

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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3. Date of Report and Period Covered

Date of report: April 30, 2010

Period covered: January 1, 2010 – March 31, 2010 (Budget Period 2 – Q2)

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 sequestration. Because of this dual-mode capture ability, capacity can be large, and we are modifying the precursor structure using structure-property relationships to optimize both physical and thermodynamic properties. By incorporating silanes in the molecules we reduce viscosity, thereby improving the mass transfer rates of CO₂ absorption and decreasing the processing costs for pumping the solvent.

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

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

- We have completed the FT-IR data collection examining the chemical and physical absorption of CO₂ in the 4 silyl-amine based reversible ionic liquids (RevILs): (3-aminopropyl)trimethoxysilane, (3-aminopropyl)triethoxysilane, (3-aminopropyl)triethylsilane, and (3-aminopropyl)tripropylsilane. Operating pressures up to 1000 psi and temperatures of 35, 50, 75, 100, and 125°C were examined using attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy and our Generation 3 custom made high pressure reaction vessel. (**TASK 4**)
- We have begun characterizing (3-aminopropyl)diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane and (3-aminopropyl)trihexylsilane and we have identified four additional silyl-amine based RevILs to be synthesized. (**TASK 2**)
- We collected the simultaneous ¹H NMR and FT-IR experiments for the four first and second generation RevILs for analysis of the thermodynamics from the chemical absorption data measured using ATR FT-IR. (**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. The general reaction scheme for the synthesis of silyl-amine based RevILs is shown (Figure 1).

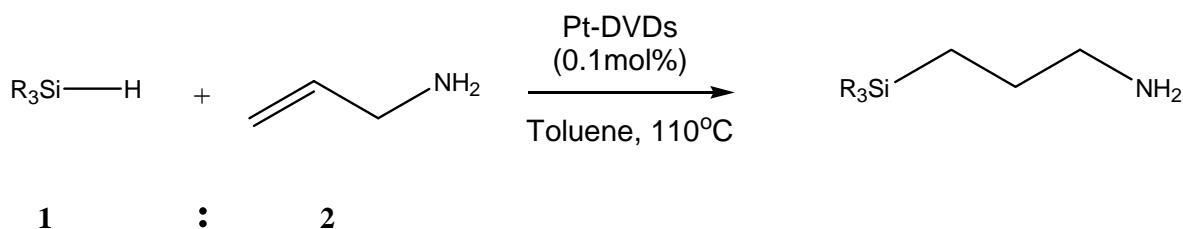


Figure 1. One-step synthetic scheme for silyl-amine based RevILs.

The synthetic scheme being employed affords two main benefits for the production of RevILs for CO₂ capture from flue gas: (1) the synthesis is simple and efficient and (2) the molecular architecture of the RevILs can be easily tuned by using silanes with different substitution. This allows for the development of a plethora of compounds to be tested for application to CO₂ capture, as well as ensuring that the optimal candidate will be capable of scaling to synthesis on an industrial level. Additionally, as progress is made on existing compounds, we can identify molecular structures for improved absorption capacities and processing properties and alter the current synthetic techniques by simple substitution of silanes. ***The progression on molecular structure that will allow for the development of an optimal CO₂ capture solvent resulting in a drastic reduction in operating costs (relative to monoethanolamine absorption) and lower capital cost (through increasing capacity).***

After synthesis and isolation, we first characterize each compound to ensure the candidate is viable for use as a reversible ionic liquid solvent for the removal of CO₂ from power plant flue gas. The first study conducted is the confirmation of reaction with CO₂ (confirmed by both ¹H and ¹³C NMR) to produce an ionic liquid capable of further physi-sorption (Figure 2).

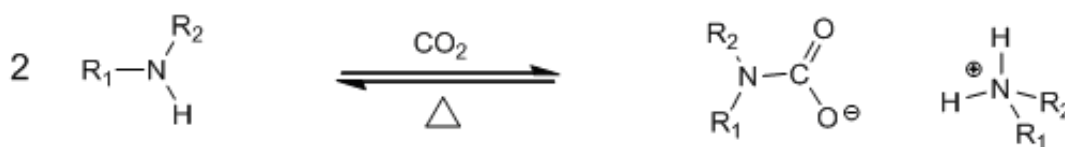


Figure 2. Reaction of custom-made amine with CO₂ to form reversible ionic liquids.

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 a good measure of 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.

The loss of CO₂ upon heating and thermal stability of the amines 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 5°C/min from 20°C initial temperature to 400°C final temperature. The first endotherm was taken to represent the loss of CO₂ with the second endotherm representing the decomposition of the molecular liquid.

Although 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. Stability will be monitored using ¹H NMR.

Additionally, we shall 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 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 chemical and physical absorption CO₂ capacity, both used for the determination of the thermodynamic properties of the solvent.*** 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 Prof. Sergei Kazarian of Imperial College London. We are now using a custom designed and built Generation 3 stainless steel reactor, which has been successfully tested at temperatures to 150°C and pressures to 1500psi. To quantify the chemical absorption capacity measured with ATR FT-IR, simultaneous ¹H NMR and FT-IR measurements will be collected for each compound at an intermediate conversion (a mixture of molecular and ionic liquids). The 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. Changes in penetration depth will be accounted for by examining the refractive indices of the samples in both molecular and ionic forms. Density changes in the samples arising from conversion to ionic liquid and swelling of the liquid due to physical absorption will be corrected by examining the C-H stretch vibrational frequencies (<3000 cm⁻¹) in the samples. 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 amount of CO_2 that is physically absorbed into the ionic liquids using the FT-IR data that is collected for the conversion measurements. The CO_2 that is in solution and not chemically bound to the amine (referred to as “free CO_2 ”) 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 and molar absorptivity of the ionic liquid is required. Density measurements will be conducted in our laboratory using an Anton Paar DMA 38 Laboratory Density Meter. Molar absorptivities will be calculated for the samples from the simultaneous ^1H NMR and FT-IR measurements, using the refractive index information to calculate path length.

Initial experiments use pure CO_2 feed streams. As we determine the equilibrium constants at multiple temperatures, we shall 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 must examine the non-ideality of our ionic liquids solutions. We are measuring concentrations, but in fact the equilibrium constant is a ratio of activities, so some measure or estimate of activity coefficients is required. We have begun looking at available data and models, and this work is described below. Such 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 previously reported, 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 Rheosys Merlin II Viscometer, located in our laboratory. Measurements are currently being done to identify a proper method to evaluate the isothermal viscosities of both molecular and ionic liquids. Once complete, the viscosities will be measured for the all candidates that have been successfully characterized. To ascertain the affect of conversion on viscosity, we will examine the viscosities of (3-aminopropyl)tripropylsilane at various conversions. The conversion of the samples will be measured using ¹H NMR.

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

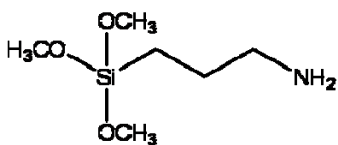
more than a 30% increase in cost. We are using the monoethanolamine (MEA) process as a basis for comparison, and are altering the operating conditions to give us targets for the development of one component reversible ionic liquids. The parameters we look to optimize are the enthalpy of capture and release, 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.

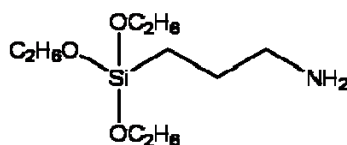
b. Results and Discussion

1- Synthesis and Characterization of Custom Reversible ILs

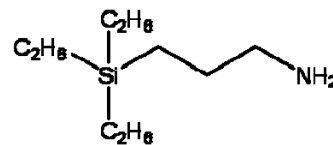
We have currently synthesized and *fully characterized* four reversible ionic liquid candidates: (3-aminopropyl)trimethoxysilane, (3-aminopropyl)triethoxysilane, (3-aminopropyl)triethylsilane, and (3-aminopropyl) tripropylsilane, as previously reported (Figure 3).



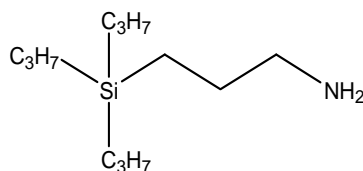
(3-aminopropyl)trimethoxysilane



(3-aminopropyl)triethoxysilane



(3-aminopropyl)triethylsilane.



(3-aminopropyl)tripropylsilane

Figure 3: Structures of first and second generation silyl-amine based RevILs.

Characterization of the first and second generation silyl-amine based RevILs lead to the identification, synthesis and isolation of three more candidates to be tested as CO₂ capture agents (Figure 4): (3-aminopropyl)ethyldimethylsilane, (3-aminopropyl) trihexylsilane, and (3-aminopropyl) diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane. (TASK 2) The characterization has been initiated on (3-aminopropyl)trihexylsilane, and (3-aminopropyl) diisopropyl (1H,1H,2H,2H-perfluoropentyl)silane. The compound (3-aminopropyl) ethyldimethylsilane has been dismissed from further characterization due to solid formation during absorption with CO₂ and reversion to molecular liquid upon melting.

The candidates in Figure 4 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 have indicated that swelling of the ionic liquids and 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 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.

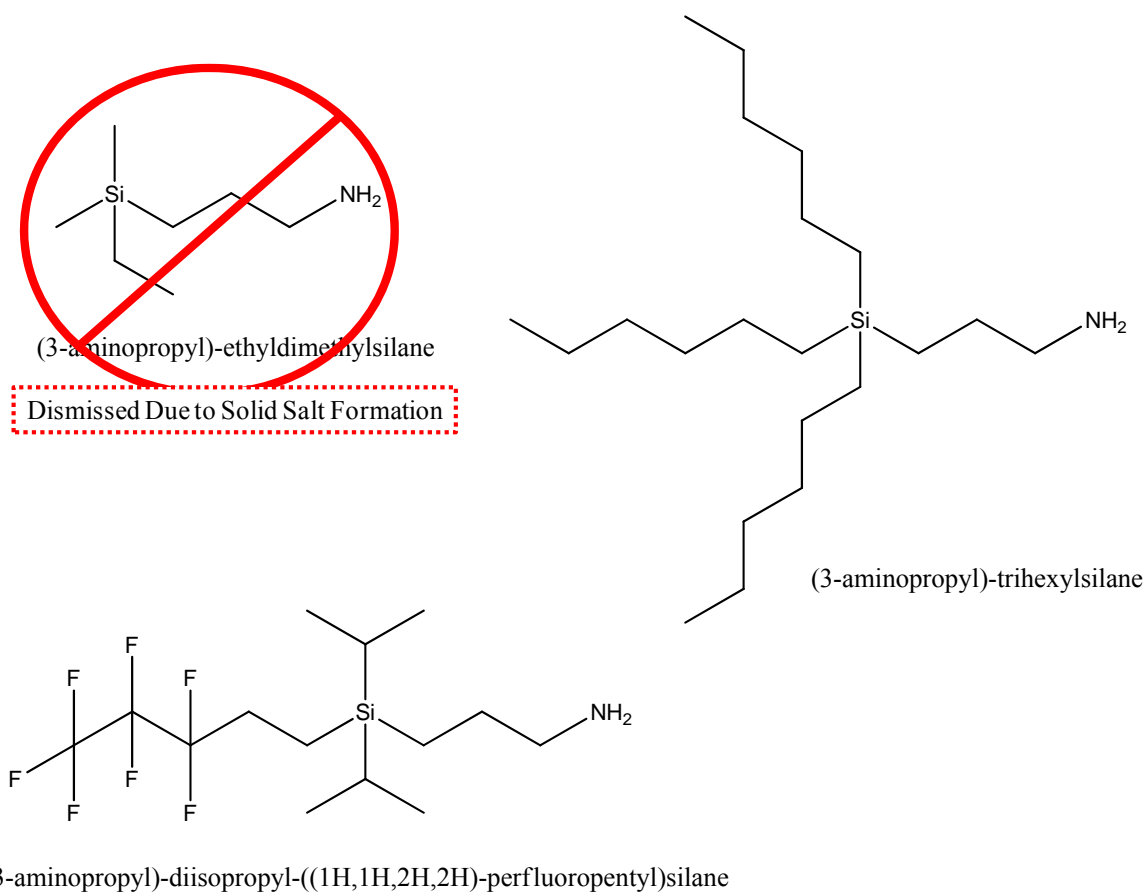


Figure 4. Structures of third generation silyl-amine based RevILs.

Although the (3-aminopropyl)ethyltrimethylsilane structure was dismissed due to solid salt formation, we propose three additional compounds as CO₂ capture to explore the effect of asymmetry on the physical and chemical properties (Figure 5):

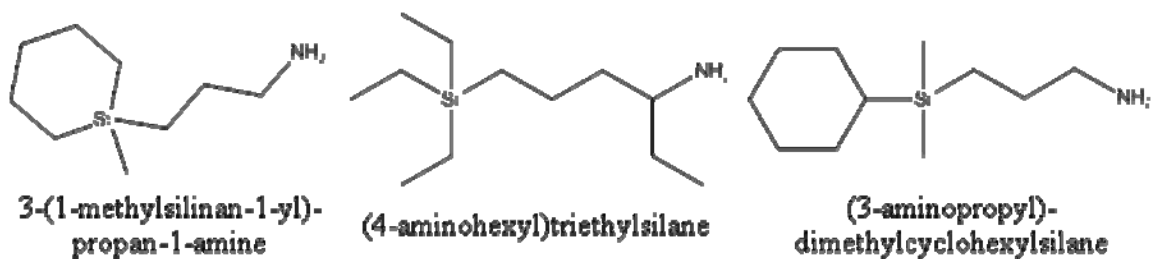


Figure 5. Structures of asymmetric silyl-amine based RevILs.

Maintaining ease of synthesis as a priority, thereby ensuring the capability for production on an industrial scale, all of the asymmetric silyl-amine based RevILs follow the same Pt-DVDs catalyzed scheme as before. The silane for 3-(1-methylsilylan-1-yl)propan-1-amine is prepared through Grignard additions to dichloromethylsilane, the dimethylcyclohexylsilane is commercially available, and (4-aminoethyl)triethylsilane is prepared by substituting 4-amino-1-butene for allyl amine. All materials have been ordered, and synthesis will proceed once the shipments have been received.

In an attempt to decrease the viscosities of the ionic liquids (enabling facile processing) and to increase capacity by lowering the molecular weight of the amine, we propose to examine the isomers of (3-amino-1-propenyl)triethylsilane (Figure 6):

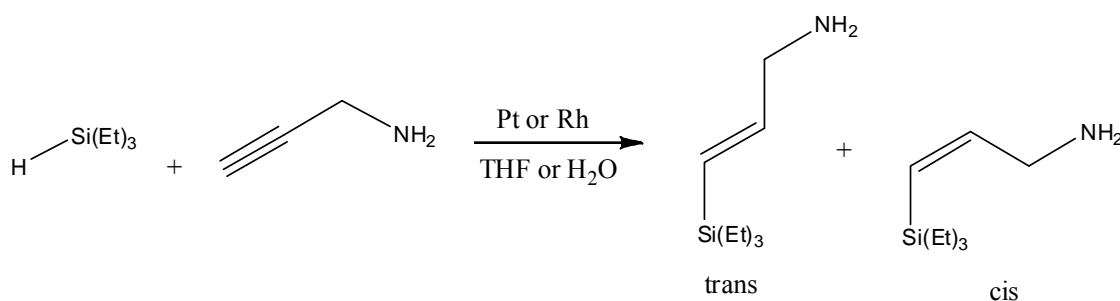


Figure 6. Synthetic scheme for *cis*- and *trans*- (3-amino-1-propenyl)triethylsilane.

Again, the synthesis of (3-amino-1-propenyl)triethylsilane is simple and efficient, and the distribution of *cis*:*trans* isomers can be controlled by altering the catalyst. We look to explore the affects of mixtures on the physical and chemical properties of the amine.

We previously proposed the use of an alkanolguanidine (Figure 7) as a reversible ionic liquid for CO_2 capture.

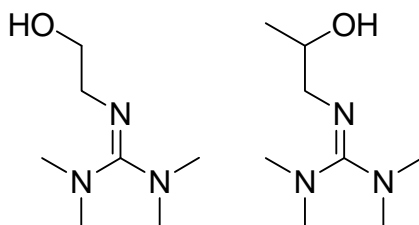


Figure 7. Proposed alkanol-guanidine reversible ionic liquid precursors.

However, we found that this type of molecule does not have desirable properties for carbon capture. First, the synthesis of two similar alkanolguanidines was attempted without significant yields of the desired products. In addition to the difficulty in synthesizing these precursors, our collaborators recently discovered and published other problems with using alkanolguanidines (Figure 8).^a

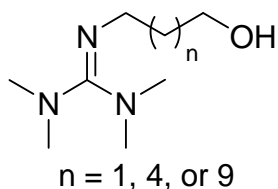


Figure 8. Structure of alkanolguanidines reported by our collaborators.

When a short alkane chain (3 carbons) was used to connect the alcohol and guanidine moieties, reaction with CO₂ led to the formation of a non-reversible cyclic carbonate (Figure 9):

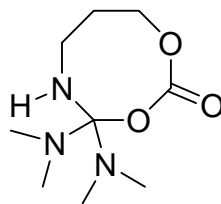


Figure 9. Proposed structure of cyclic carbonate product of short-chain alkanolguanidine reacted with CO₂.

The use of a longer alkane chain (11 carbons) resulted in a waxy solid upon the addition of CO₂. Finally, when a medium alkane chain length (6 carbons) was used, reaction with CO₂ provided a reversible ionic liquid. However, the CO₂ absorption capacity was found to be low (~10% by weight) due to entropic effects. Due to the limitations of working with alkanolguanidines, we chose to move on to other compounds with greater potential for CO₂ capture.

^a David J. Heldebrant, Phillip K. Koech, M. Trisha C. Ang, Chen Liang, James E. Rainbolt, Clement R. Yonker, and Philip G. Jessop, "Reversible zwitterionic liquids, the reaction of alkanol guanidines, alkanol amidines, and diamines with CO₂," *Green Chemistry*, 713-721 (2010).

2- Thermodynamics of CO₂ Capture

The ATR FT-IR measurements for (3-aminopropyl)trimethoxysilane, (3-aminopropyl)triethoxysilane, (3-aminopropyl)triethylsilane, and (3-aminopropyl) tripropylsilane have been *completed*. Operating pressures up to 1000 psi and temperatures of 35, 50, 75, 100, and 125°C were examined using attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy and our Generation 3 custom made high pressure reaction vessel. Measurements have been initiated for the (3-aminopropyl) diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane and (3-aminopropyl)trihexylsilane.

We are currently processing the data that has been completed for the first and second generation RevILs. The amount of CO₂ captured through physical absorption can easily be quantified through application of the methanol/CO₂ calibration curve, as discussed in the “Approach” section of this report. However, we must know the molar absorptivity of the sample. This information will be calculated from the simultaneous ¹H NMR and FT-IR experiments, which have been *completed* for the first and second generation RevILs. An example of the ¹H NMR spectra for an intermediate conversion of (3-aminopropyl)triethoxysilane is shown in Figure 10, illustrating the splitting of peaks when the amine forms the carbamate. The ¹H NMR in Figure 10 indicates a conversion of molecular form to ionic form of 69%.

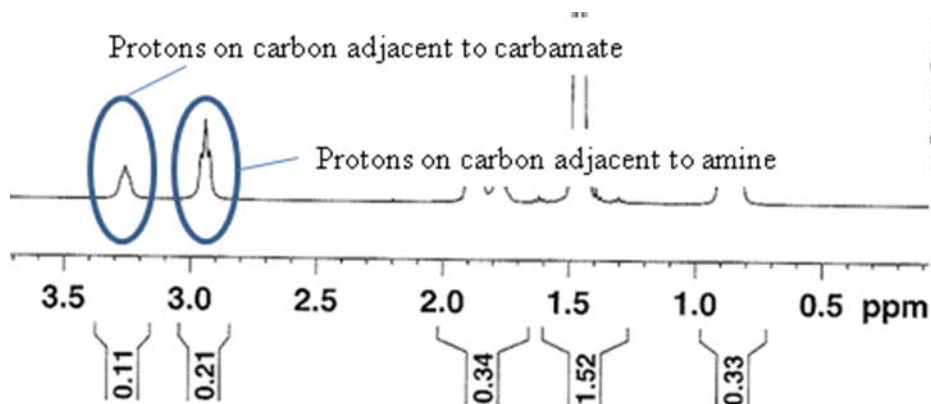


Figure 10. ¹H NMR of incomplete conversion of (3-aminopropyl)triethoxysilane to IL.

In order to properly analyze the FT-IR data, we need the density of the molecular form of the RevILs and the penetration depth of the ATR (which is dependent on refractive index). As of

this report, we have submitted an order for an Anton Paar DMA 38 Laboratory Density Meter and a Reichert Arias 500 Refractometer. Once quantification of physical and chemical absorption is complete for the first and second generation RevILs, the information will be used with the appropriate model to determine the thermodynamic properties of CO₂ capture.

In evaluating the equilibrium constant (K), we shall use the conversion of the molecular liquid to ionic liquid as well as the dissolved CO₂ concentration as measured by the FT-IR. We shall evaluate the equilibrium constant with an activity based approach to account for the nonideality of the mixture. We expect the system to exhibit nonideal behavior because of the highly polar nature of the liquid phase and the dissimilarity of the molecules in the system (CO₂, the amine precursor, and the highly polar and viscous ionic liquid).

Evaluation of the equilibrium constant involves the estimation of the activity coefficient (γ) with excess Gibbs energy or equation of state models. Conventionally, such models contain one or more adjustable parameters that are optimized to best fit experimental data. In ternary systems, the binary interaction parameters may first be obtained from experimental Vapor-Liquid Equilibria (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 currently reviewing published data and thermodynamic models for ionic liquids-CO₂, organics-ionic liquids, electrolyte solutions, and ternary systems including variations of these components. We are considering various thermodynamic models that represent mixtures containing polar and non-polar components such as the Universal Quasichemical (UNIQUAC) and Statistical Associating Fluid Theory (SAFT).

UNIQUAC is used to model phase equilibria of binary and ternary systems containing ionic liquids, hydrocarbons, and CO₂¹⁻⁴. UNIQUAC utilizes the volume and surface area of molecules, which can be calculated through variety of theoretical methods, and a binary interaction energy parameter fitted to experimental data. A similar method, Universal Functional Activity Coefficient (UNIFAC), has also been reported for systems containing ionic liquids however, the method relies on infinite dilution data which could be challenging to measure in our

systems. Another method that could be used is the group contribution (GC) method, which represents the physical properties of the molecule by the summation of the interactions between specific functional groups within the molecule. A molecule is broken down into its functional groups (CH₂, C=O, etc.) and reported or calculated values are used to estimate interaction values for each functional group⁵. The principle of group contribution can be implemented into other thermodynamic models such as linear solvation energy relationships⁶

SAFT assumes that molecules consist of freely joint spherical segments and it has been widely used to represent complex mixtures. It is reported for vapor-liquid equilibria of binary and ternary mixtures of polymers-solvents-gases⁷⁻⁸, and ionic liquids-CO₂ (Andreu and Vega – 2007) systems⁹⁻¹⁰. For nonpolar non-associating fluids, the method requires three parameters: the molecule's segment diameter (σ), the number of segments representing each molecule (m), and the segment energy parameter (ϵ). The pure component parameters are obtained from vapor pressure data and liquid densities for volatile liquids. For relatively non-volatile molecules (polymers and ionic liquids), the parameters are obtained by simultaneously fitting liquid densities and binary phase equilibrium data. Additional parameters are required for associating systems (hydrogen bonding) and polar interactions (dipole and quadrupole). The two main advantages of this method: 1) its wide applicability and acceptance and 2) semi-predictive power. On the negative side, method requires accurate and available experimental data, which is not optimal for newly synthesized molecules screening.

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 solvent for CO₂ capture.

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3- Viscosity Studies

We are currently 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. Previously, we had taken data on the MCR300 controlled stress rheometer supplied by Anton Paar, located in the Complex Fluids Group Laboratory at Georgia Tech. We have some data from this, and we have shown in all cases measured that the fluids are Newtonian – no variation of viscosity with shear rate. However, the equipment is shared and has recently been heavily used and poorly maintained. To ensure both integrity of our measurements and speed of data collection, we have ordered and received a Rheosys Merlin II Viscometer for the sole purpose of measuring the viscosities of the RevILs.

As of this report, the machine has been received and training has been completed. We are currently developing a method, and once complete, we will verify the data collected on the first and second generation silyl-amines. 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.

Significant accomplishments were made during the 6th Quarter of the project by identifying four additional silyl-amine based RevILs that we believe could reduce operating and capital costs of a CO₂ capture process by offering favorable chemical and physical properties.. 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. Once a method has been developed, the use of an in-house viscometer will allow for the viscosity measurements to be rapidly 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, which has been supported by the published findings of our collaborators. (**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.