

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

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Co-PI: Dr. Charles L. Liotta

3. Date of report and period covered

Date of report: January 27, 2009

Period covered: October 1, 2008 – December 31, 2008

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 physisorption 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.

Great progress has been achieved in the first quarter of effort on this project. Our major contributions include:

- We have added and trained additional staff to meet the demands of this project. These include a new Research Scientist (chemist) and Postdoctoral Fellow (chemical engineer) plus multiple new PhD students and undergraduate assistants from both disciplines, who will work with our more experienced personnel over the course of the project.
- We have made substantial progress on our Task 2 – Synthesis & characterization of one component silyl amine based reversible ionic liquids. We report the synthesis and chemical characterization of precursors for some novel reversible ionic liquids – (3-aminopropyl) trimethoxysilane, (3-aminopropyl) triethoxysilane, and (3-aminopropyl)-triethylsilane and the corresponding ionic liquids. We have published our first paper on this topic in Chemical Communications, appearing in January, 2009. Further we have started making viscosity measurements on the reversible ionic liquids
- We have gotten an excellent head start on Task 4 – Measurement of thermodynamic properties of ionic liquids synthesized. Although this task is not slated to begin until later in the year, to achieve this we have designed, ordered, and just as of this writing, received in late January, 2009, the necessary commercial equipment. Also we have designed and submitted for machining a novel sample vessel for the FTIR measurements. Having this started will now permit us to set up, receive training, and start later in the second quarter on this task.

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 35% 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. *Three candidates were synthesized and characterized (Figure 1):* 1) (3-aminopropyl)trimethoxysilane, 2) (3-aminopropyl)triethoxysilane, and 3) (3-aminopropyl)triethylsilane.

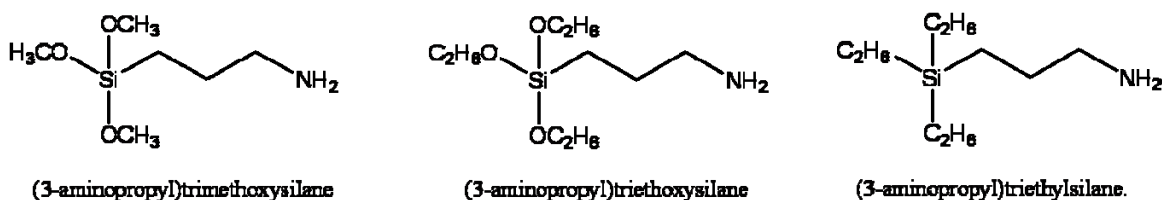


Figure 1. Synthesized candidates for CO₂ capture.

Each of these candidates was tested for CO₂ capture, yielding reversible ionic liquids as illustrated by the general reaction scheme in Figure 2. The resulting reversible ionic liquids are being fully characterized (NMR, Elemental analysis, IR, MS, solvatochromic polarity measurements). The loss of CO₂ upon heating will be explored using NMR and DSC/TGA. The stability of the custom-made reversible ionic liquids will be investigated as a function of time, water content (0 and 10 % water) and temperature (4°C, 25°C, and 50°C). Small aliquots will be taken weekly and analyzed via ¹H NMR to determine the extent of degradation, if any.

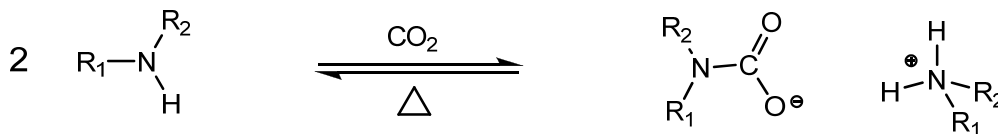


Figure 2. Reaction of custom-made amine with CO₂ to form reversible ionic liquids.

Additionally, we will look to capture ¹³C labeled CO₂ to differentiate and quantify the chemisorbed (single or multiple reactions) and physisorbed CO₂ present in the reversible ionic

liquid. We anticipate capacities to exceed the 1:2 CO₂ to solvent ratio achieved by single reaction stoichiometry. Quantitative ¹³C NMR will be used to perform the analysis and the results will be compared with FTIR data.

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. The equilibrium constant K representative of the capture of CO₂ can be determined from the following expression:

$$K = \frac{x}{(1-x)^2 P_{CO_2}}$$

We will be using attenuated total reflectance (ATR) fourier-transform infrared (FT-IR) spectroscopy. The ATR FT-IR optics bench used for data collection will be the Heated Golden Gate ATR 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. *We manufactured in-house a high pressure stainless steel reactor* that will contain the sample and high pressure gas. The reactor contains a thermocouple epoxied into place with J-B Weld cold weld epoxy, which has a rating of up to 600°F and 3960 psi. *The cell has been successfully tested to hold 1500 psi at 150°C.* This is due to limitations of the current Specac device which is only rated to 250°C, as we are awaiting the arrival of the new model rated up to 300°C *which is to be delivered the last week of January, 2009.* After the installation and calibration of the instrument, the data will be collected at operating conditions of 200°C and 1500psi.

The FT-IR spectra will be collected on a Shimadzu IR Prestige, *which was delivered on January 22, 2009*. After setup and training, we shall begin studying the reaction of the custom-made (3-aminopropyl)triethylsilane and CO₂ with 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. From this point, we will only need to collect one (1) simultaneous NMR/IR spectra for each unique molecular liquid examined. 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.

Experimentation will follow starting with the custom-made candidates: (3-aminopropyl)trimethoxysilane and (3-aminopropyl)triethoxysilane and using pure CO₂ 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 CO₂. The custom reversible ionic liquids that show promising pure CO₂ capacities and reaction enthalpies will be investigated with altered feed streams to examine the effects of mixed N₂/CO₂ 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. 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. Previous studies on the equimolar mixture of N-butyl-N,N,N,N-tetramethylguanidine and methanol have shown that the viscosity can change by as much as three orders of magnitude as the molecular liquid is completely converted to the ionic form upon reaction with CO₂. *These results 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 candidates will be measured using a MCR300 controlled stress rheometer supplied by Anton Paar, located in the Complex Fluids Group Laboratory at Georgia Tech.

4- Scrubber Process Design

An ASPEN simulation to treat a *model coal-fired power plant flue gas stream is being developed*. 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

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

The characterization of the (3-aminopropyl)trimethoxysilane and the (3-aminopropyl)triethoxysilane and the corresponding ionic liquids were performed by using NMR, IR, and elemental analyses. Since the (3-aminopropyl)trimethoxysilane and the (3-aminopropyl)triethoxysilane were purchased, routine ¹H and ¹³C NMR were performed to confirm the structure and the purity. The NMR spectra were consistent with expected structure of the alkoxy-silylamine molecules. The formation of the corresponding ionic liquids was performed

upon reaction with CO₂ at ambient conditions. The ionic liquid products were characterized by ¹H, ¹³C NMR, IR, and elemental analysis. The appearance of the characteristic carbamate carbon peak in ¹³C NMR was observed. The characteristic infra red signatures, -NH₃⁺ (3400-2400 cm⁻¹) and -CO₂⁻ (~1570 cm⁻¹ asymmetric stretch; 1471 cm⁻¹ symmetric stretch) were observed, validating the formation of the ionic species products. Elemental analyses (C, N, H, Si) were consistent with the calculated elemental analysis. Furthermore, thermogravimetric analyses (TGA), differential scanning calorimetry (DSC), viscosity, and solvatochromic polarity measurements were performed on the amines and the corresponding ionic liquids.

The (3-aminopropyl)-triethylsilane is not commercially available and was therefore synthesized in our laboratories from triethylsilane and allylamine (Figure 3).

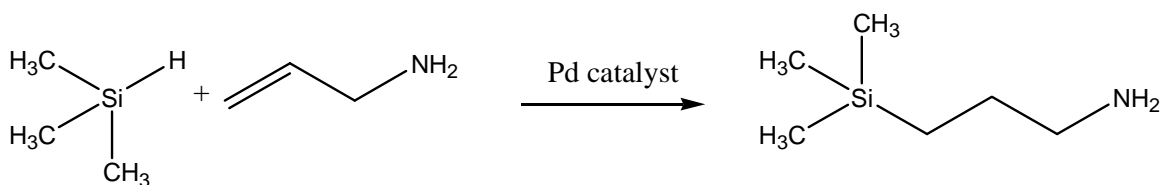


Figure 3. Synthesis of the (3-aminopropyl)-triethylsilane

The characterization of the (3-aminopropyl)-triethylsilane and the corresponding ionic liquid was performed by ¹³C NMR, ¹H NMR, IR spectroscopy, Maldi mass spectroscopy, TGA, and DSC analyses. Interestingly, the DSC analyses indicates a higher reversal temperature (or loss of CO₂) for the ionic liquid bearing three ethyl groups (143°C) compare to three ethoxyl groups (108°C). The viscosity and solvatochromic polarity measurements and elemental analyses are currently being performed.

2- Thermodynamics of CO₂ capture (measurements)

A high pressure stainless steel reactor was manufactured in house. Figure 4 shows a schematic of the reactor and Figure 5 is an actual picture of the reactor. The reactor consists of a stainless steel body, two 1/16" perforations (for temperature reading, and for inlet and outlet of chemicals), and three cavities: 1) for the reaction, which will be in direct contact with the ATR crystal, 2) for pressure upkeep (O-ring) and 3) for localization and upkeep of the whole reactor during analyses).

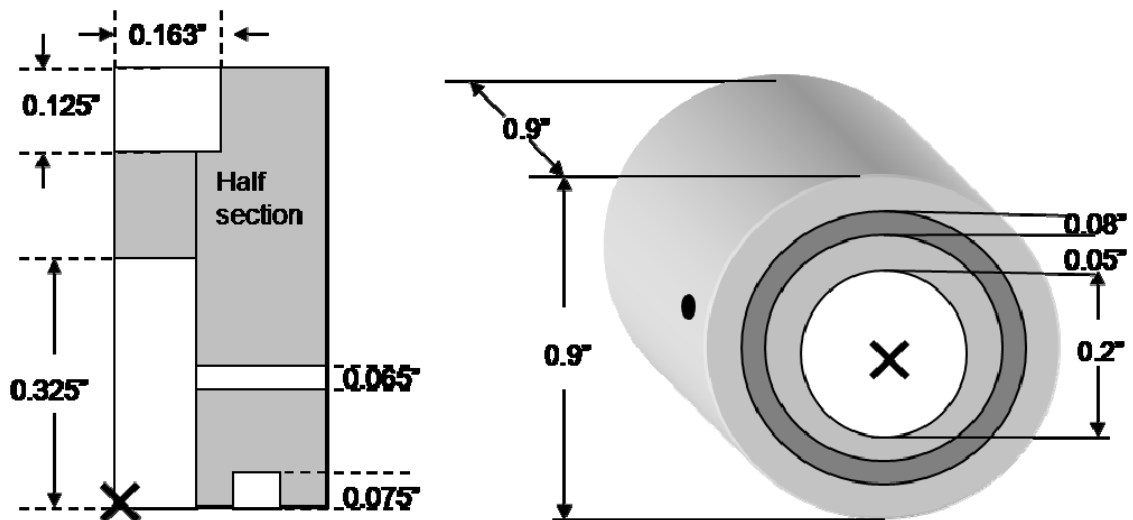


Figure 4. Schematic of the high pressure stainless steel reactor.

A thermocouple was epoxied with J-B Weld cold weld. In addition, a 1/16 standard metal connection was welded to the second connection of the system. Further connections (not shown in the schematic) were also performed to obtain CO₂ flow control and pressure reading. The pressure is measured by a Druck PDCR 4010 pressure transducer connected to a Druck DPI 260 pressure displayer. High pressure products (HIP) needle valves 15-11AF1 were connected throughout the system for flow control.

Preliminary testing have shown that the system can successfully and safely hold pressures up to 1500 psi at 150°C. An additional reactor is currently being built; furthermore, other reactors can be manufactured in-house as needed.

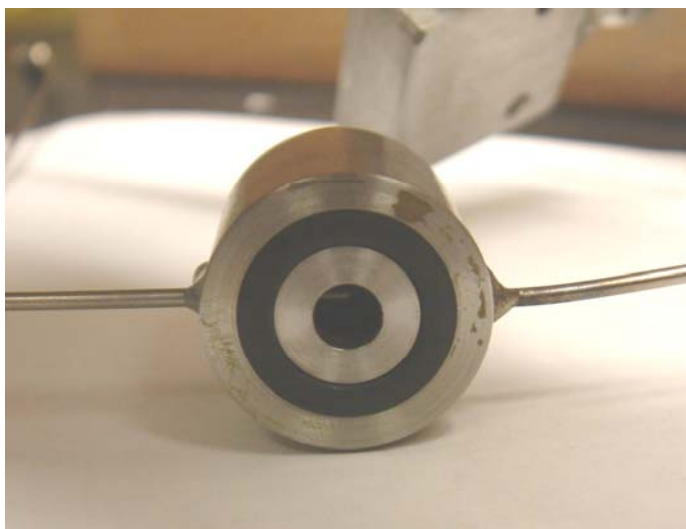


Figure 5. Frontal view of the volume of reaction, O-ring and connections.

c. Conclusion

We report the successful synthesis and chemical characterization of precursors for three novel reversible ionic liquids and for the corresponding ionic liquids. We have published our first paper on this topic in *Chemical Communications*, appearing in January, 2009. Further we have started making viscosity measurements on the reversible ionic liquids

We have designed, ordered, received the necessary FTIR equipment to make the thermodynamic and rate measurements on the new reversible ionic liquids.. Also we have designed and had machined a novel sample vessel for the FTIR measurements.

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:

ID	Milestone Description	Planned Completion	Verification Method
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 ahead of schedule, with the complete laboratory synthesis and characterization of three new single-component silyl amine-based reversible ionic liquids.

We fully anticipate that Milestone C will also be completed on during Year One.

8. Summary of Significant Accomplishments

The significant accomplishments are:

- Prepare, isolate, purify and characterize three custom-made amines and reversible ionic liquids for CO₂ capture
- Put in place all the accounting infrastructure that allowed the orders to be placed and processed
- Identify and purchase FTIR spectrometer (Shimadzu IR prestige) and heated golden gate ATR accessory (Specac)
- Manufacture and test two high pressure stainless steel reactors to be coupled with heated golden gate ATR
- Develop an Aspen model for first evaluation of targets set by DOE (90% CO₂ capture with no more than a 35% increase in cost)

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

We have not had any problems or delays, and because we are able to stay ahead of schedule, we do not anticipate any problems or delay.

10. Products produced

a. Publications

One paper was submitted and now has been published in early 2009:

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.

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.

d. Technologies/Techniques

We designed and developed custom stainless steel reactors that will fulfill our experimental needs: it will hold high pressure (up to 15,000 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 filling for the one-component reversible ionic liquids is in process.