular and ionic forms of all six candidates

- Identify and synthesize promising target molecules for future synthesis and characterization based on evidence collected during the first 3 Quarters of the project
- Completed stability tests that showed our custom-made compounds had superior degradation resistance than the commercially available compounds
- Recent advancements have resulted in a submittal for publications in scientific journals and presentations at scientific conferences

9. Actual or anticipated problems or delays, and actions taken

We have only the minimal synthetic delay discussed above in completing Milestone 3, but overall we have been able to stay well ahead of schedule. We do not anticipate any future problems or delays.

10. Products produced

a. Publications

Papers published:

Vittoria M. Blasucci, Ryan Hart, Pamela Pollet, Charles L. Liotta, and Charles A. Eckert, "Reversible ionic Liquids for Facile Separations," *Fluid Phase Equilib*, accepted (Jan 2010).

Vittoria Blasucci, Cerag Dilek, Hillary Huttenhower, Ejae John, Veronica Llopis-Mestre, Pamela Pollet, Charles A. Eckert, and Charles L. Liotta, "One Component, Switchable, Neutral to Ionic Liquid Solvents Derived from Siloxylated Amines," *Chem Comm*, 116-119, 2009.

Vittoria Blasucci, Ryan Hart, Veronica Llopis-Mestre, D. Julia Hahne, Melissa Burlager, Hillary Huttenhower, Reginald Thio, Charles L. Liotta, and Charles A. Eckert, "Single Component, Reversible Ionic Liquids for Energy Applications," *Fuel*, in press.

Ryan Hart, Pamela Pollet, Veronica Llopis-Mestre, Ejae John, Vittoria Blasucci, Hillary Huttenhower, Dominique Julia Hahne, Walter Leitner, Charles A. Eckert, Charles L. Liotta, "Benign Coupling of Reactions and Separations with Reversible Ionic Liquids," *Tetrahedron*, in press.

Papers presented:

Charles A. Eckert and Charles L. Liotta, "Reversible Ionic Liquids as Double-Action Solvents for CO₂ Capture," Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 24, 2009.

Vittoria Blasucci, Cerag Dilek, Hillary Huttenhower, Ejae John, Veronica Llopis-Mestre, Pamela Pollet, Charles L. Liotta, and Charles A. Eckert "One-Component, Switchable, Neutral to Ionic Liquid Solvents Derived from Siloxylated Amines," 237th National Meeting, ACS, Salt Lake City, UT, March, 2009.

Vittoria Blasucci, Ryan Hart, Cerag Dilek, Hillary Huttenhower, Veronica Llopis-Mestre, Pamela Pollet, Eduardo Vyhmeister, Charles L. Liotta, and Charles A. Eckert, "Reversible Ionic Liquids as Double-Action Solvents for Efficient CO₂ Capture," AIChE Spring National Meeting, Tampa, FL, April 2009

Philip G. Jessop, Michael Cunningham, Charles A. Eckert, and Charles L. Liotta "CO₂ as a Trigger for Switchable Chemistry, International Conference on Carbon Dioxide Utilization, China, May 2009.

Ali Fadhel, Vittoria Blasucci, Cerag Dilek, Ryan Hart, Hillary Huttenhower, Veronica Llopis-Mestre, Pamela Pollet, Eduardo Vyhmeister, Charles A. Eckert, and Charles L. Liotta "Designer Reversible Ionic Liquids for CO₂ Capture," 13th Annual Green Chemistry & Engineering Conference, Washington, DC, June 2009.

Ryan Hart, Vittoria Blasucci, Charles A. Eckert, and Charles L. Liotta, "Development of One-Component Reversible Ionic Liquids for Energy Applications," 2009 Annual AIChE Meeting, Poster, Nashville, TN, November 2009.

Invited paper:

Charles A. Eckert, Ryan Hart, Vittoria Blasucci, and Charles L. Liotta, "'Smart' Solvents for Extractions and Purifications", 2009 Annual AIChE Meeting, "New Developments in Extractive Separations," Nashville, TN, November 2009.

b. Websites

Webpages have been prepared and posted within the Eckert/Liotta group website (<http://www.chbe.gatech.edu/eckert/projects.html>).

c. Networks or collaboration fostered

The DOE grant has fostered an intracampus collaboration between the Eckert-Liotta Joint Research Group and the Breedveld Complex Fluids Group. Dr. Victor Breedveld is very talented regarding the flow behaviors of complex fluids, and has the equipment necessary for the evaluation of the viscosity change as a function of conversion for our reversible ionic liquid systems. Following his recommendations and direction, we have been able to properly select, validate, and test a method using his rheometer to obtain information that is quite valuable for the design of a CO₂ capture facility utilizing liquid sorbents for capture.

Additionally, we have been contacted by a commercial entity, Gas Technology Institute, to develop our carbon-capture technology on an industrial scale.

d. Technologies/Techniques

We designed and developed custom stainless steel reactors that will fulfill our experimental needs: they will hold high pressure (up to 2,000 psi), high temperature (up to 300°C) with a volume of about 5 ml and adapt easily onto the heated golden gate ATR cell.

This set-up is user-friendly: as it allows for fast and accurate measurements, easy set-up and easy cleaning between runs (limiting potential cross-contamination).

e. Inventions/Patents

Patent filing for the one-component reversible ionic liquids is in process.