

## **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 CO<sub>2</sub> Capture

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Co-PI: Dr. Charles L. Liotta

### **3. Date of Report and Period Covered**

Date of report: October 31, 2009

Period covered: July 1, 2009 – September 30, 2009 (Q4)

### **4. Executive Summary**

The objective of this project is to develop reversible ionic liquids as solvents for post-combustion recovery of CO<sub>2</sub> from fossil fuel-fired power plants. These novel solvents are neutral molecules which react with CO<sub>2</sub> to form an ionic liquid, which then dissolves additional CO<sub>2</sub> by a physi-sorption mechanism. Subsequently modest elevations in temperature reverse the reaction and yield pure CO<sub>2</sub> 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 CO<sub>2</sub> 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 fourth quarter of this project, meeting or exceeding projected achievements. Our major contributions for the fourth quarter include:

- We continue to collect data for the absorption of CO<sub>2</sub> 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 a temperature of 35°C. Experiments have been initiated at 50°C over the aforementioned pressure range. (**TASK 4**)
- We have successfully synthesized and purified three additional silyl-amine based reversible ionic liquids: (3-aminopropyl)ethyltrimethylsilane, (3-aminopropyl) trihexylsilane, and (3-aminopropyl)diisopropyl(undecafluoropentyl)silane. The characterization of these compounds has been initiated. (**TASK 2**)

Our goal remains to minimize the cost and energy requirements of CO<sub>2</sub> capture to help DOE meet its goal – 90% CO<sub>2</sub> 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 CO<sub>2</sub>. 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 CO<sub>2</sub> capture agents (Figure 1): (3-aminopropyl)ethyldimethylsilane, (3-aminopropyl)trihexylsilane, and (3-aminopropyl)diisopropyl(undecafluoropentyl)silane.

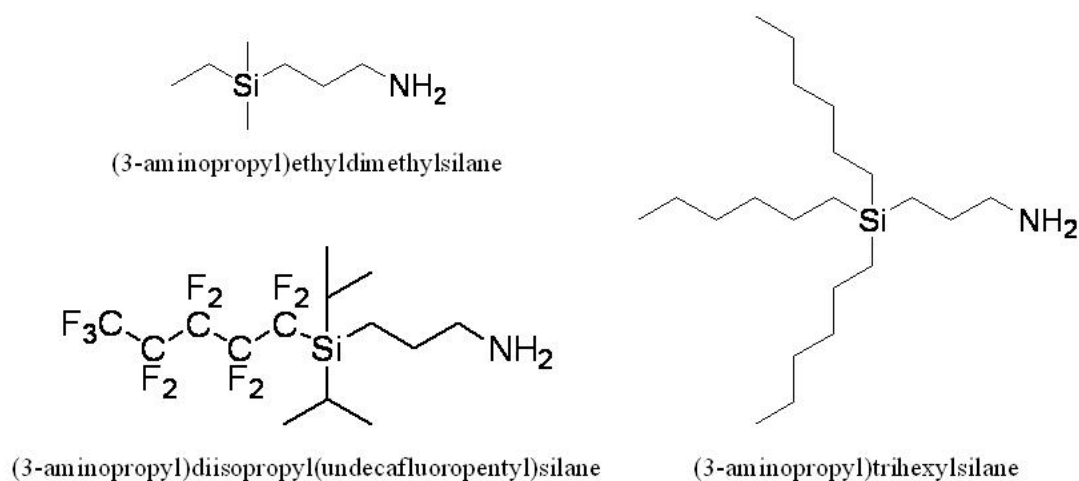


Figure 1. Structures of the newly synthesized silyl-amine based reversible ionic liquids.

The candidates in Figure 1 were chosen to increase CO<sub>2</sub> capacity of the solvents and, in the case of (3-aminopropyl)diisopropyl(undecafluoropentyl)silane, to apprehend structure/property relationship (via the fluorinated side chain electronic effect) on the capture and release of CO<sub>2</sub>. 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 CO<sub>2</sub> 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)ethyltrimethylsilane and increased bulkiness of (3-aminopropyl)triethylsilane. And in an attempt to understand how strong of an influence the side chains on the Si- group have on the thermodynamics of CO<sub>2</sub> capture and release we will examine (3-aminopropyl)diisopropyl(undecafluoropentyl)silane.

As synthesized, each of these candidates will be tested for CO<sub>2</sub> 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 ( $\lambda_{max}$ ) for the probe in a given solvent is relative to the polarity of the solvent. The  $\lambda_{max}$  of Nile Red has been found and reported for hundreds of solvents, making this an efficient approach for determination of solvent polarity.

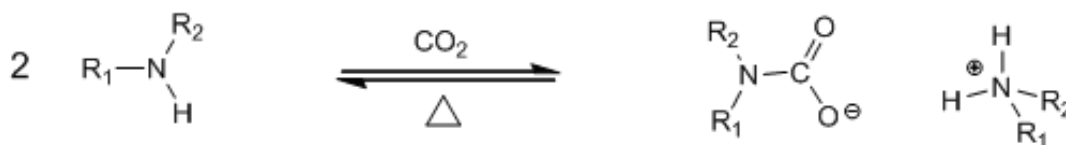


Figure 2. Reaction of custom-made amine with CO<sub>2</sub> to form reversible ionic liquids.

The loss of CO<sub>2</sub> 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°C/min or 30°C/min ramp rates from 20°C initial temperature to

300°C or 400°C final temperature. The first endotherm was taken to represent the loss of CO<sub>2</sub> with the second endotherm representing the evaporation 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 <sup>13</sup>C labeled CO<sub>2</sub> to differentiate and quantify the chemisorbed (single or multiple reactions) and physisorbed CO<sub>2</sub> present in the reversible ionic liquid. We anticipate capacities to exceed the 1:2 CO<sub>2</sub> to solvent ratio achieved by single reaction stoichiometry. Quantitative <sup>13</sup>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 CO<sub>2</sub> capture agents (such as usable liquid range, stability, capability to release CO<sub>2</sub>, etc.) will then be tested for determination of thermodynamic properties, viscosity, and capacity.

## **2- Thermodynamics of CO<sub>2</sub> 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 CO<sub>2</sub> capture capacities. The equilibrium constant K representative of the capture (and release) of CO<sub>2</sub> can be found by measuring the

conversion of the precursor molecule to ionic liquid at a given temperature and CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> using simultaneous <sup>1</sup>H, <sup>13</sup>C NMR and IR spectra being collected on the same sample. The <sup>1</sup>H, <sup>13</sup>C 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  $^1\text{H}$  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  $\text{CO}_2$  that is physically absorbed into the ionic liquids using the FT-IR data that is collected for the equilibrium measurements. The  $\text{CO}_2$  that is in solution and not chemically bound to the amine (referred to as “free  $\text{CO}_2$ ”) has a very distinct absorption band in the mid-infrared region (the  $\nu_3$  band of  $\text{CO}_2$  at *ca.*  $2335\text{ cm}^{-1}$ ). Following the Beer-Lambert Law, the absorbance of this band is directly proportional to the concentration of this “free  $\text{CO}_2$ ” absorbed in solution. A calibration curve relating the absorbance of  $\text{CO}_2$  and the concentration was obtained for a methanol/ $\text{CO}_2$  system using VLE data found in literature to calculate the concentration of  $\text{CO}_2$  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  $\text{CO}_2$  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<sub>2</sub>. For example, the compound (3-aminopropyl) diisopropyl(undecafluoropentyl)silane will allow for us to determine the effect of fluorinated side chains on the enthalpic properties of the CO<sub>2</sub> capture candidates. The custom reversible ionic liquids that show promising pure CO<sub>2</sub> capacities and reaction enthalpies will be investigated with altered feed streams to examine the effects of mixed N<sub>2</sub>/CO<sub>2</sub> streams, water, SO<sub>x</sub>, NO<sub>x</sub>, 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, namely the SAFT model. *Preparation of a modified SAFT model has been initiated, and as data are collected and analyzed from the FT-IR we will start to incorporate the experimental data into the model for evaluation.* 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 CO<sub>2</sub> capture and, more importantly, release.

### **3- Viscosity Studies as a function of CO<sub>2</sub> capture**

The change in viscosity as a function of CO<sub>2</sub> 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.*

#### **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 CO<sub>2</sub> capture agents to meet the goal of 90% CO<sub>2</sub> 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, CO<sub>2</sub> 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.

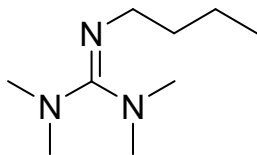
Additional design issues that we plan to consider in the future are the effects of the presence of SO<sub>2</sub>, NO<sub>2</sub>, and carryover gypsum particles from the scrubber in the gas. We do know that our reversible ionic liquids will also absorb SO<sub>2</sub>, but the thermodynamics and kinetics have not yet been investigated. We suspect that the NO<sub>2</sub> 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**

### ***1- Synthesis and Characterization of Custom Reversible ILs***

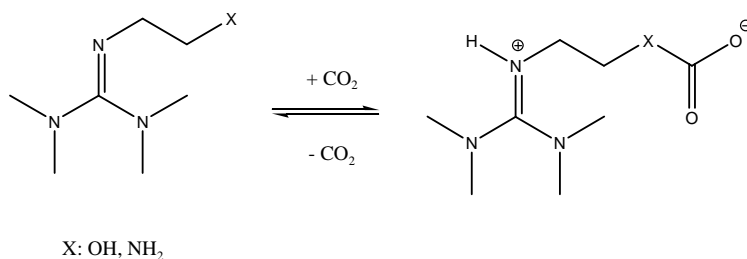
Three additional silyl-amine based reversible ionic liquids have been successfully synthesized and isolated, as evidenced by <sup>1</sup>H NMR. The characterization of all three compounds has begun, and includes: confirmation of liquid salt formation via visual inspection with <sup>13</sup>C and <sup>1</sup>H NMR, confirmation of reversal and determination of reversal temperature with DSC, FT-IR of both the molecular and ionic liquids, solvatochromic polarity measurements using Nile Red and UV-Vis spectroscopy, viscosity measurements of molecular and ionic liquids, density measurement of ionic liquid, and measurement of the refractive index at the range of temperatures the material will be tested in the ATR FT-IR measurements (**TASK 2**).

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 %.



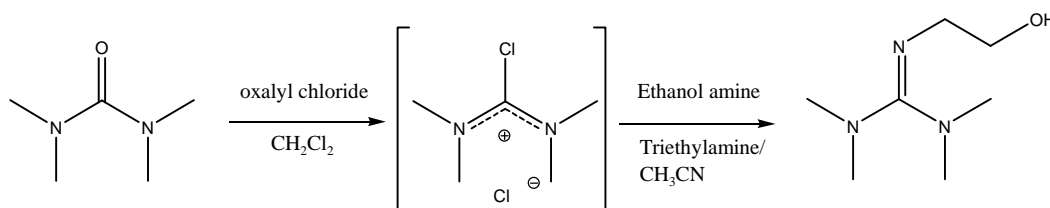
**Figure 3.** Tetramethylbutylguanidine, benchmark compound for synthesis of one component guanidine based reversible ionic liquids.

Our group demonstrated that equimolar mixtures of TMBG with alcohols react *reversibly* with CO<sub>2</sub> to form ionic liquids (guanidinium alkylcarbonates). By analogy, we shown that TMBG:water (1:1) mixture forms an ionic guanidinium bicarbonate upon reaction with CO<sub>2</sub>. 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.

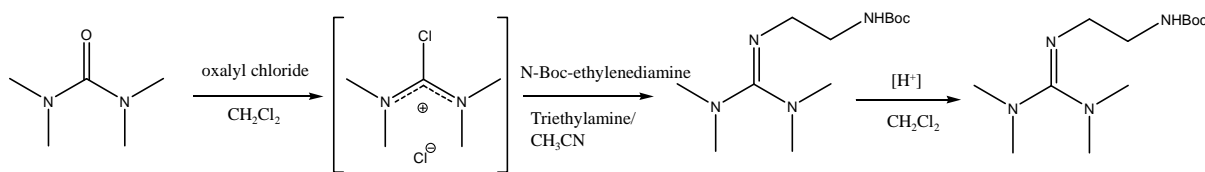
The synthesis of the N''-(2-hydroxy-ethyl)-N,N,N',N'-tetramethyl-guanidine (Figure 5) was carried out from the N,N,N',N'-tetramethyl-urea. Upon reaction with oxalyl chloride in anhydrous dichloromethane, the chloride intermediate salt ((chloro-dimethylamino-methylene)-dimethyl-ammonium) was synthesized. The dichloromethane solvent is removed in vacuo and replaced by anhydrous acetonitrile. In the second step, the chloride salt is reacted with ethanolamine in the presence of triethylamine (an HCl scavenger). The analysis of the crude product via  $^1\text{H}$  and  $^{13}\text{C}$  NMR showed the formation of the desired product. However, many by-products were also formed. Purifications by silica gel chromatography or distillation failed to provide sizable quantities of the N''-(2-hydroxy-ethyl)-N,N,N',N'-tetramethyl-guanidine. The reaction conditions are currently being optimized to improve the chemoselectivity of the reaction toward the formation of the desired alcohol-guanidine.



**Figure 5.** Synthesis of N''-(2-hydroxy-ethyl)-N,N,N',N'-tetramethyl guanidine

In the synthesis of the N''-(2-amino-ethyl)-N,N,N',N'-tetramethyl-guanidine (Figure 6), N,N,N',N'-tetramethyl-urea reacts with oxalyl chloride under anhydrous conditions to afford the chloride salt intermediate ((chloro-dimethylamino-methylene)-dimethyl-ammonium). The dichloromethane solvent is then removed in vacuo and replaced by anhydrous acetonitrile for the second step. Upon reaction with N-Boc-ethylenediamine, the Boc-protected-2-aminoethyl-N,N,N',N'-tetramethyl-guanidine is prepared. The desired guanidine can be obtained upon the acid-catalyzed Boc-deprotection of the amine group. Although the first step took place

quantitatively, the second step yielded to the formation of by-products along with the desired guanidine product (using  $^1\text{H}$  and  $^{13}\text{C}$  NMR). Purification via distillation resulted in the decomposition of the guanidine product. The reaction conditions (temperature, solvent, reaction time, order of addition of the reagents) and other purification techniques are currently being altered in order to optimize the formation of the amine-guanidine product.



**Figure 6.** Synthesis of N''-(2-amino-ethyl)-N,N,N',N'-tetramethyl-guanidine

## 2- Thermodynamics of CO<sub>2</sub> Capture

Data is currently being collected to determine the conversion and concentrations of CO<sub>2</sub> in the reversible ionic liquids at temperatures up to 150°C and pressure up to 70 bar 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 CO<sub>2</sub> capture. To date, the experiments have been successfully performed for the pressure range of 0-70 bar at 35°C for all 4 compounds and at 50°C for (3-aminopropyl)tripropylsilane. The ATR FT-IR experiments indicate that at the temperature of 35°C, which is where absorption towers typically operate, nearly all the CO<sub>2</sub> absorbed into solution is completely reacted suggesting a large equilibrium constant (i.e  $K \gg 1$ ). This behavior is evidenced by comparing Figure 7 and Figure 8 for (3-aminopropyl)triethylsilane at 35°C. Figure 7 shows the increase of the carbonyl peak with CO<sub>2</sub> pressure. The carbonyl peak is indicative of formation of the ionic liquid, and we are currently performing the corresponding NMR experiments to quantify the

extent of conversion. Figure 8 shows the free CO<sub>2</sub> in solution for (3-aminopropyl)triethylsilane at 35°C. At a CO<sub>2</sub> pressure of 1 bar, there is no evidence of conversion to molecular liquid or physical absorption of CO<sub>2</sub>. When the pressure is increased to 19.1 bar, there is still no CO<sub>2</sub> physically absorbed in solution (Figure 8) but there is a substantial increase in ionic liquid formation (Figure 7). Up to a pressure of 48.5 bar it appears there is further conversion to ionic liquid, with a minor amount of CO<sub>2</sub> physically absorbed in solution. At 58.6 bar the molecular liquid is fully converted to the ionic liquid, and substantial amounts of CO<sub>2</sub> are now being physically absorbed in the solution.

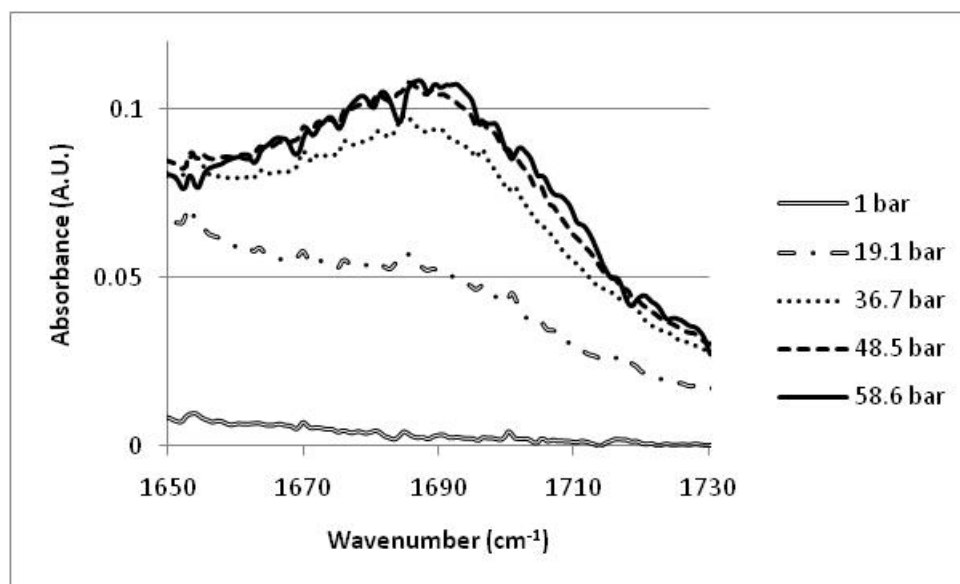


Figure 7. Carbonyl peak of ionic liquid formation of (3-aminopropyl)triethylsilane at 35°C.

Figures 7 and 8 also illustrate the powerful measurement technique being employed. Gravimetric techniques for measuring capacity are incapable of differentiating between chemical absorption and physical absorption. It has been clearly shown that for the silyl-amine based reversible ionic liquids both phenomena take place, and knowledge of both quantities allows for the determination of the thermodynamic properties.

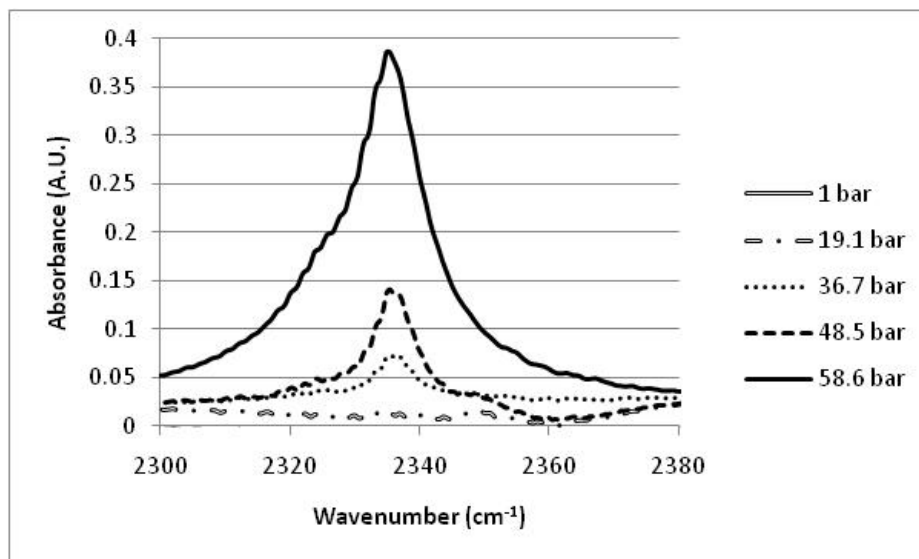


Figure 8. Free CO<sub>2</sub> physically absorbed in (3-aminopropyl)triethylsilane at 35°C.

The capability of the reversible ionic liquids to physically absorb CO<sub>2</sub> results in enhanced capacities. The system of CO<sub>2</sub> and methanol has been used to determine a calibration curve for the intensity of CO<sub>2</sub> versus absorbed concentration. This calibration curve has been used to quantify the amount of free CO<sub>2</sub> in solution. Figure 9 shows the amount of free CO<sub>2</sub> in (3-aminopropyl) tripropylsilane at two temperatures, 35°C and 50°C.

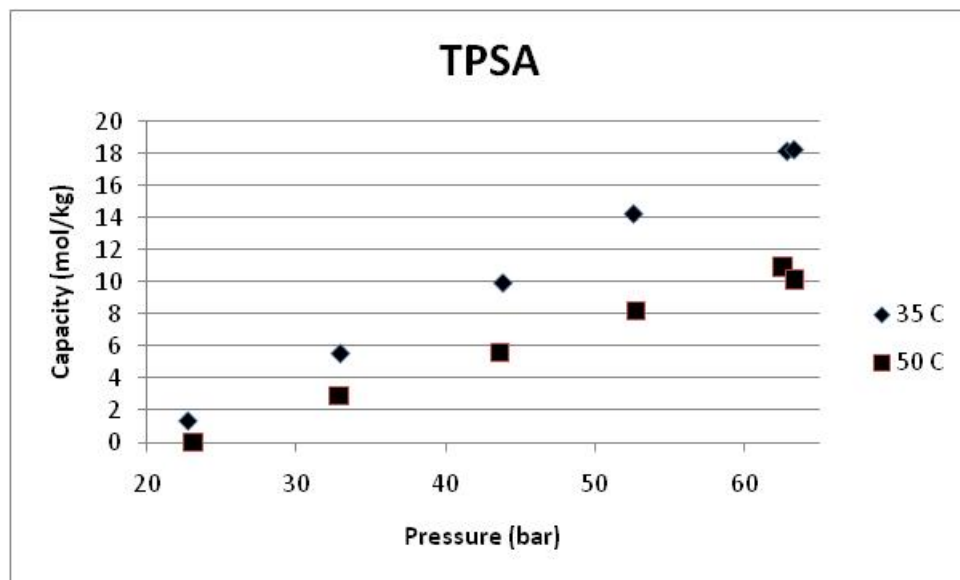


Figure 9. Physically absorbed CO<sub>2</sub> capacities in (3-aminopropyl)tripropylsilane.

We are continuing with the testing of the 4 silyl-amine based reversible ionic liquids at temperatures up to 150°C, and will begin testing other compounds after they are completely characterized.

### **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. 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% CO<sub>2</sub> 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 *Tetrahedron*.

Significant accomplishments were made during the 4<sup>th</sup> Quarter of the project by successfully synthesizing and isolating 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 three milestones listed in the Project Management Plan for Year One are as follows:

<b>ID</b>	<b>Milestone Description</b>	<b>Planned Completion</b>	<b>Verification Method</b>
A	Complete Project Management Plan	10/01/08	PMP approved by DOE COR
B	Complete laboratory synthesis and characterization of one new single-component silyl amine-based reversible ionic liquid.	6/30/09	laboratory synthesis and characterization of single-component silyl amine-based reversible ionic liquid.
C	Complete laboratory synthesis and characterization of one new single-component silyl guanidine-based reversible ionic liquid.	9/30/09	Progress Report describing laboratory synthesis and characterization of one new single-component silyl guanidine-based reversible ionic liquid

At this time, Milestone A has been completed on schedule with the approval of the Project Management Plan.

Also, Milestone B has been completed and expanded upon ahead of schedule, with the complete laboratory synthesis and characterization of four new single-component silyl amine-based reversible ionic liquids.

Work on Milestone C has met with synthetic difficulties, but these are now being overcome and the work should be completed shortly. However, it now appears that for the purposes of this project the single-component silyl amine-based reversible ionic liquid may be superior to those that are guanidine based, and as we assay that difference we may take advantage of it.

## 8. Summary of Significant Accomplishments

The significant accomplishments are:

- Prepare, isolate, purify and *fully characterize* four total amine-based reversible ionic liquids for CO<sub>2</sub> 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 four 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 a scientific journal

## 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 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*, accepted (June 2009).

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*, accepted (Oct 2009).

Papers presented:

Charles A. Eckert and Charles L. Liotta, "Reversible Ionic Liquids as Double-Action Solvents for CO<sub>2</sub> Capture," Annual NETL CO<sub>2</sub> 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," 237<sup>th</sup> 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 CO<sub>2</sub> Capture," AIChE Spring National Meeting, Tampa, FL, April 2009

Philip G. Jessop, Michael Cunningham, Charles A. Eckert, and Charles L. Liotta "CO<sub>2</sub> 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 CO<sub>2</sub> Capture,” 13<sup>th</sup> Annual Green Chemistry & Engineering Conference, Washington, DC, June 2009.

Papers to be presented:

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 CO<sub>2</sub> capture facility utilizing liquid sorbents for capture.

#### **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.