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_2 Capture

PI: Dr. Charles. A. Eckert

Co-PI: Dr. Charles L. Liotta

3. Date of Report and Period Covered

Date of report: July 31st 2011

Period covered: April 1st, 2011 – June 30th, 2011 (Budget Period 3 – Q3)

4. Executive Summary

The objective of this project is to develop reversible ionic liquids as solvents for post-combustion recovery of CO_2 from coal-fired power plants. These novel solvents are neutral molecules which react with CO_2 to form an ionic liquid, which then absorbs additional CO_2 by a physisorption mechanism. Subsequently, modest elevations in temperature reverse the reaction and yield pure CO_2 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 CO_2 absorption/desorption and decreasing the processing costs for pumping the solvent.

We have designed, tested, and optimized reversible ionic liquids for application to CO_2 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 throughout the third year of this project, meeting or exceeding projected achievements. Our major contributions through this quarter include:

- We have calculated the equilibrium constants for CO_2 capture reactions at various temperatures (**TASK 4.**)

- We have refined the results for the physisorption of CO_2 (**TASK 4**) and verified our physisorption experimental technique by comparing values of CO_2 physisorption in [Bmim][PF$_6$] published in the literature.

- We have also analyzed the effects of mass transfer on CO_2 absorption times and capacity through flowrate and diffuser tube studies (**TASK 5.**)
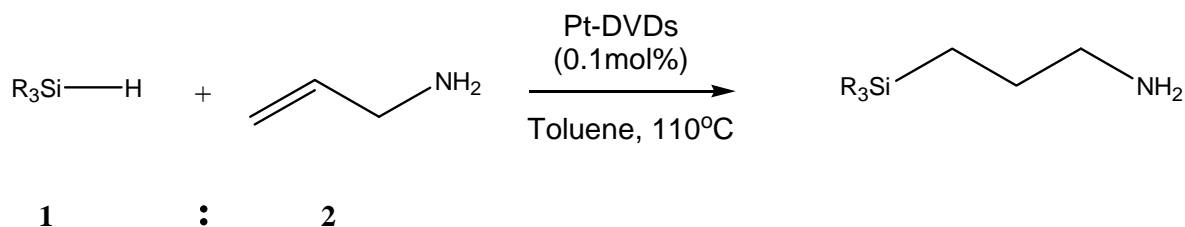

Our goal remains to minimize the cost and energy requirements of CO_2 capture to help DOE meet its goal – 90% CO_2 capture with no more than a 30% increase in cost by 2020.

5. Results of Work

a. Approach

1- Synthesis and Characterization of Custom Reversible ILs

One of the important requirements for a commercially viable CO_2 capture solvent is a simple synthesis route which can be easily scaled up to provide adequate capture fluid for the high volumes of CO_2 released from power plants. The primary scheme (Scheme I) that we use for the synthesis of our silyl-amine based molecular solvent is (Figure 1).

R₃Si—H + [allylamine structure] NH₂   →(Pt-DVDs (0.1mol%), Toluene, 110°C)→   R₃Si [propyl chain] NH₂

R₃Si——H   +   ⌒⌒NH₂   →[Pt-DVDs (0.1mol%) / Toluene, 110°C]→   R₃Si⌒⌒⌒NH₂

1   :   2

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

The above synthetic scheme offers two main benefits for the production of RevILs for CO_2 capture from flue gas: (1) the synthesis is simple and efficient and (2) the structure can be easily modified by simply changing the substitution on the starting silane. This allows us to systematically introduce changes to the structure and to improve the properties for CO_2 capture application. ***With progressive improvements to the molecular structure we aim to develop an optimal CO_2 capture solvent with significant decrease in the operating costs (relative to monoethanolamine absorption).***

After synthesis and isolation, each compound was thoroughly characterized via ^1H, ^{13}C NMR, elemental analysis, FT-IR, and DSC/TGA thermograms. Then, each molecular liquid was reacted with CO_2 to produce an ionic liquid capable of further physisorption (Figure 2). The

resulting ionic species (liquid or solid) was characterized by ^{1}H and ^{13}C NMR, melting point (if applicable), FT-IR, and solvatochromatic measurements.
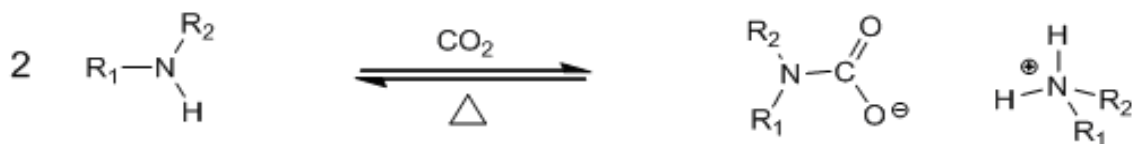
Figure 2: Reaction of custom-made amine with CO_2 to form reversible ionic liquids.

The release of CO_2 upon heating and thermal stability of the amines were explored using NMR and differential scanning calorimetry (DSC). The DSC experiments were performed on a Q20 TA Instruments machine, with a temperature profile of 5°C/min from an initial temperature of -40°C to a final temperature of 400°C.

2- Thermodynamics of CO_2 Capture

Thermodynamics of these systems is summed up by three main quantities of interest: the equilibrium constant $K(T)$, the difference between the reversion temperature and CO_2 capture temperature $\Delta T = T_{rev}-T_{fwd}$, and the enthalpy required for regeneration of silyl-amine from the ionic liquid $\Delta H_{regenration}$. These quantities are highly interrelated to each other. The equilibrium constant $K(T)$ determines the equilibrium conversion of the molecular precursor (silyl-amine) at a given temperature and is independent of CO_2 pressure. A favorable silyl-amine will have a high K (K>1) at the CO_2 capture temperature (T_{fwd}) to ensure maximum conversion of the molecular precursor to the ionic liquid, and a low K value (K<1) at the reversion temperature (T_{rev}) to ensure regeneration of the silyl-amine. These K values are also related to the reaction enthalpies by

$$\frac{d\,\ln K(T)}{d\,T} = \frac{\Delta H_{rxn}}{RT^2} \qquad (1)$$

where ΔH_{rxn} is the enthalpy of reaction between the molecular liquid and CO_2 to give ionic liquid (and vice versa). The above equation implies that if the K values are extremely high (K>>1) or extremely low (K<<1), ΔH_{rxn} will be large leading to huge energy penalty ($\Delta H_{regeneration}$) for regeneration of the silyl-amine.

The second quantity of interest is $\Delta T = T_{rev}-T_{fwd}$, where T_{fwd} is the temperature at which CO_2 is captured and T_{rev} is the reversal temperature. This quantity determines the heat input required to raise the temperature of the ionic liquid to the T_{rev},

$$Q = mC_p\,\Delta T \qquad (2)$$

m is the mass of the ionic liquid and C_p is the heat capacity. In the actual absorber unit, T_{fwd} will be dictated by the temperature of flue gas stream, hence we will choose T_{fwd} as a basis temperature (say 40°C) for all our compounds. The quantity that will change with the choice of molecular liquid will be T_{rev}. To minimize the heat input for heating the ionic liquid, we would prefer lower values of T_{rev}, however Equation (1) also implies that small values of ΔT (hence T_{rev}) will lead to large reaction enthalpies for regeneration. Therefore, we are looking for compounds that give optimum values of $T_{rev.}$

Since our compounds capture CO_2 through dual mode, two kinds of enthalpies constitute the enthalpy required for regeneration of the molecular liquid: $\Delta H_{regenration} = \Delta H_{rxn} + \Delta H_{dissolution}$. ΔH_{rxn} is associated with removing the chemisorbed CO_2 and $\Delta H_{dissolution}$ with the physisorbed CO_2.

The equilibrium constant, K(T), representative of the capture (and release) of CO_2 is found by measuring the equilibrium concentrations of reactants (the precursor molecule and CO_2), and the product (ionic liquid) at a given temperature, and then correcting for the nonideal behavior of these species.

$$K = \frac{a_{IL}}{a_{ML}^2 \, a_{CO_2}} = \frac{x_{IL}\gamma_{IL}}{(x_{ML}\gamma_{ML})^2 \cdot \frac{f_{CO_2}}{f^\circ_{CO_2}}} = \frac{x_{IL}\gamma_{IL}}{(x_{ML}\gamma_{ML})^2}$$

(3)

where x_i is the mole fraction of the species and γ_i the activity coefficient, and f_{CO2} and $f°_{CO2}$ are the fugacity and standard state fugacity of CO_2. Since $f°_{CO2}$=1bar, for K evaluated at 1bar (hence f_{CO2}=1bar), the equation reduces to the ratio of activities of IL and the square of activities of ML. For evaluating x_i, we use the conversion of the molecular liquid to ionic liquid found gravimetrically as well as with ATR FT-IR. Gravimetric measurements are performed by sparging CO_2 at one bar pressure in a vial containing the solvent maintained at a constant temperature in a sand bath. There are two regions in the IR spectrum that are used to determine molecular and ionic liquid mole fractions: the broad ammonium stretch vibration between 3100-2600 cm^{-1} and the presence of a C=O stretch from the carbamate between 1740-1520 cm^{-1}.

To account for the nonideality (γ_i) of the mixture (deviations from Raoult's Law) i.e. to reflect the highly polar nature of the liquid phase and the dissimilarity of the molecules in the system, we have used data from one of our *collaborations outside this project*. COSMO-RS approach[1,2] which assesses the thermodynamic properties of a system through a combination of statistical mechanics calculations and unimolecular quantum chemistry, is used for this purpose. These

---

[1] Klamt, A. The COSMO and COSMO-RS solvation models. *Comput. Mol. Sci. Res.* **2011** (DOI: 10.1002/wcms.56)

[2] Diedenhofen, M.; Klamt, A. COSMO-RS as a tool for property prediction of IL mixtures—A review. Fluid Phase Equilibria **2010**, 294, 31–38.

calculations are jointly performed by researchers from the Eckert-Liotta group at Georgia Institute of technology and Palomar and Rodriguez group from Universidad Complutense de Madrid & Universidad Autónoma de Madrid. The collaboration is *not* part of the current DOE project, however the data is used here as from an external source to compliment the FT-IR and gravimetric experiments.

We use Differential Scanning Calorimetery (DSC) for calculation of $\Delta H_{regeneration}$ and T_{rev}. As before, the preformed ionic liquid is heated in a DSC pan from -40°C to 400°C at a rate of 5°C/min. $\Delta H_{regenation}$ is measured by calculating the total heat flow during the reversal, while T_{rev} is measured as the onset point of reversion event. DSC also helps us determine the temperature range at which the molecular liquid evaporates. In addition, a simultaneous Thermogravimetric (TGA) on the preformed ionic liquids tells us the weight loss during the reversal and evaporation events, and hence the solvent loss during evaporation.

3- CO$_2$ Capture Capacities

Our objective in this project is to enhance the CO_2 capture capacities of our compounds through chemisorption and physisorption, with minimal increase in the process costs. The amount of CO_2 captured through chemisorption (reaction with the amine) depends on the stoichiometry and the equilibrium constant (K) at the reaction temperature. All the silyl-amines discussed in this report contain a single amine functionality, hence at complete conversion, two moles of these compounds react with a single mole of CO_2. The physisorption, on the other hand, depends on the intermolecular void space in these silyl amines, their van der Waals attractions with CO_2, and the partial pressure of the CO_2 gas stream in contact with the compound. We have systematically altered the structure of our compounds to enhance the physisorption capacities.

We have employed gravimetric technique for determining the overall capture capacity of each compound. For these experiments, CO_2 or a N_2+CO_2 (simulated flue gas mixture) at 1 bar total pressure was sparged through the molecular liquid (silyl-amine) at room temperature. The overall capture capacity is determined by the net weight gain at the end of sparging. This, for a given temperature, represents the combined chemisorption at maximum conversion and the physisorption corresponding to the partial pressure of CO_2. We have used two methods of sparging: 18 gauge needle and a diffuser tube. The diffuser tube is 1 cm in diameter, and consists of fritted glass with 24-50 μm porosity. The use of a diffuser tube instead of a needle allows for a better dispersion of the CO_2 throughout the liquid sample, in the form of much smaller bubbles, than what a needle can provide at a similar flowrate. Researchers elsewhere have also shown that by increasing the dispersion of the gas into a switchable solvent, they could much easier switch the hydrophobicity/philicity properties of the solvent when compared to a needle[3].

Additionally, we are using attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectroscopy to *simultaneously measure of chemical and physical CO_2 absorption capacity*. Determination of chemisorption was discussed in the previous section. For physisorption, a preformed RevIL sample was placed in a custom-designed ATR cell, and equilibrated at constant temperature and CO_2 pressure. CO_2 concentration is measured by evaluating absorbance of the asymmetric CO_2 stretch between 2400-2200 cm^{-1}. Beer-Lambert Law relates the absorbance to the concentration of the physisorbed CO_2. For Beer-Lambert Law calculations, we also require density, refractive index, and molar absorptivity of the ionic liquid. Physisorption x_{CO2} is reported in terms of Henry's Law constants:

[3] S.M. Mercer, P.G. Jessop, "Switchable water": Aqueous solutions of switchable ionic strength, ChemSusChem, 3 (2010) 467-470.

$$y_{CO_2} P = x_{CO_2} H$$

<div align="right">(4)</div>

The ATR FT-IR optics bench used for data collection is 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 performed by using a custom-designed and -built ATR FT-IR high pressure reactor. 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.

4- Kinetics and Mass transfer

For all our RevILs, the CO_2 absorption times were found to be mass transfer limited. The actual reaction of the silyl-amine with CO_2 is almost instantaneous. Detailed Analysis of this was given in the last report and the follow up is given in the results section.

5-   Other important Structure-Property relationships: Viscosity, Refractive index, and Density

One of the main challenges in the applicability of our solvents for CO_2 capture is the high viscosities of the ionic liquids formed by CO_2 absorption. However, the viscosity decreases significantly at higher temperatures as shown in the Quarter 7 report. Our preliminary experiments had shown that the viscosity is a non linear function of conversion (extent of chemisorption). In addition, the refractive index was found to be highly correlated to the conversion and hence the viscosity. In quarter 10, we performed extensive studies to systematically prove these findings.

<u>Viscosity</u>

Viscosity of each compound was measured using a Rheosys Merlin II Viscometer, located in our laboratory. The results for both the molecular and the ionic liquids were presented in the seventh quarterly report.

<u>Refractive Index</u>

The refractive indices for both the molecular and ionic liquid forms were measured using a Reichert Arias 500 Abbe-style refractometer, connected to a circulated cooling bath with glycol as the heat transfer fluid, enabling measurements from 0°C to 75°C. The refractometer is a semi-automatic design which eliminates the need for users to interpret the shadowline intercept, resulting in an accuracy of ±0.0001 regardless of user. This will prove important for establishing refractive index as a measure of conversion.

6- **Scrubber Process Design**

An ASPEN HYSYS 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_2 capture agents to meet the goal of 90% CO_2 capture with no more than a 30% increase in cost. We shall use the monoethanolamine (MEA) process as a basis for comparison, and alter the operating conditions to give us targets for the development of one component reversible ionic liquids. The parameters we seek to optimize are the CO_2 capture capacities, enthalpy of capture and release, capture and release temperatures, solvent boiling point and vaporization during regeneration, 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.
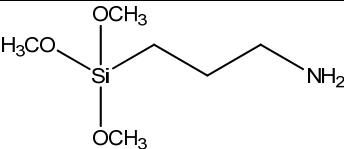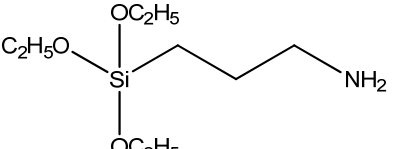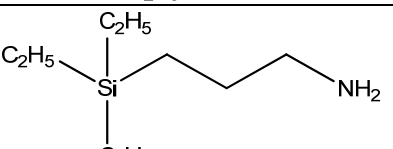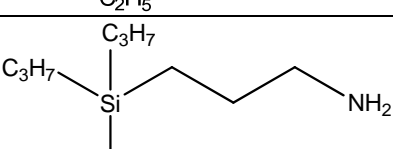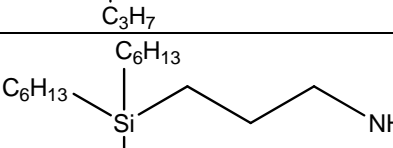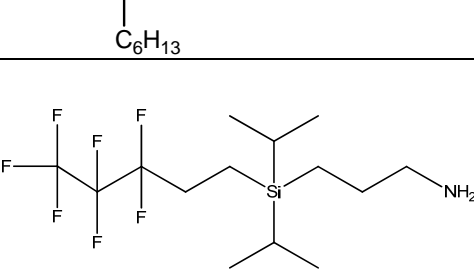
Additional design issues that we plan to consider in the future are the effects of the presence of SO_2, NO_2, and carryover gypsum particles from the scrubber in the gas. We believe that our reversible ionic liquids will also absorb SO_2, but the thermodynamics and kinetics have not yet been investigated. We suspect that the NO_2 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.
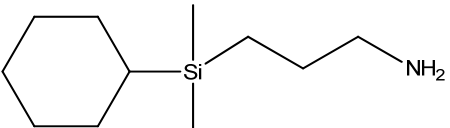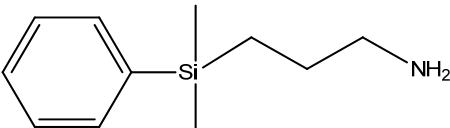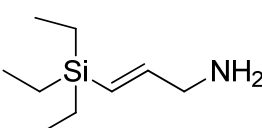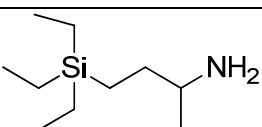
b. Results and Discussion

1- Synthesis and Characterization of Custom Reversible ILs

Till now, we have successfully performed synthesis, characterization, and analysis of ten compounds. These have been listed in Table 1.

Table 1 Molecular Liquid Library for Silyl-Amine based CO_2 capture solvents

Compound	Molecular liquid	Structure	Acronym
1	(3-aminopropyl) trimethoxysilane		TMSA
2	(3-aminopropyl) triethoxysilane		TESA
3	(3-aminopropyl) triethylsilane		TEtSA
4	(3-aminopropyl) tripropylsilane		TPSA
5	(3-aminopropyl) trihexylsilane		THSA
6	(3-aminopropyl) diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane		FSA

Compound	Molecular liquid	Structure	Acronym
7	(3-aminopropyl) cyclohexyldimethylsilane		CHDMSA
8	(3-aminopropyl) phenyldimethylsilane		PDMSA
9	(E)-3-(triethylsilyl)prop-2-en-1-amine		TEtPESA
10	4-(triethylsilyl) butan-2-amine		αM-TEtSA

2- Thermodynamics of CO$_2$ Capture

We have successfully calculated the equilibrium constants (K) for (3-aminopropyl) tripropylsilane at various temperatures. As mentioned in the approach section, this requires determination of equilibrium mole fractions of molecular and ionic liquid (Kc) and corrections for non-ideality of the system (Kγ). There are two regions in the IR spectrum that are used to determine molecular and ionic liquid mole fractions: the broad ammonium stretch vibration between 3100-2600 cm^{-1} and C=O stretch from the carbamate between 1740-1520 cm^{-1}. These regions are denoted Region I and Region III on the FT-IR spectrum of TPSA in Figure 3. The peak areas are used to determine the mole fractions using Beer-Lambert law. In Region I, contribution to the peak areas from the molecular liquid C-H stretch, ionic liquid C-H stretch,

13

and ammonium peak are considered. Likewise, in Region III the peak area is a result of the N-H

stretch of the molecular liquid as well as the overlapping carbamate stretch
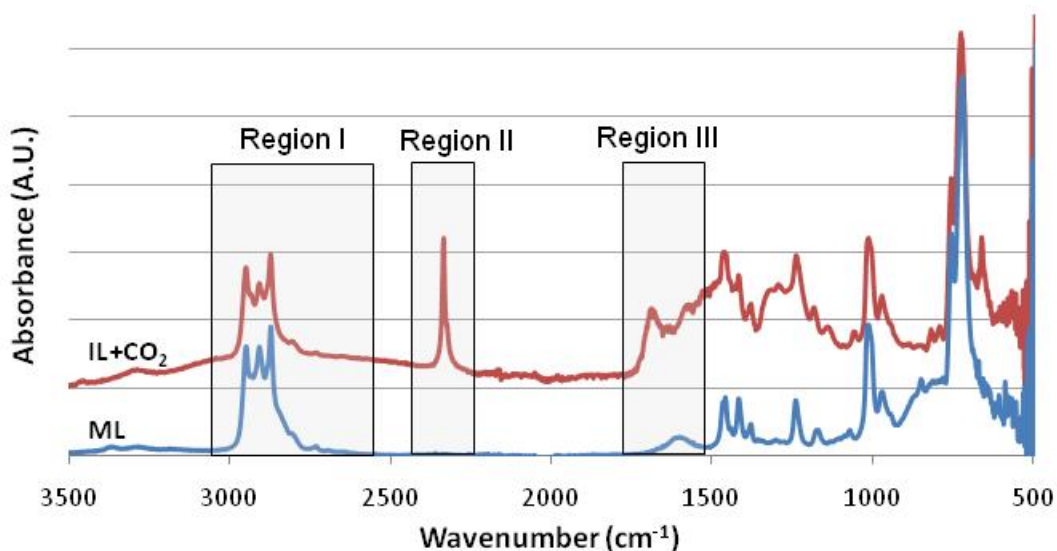
Figure 3: ATR-FTIR spectrum for TPSA (a) Blue: molecular liquid (b) Red: ionic liquid + physisorbed CO_2

Values for Kc at 60, 65, 70 and 80˚C, are shown below in

Table 2.

Temperature (°C)	X_{IL}	Kc
60	0.80	28.6
65	0.66	7.4
70	0.53	2.9
80	0.20	0.3

Table 2: Experimental values of Kc for TPSA

A linear plot between reciprocal temperature and log K (van't Hoff equation), is used to

determine the equilibrium constants and hence equilibrium conversions at other unknown

temperatures. The slope of the graph gives the reaction enthalpy. If Kc is plotted against the

reciprocal temperature, though the graph is linear, the slope gives enthalpy of -213 kJ/mol of

CO_2. As mentioned in the eighth quarterly report, enthalpy from DSC measurements is equal to -114 kJ/mol of CO_2. To avoid this discrepancy, we need to account for the non-ideal behavior of the system through $K\gamma$ described in the approach section. Data for $K\gamma$ was obtained using COSMO-RS through collaboration[4] *beyond this DOE project*. Table 3 lists the values of $K\gamma$ corresponding to the four Kc values reported in Table 2.

Temperature (°C)	x_{IL}	$K\gamma$
60	0.8	0.1
65	0.66	0.21
70	0.53	0.35
80	0.2	0.98

Table 3: Values of $K\gamma$ for TPSA Calculated Using COSMO-RS

The equilibrium constants K calculated as the product of Kc and $K\gamma$ were plotted against reciprocal temperature as shown below in Figure 4. The heat of reaction as calculated from the plot is equal to -111 kJ/mol of CO_2. This value falls within the experimental error of the DSC value of -114 kJ/mol of CO_2. The data validates this approach for calculating the equilibrium constants at various temperatures. These experiments aid in the thermodynamic optimization of the system as it illustrates the conversion at elevated temperatures and can be used for the determination of an optimal temperature for the stripping tower.

---

[4] Calculations were jointly performed by researchers from the Eckert-Liotta group at Georgia Institute of technology and Palomar and Rodriguez group from Universidad Complutense de Madrid & Universidad Autónoma de Madrid.
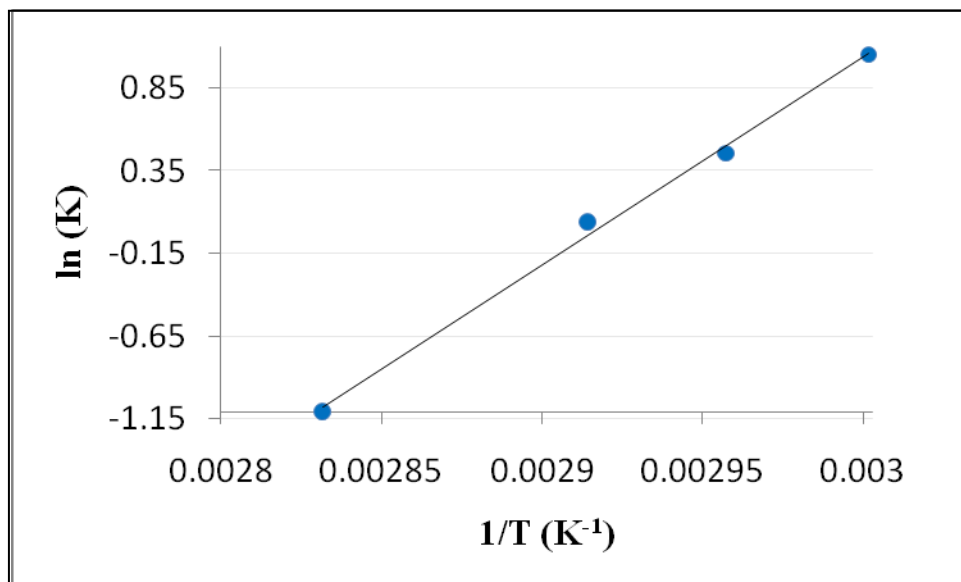
Figure 4: van't Hoff Plot of TPSA

3- CO_2 Capture Capacities

In previous quarters we have reported both on the equilibrium capacities and Henry's Law constants of our silyl-amines. A few improvements have been made to the experimental techniques, and refinements have been to both gravimetric capacities and physisorption results. Gravimetric capacities have been discussed in detail with the results for Mass transfer and Kinetics.

Figure 5 shows the mole fraction of physisorbed CO_2 in TPSA as a function of pressure calculated using asymmetric CO_2 stretch in FT-IR.
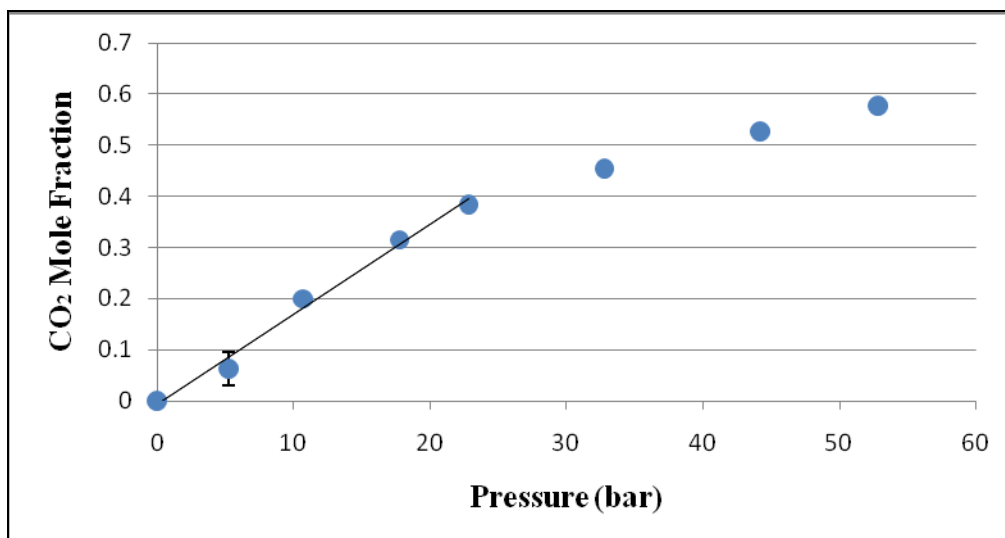
Figure 5: Mole fraction of CO_2 in TPSA as a function of pressure at 35°C

Ionic Liquid	Henry's Constant (bar)
TEtSA	73±9
TPSA	60±7
THSA	43±4
FSA	44±6

Table 4-Henry's constants for ionic liquids at 35°C

Henry's law is applicable at low concentrations, where solute-solute interactions are negligible. The straight line in the figure shows the applicability of Henry's Law up to $x_{CO2} \sim 0.4$ (25 bar CO_2). Henry's law constants are calculated as the reciprocal of the slope in the above graph. Refined results for the four reversible ionic liquids at 35°C are presented in

Table 4. The solubility of CO_2 in the ionic liquids increases with decreasing temperature. At 25°C the Henry's Law constant for TPSA was found to be 49 bar. Our technique was validated by comparing the literature value of Henry's Law constant of CO_2 in the conventional

ionic liquid, [Bmim][PF$_6$], against the one found from our FT-IR technique. At 25°C, our experiments show a value of 58 bar, which is consistent with the reported value of 53.4 bar[5].

4- Kinetics and Mass Transfer

In Quarter 10, we reported that the reaction of CO_2 with silylamines is instantaneous and the absorption times are limited by mass transfer. In this quarter, we have further explored effects of parameters such as CO_2 flowrate, and the medium of introduction of CO_2: 18 gauge needle and a diffuser tube.

CO$_2$ Flowrate: CO_2 was sparged through TPSA molecular liquid for 60 seconds at 25°C through an 18 gauge needle at flowrates from 200 to 1340 ml/min, and CO_2 uptake was measured gravimetrically. Figure 6 shows that the CO_2 uptake increases from 0.86 mol CO_2/kg ML at 200 ml/min CO_2, to 2.15 mol CO_2/kg ML at 1340 ml/min CO_2. The maximum chemisorption limit for TPSA is 2.32 mol CO_2/kg ML. At all the the flowrates, CO_2 was introduced in significant excess as to obtain the chemisorption limit, only 74 ml of CO_2 at STP is required. This suggests that the increased aggitation due to increased flowrate increases the rate of CO_2 uptake. Hence the process is mass transfer limited.

---

[5] Jessica L. Anderson, Janeille K. Dixon, and Joan F. Brennecke, *Acc. Chem. Res.* **2007,** *40,* 1208–1216
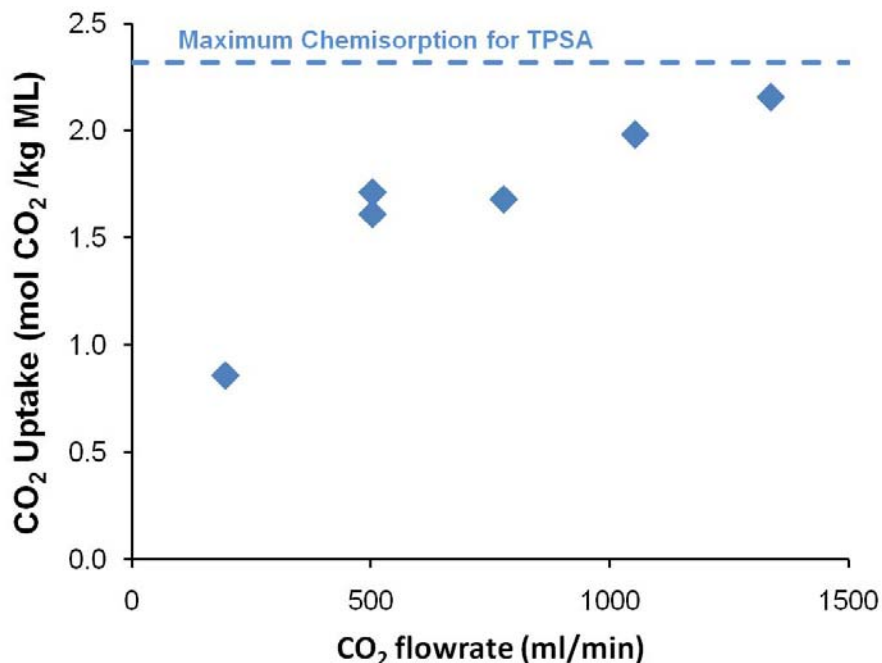
Figure 6: CO_2 uptake in TPSA in 60 sec as a function of CO_2 flowrate. Conditions: 25°C, pure CO_2, needle. Theoretical maximum chemisorption at 2.32 mol CO_2/kg ML indicated by dashed line.

Diffuser Tube Studies: In the last quarter, we showed that in 1 minute, TPSA at room temperature absorbed nearly thrice as much CO_2 when CO_2 was introduced through a diffuser tube as compared to an 18 gauge needle, at a constant CO_2 flowrate of 200 ml/min. Diffuser tube allows better CO_2 dispersion, and hence enhanced mass transfer. CO_2 uptake comparison over a longer period of time is shown in Figure 7. Complete theoretical chemical conversion was achieved in less than 90 seconds when the diffuser tube was used compared to 300 seconds with the needle. Even beyond this, the CO_2 uptake through diffuser tube continued to exceed that through a needle and at 75 minutes maximum CO_2 uptake for the samples were 2.99 mol CO_2/kg ML through the tube and 2.71 mol CO_2/kg ML for the needle.
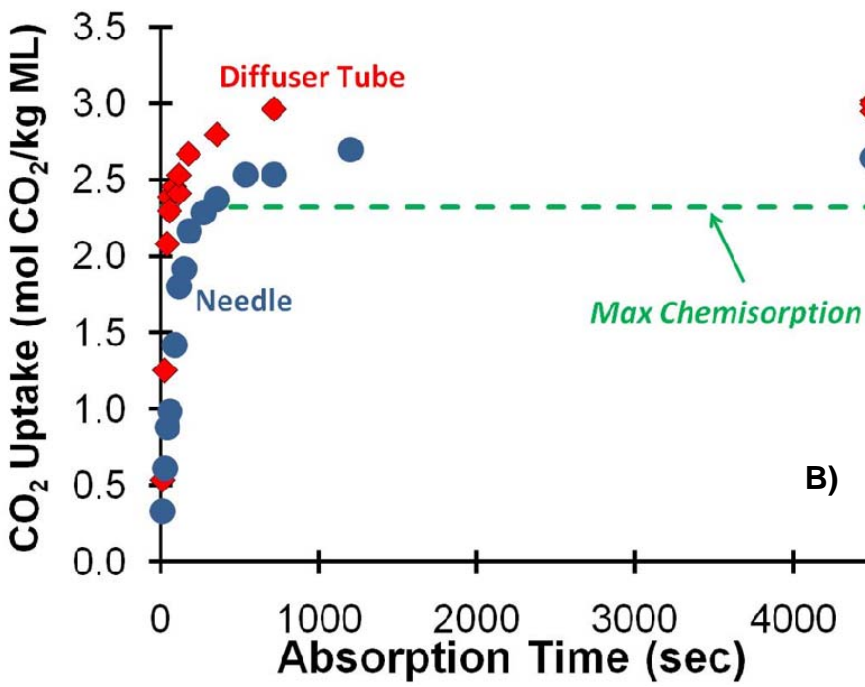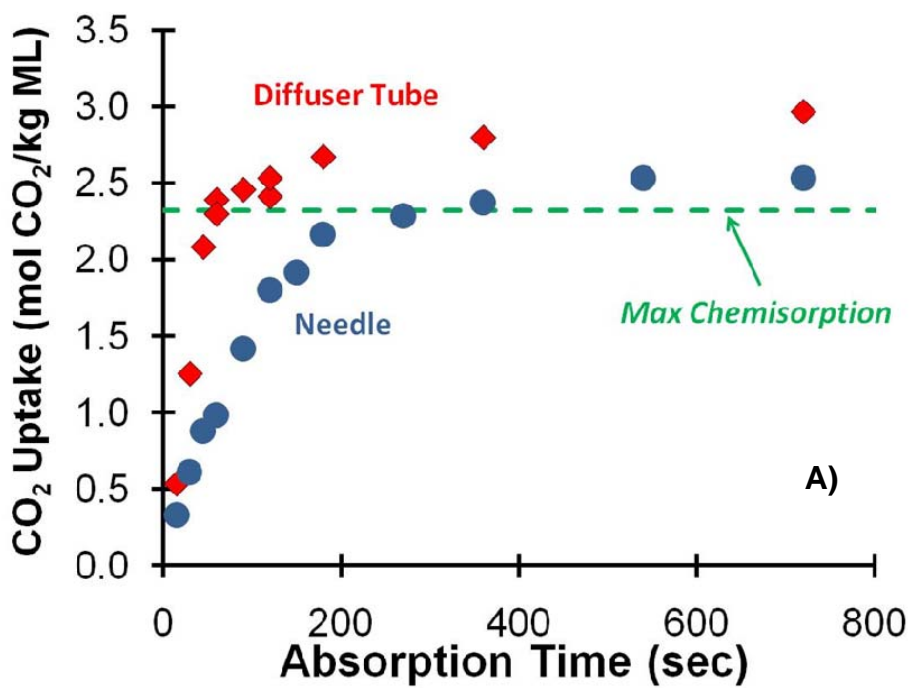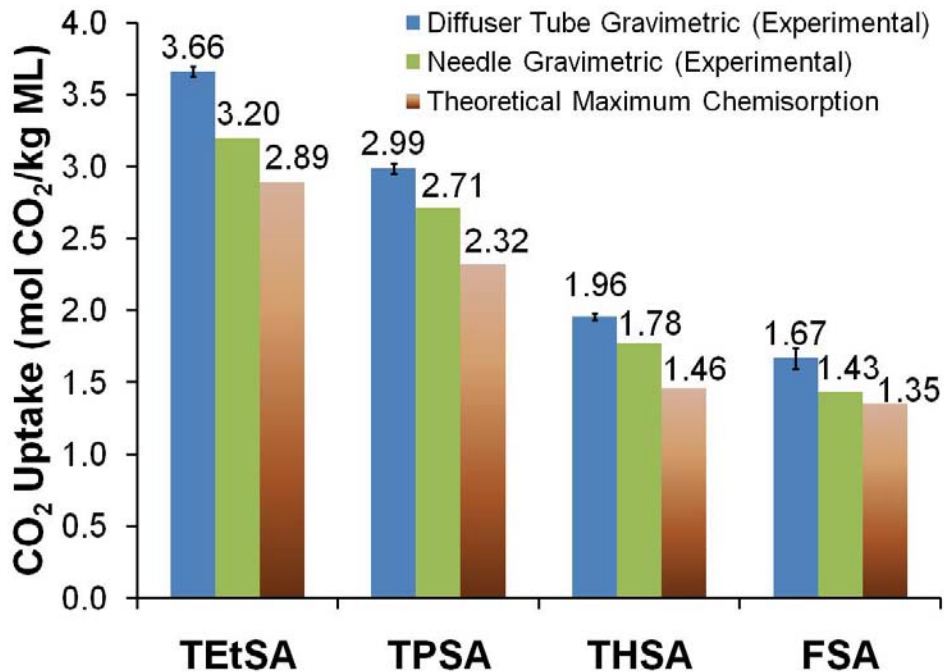
Figure 7: Comparison of diffuser tube (red diamonds) to needle (blue circles) CO_2 introduction methods as a function of time in TPSA. 200 ml/min pure CO_2, 25°C. Green dashed line indicates theoretical maximum chemisorption for TPSA. A) 15-seconds - 12 minutes. B) 15 seconds – 75 minutes.

Figure 8: CO$_2$ uptake comparison for select RevILs using both diffuser tube and needle CO$_2$ introduction methods. 25°C, 200 ml/min pure CO$_2$.

Comparison of Gravimetric Results to Thermodynamic Predictions. Comparison of theoretical chemisorption, CO$_2$ uptake through diffuser tube, and through an 18 gauge needle are given in Figure 8. Both the needle and diffuser tube gravimetric results significantly exceed the complete conversion to RevIL value. For TPSA, if we include 0.047 mol CO$_2$/kg ML of physisorption at 25°C measured by FT-IR, the combined physisorption and chemisorption should equal 2.37 mol CO$_2$/ kg ML. However, from gravimetric analyses, CO$_2$ uptake is much higher: 2.99 mol CO$_2$/kg ML through the tube and 2.71 mol CO$_2$/kg ML for the needle. Although this is highly advantageous for CO$_2$ capture from flue gas, fundamental understanding of the causal mechnism is required to fully utilize this. There are three proposed possibilities which we will try to explore in the next quarter:

1) CO$_2$ entrainment of bubbles in the viscous ionic liquid.

2) Additional chemical reaction of CO$_2$ to form a specie other than carbamate ion.

3) Moisture being introduced into the experimental system, increasing the CO_2 uptake by additional reaction with water to form carbonates and bicarbonates.

c. Conclusion

We continue to make substantial progress towards helping the DOE achieve the goal of 90% CO_2 capture with no more than a 30% increase in cost by 2020. In the 11th Quarter of the project, we have focused on refining the results for thermodynamics of our systems, and studying the effects of mass transfer on the CO_2 absorption in our silyl-amine solvents.

We have successfully calculated the equilibrium constants for (3-aminopropyl) tripropylsilane (TPSA) at four different temperatures and verified it using the vant Hoff's plot (**TASK 4.**) In addition, the results of Physisorption were refined and the physisorption calculation methodology was verified by comparing the results for a conventional ionic liquid ([Bmim][PF_6]) (**TASK 4.**) To further illustrate the influence of mass transfer on CO_2 absorption (**TASK 5,**) detailed studies were performed where the flowrate of CO_2, and the method of introduction of CO_2 were altered. Since at all the flowrates that we studied, we had excess of CO_2, faster absorption at higher flowrates was attributed to enhanced mixing (and hence enhanced mass transfer.) Diffuser tube resulted in faster and greater amount of CO_2 absorption. The overall CO_2 capture capacities were found to exceed the combined physisorption and chemisorption. Several alternate explanations of this have been proposed and will be investigated in future.

The data now being collected are giving insights to help us further modify the structure of our compounds for enhanced properties for CO_2 capture from coal-fired power plants. We hypothesize that the silyl-amine reversible ionic liquid candidates are far superior to the one

component guanidine reversible ionic liquids (**TASK 3**), and owing to their dual absorption mechanism are proving to be very promising candidates for commercializable CO_2 capture solvents.

6. Cost Status

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

1. Milestone Status

The milestones listed in the Project Management Plan for Years One and Two were 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
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	06/30/10	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	9/30/10	Progress Report describing thermodynamics of formation of new single-component silyl

	reversible ionic liquid and one new single-component silyl guanidine-based reversible ionic liquid.		amine-based and single-component silyl guanidine-based reversible ionic liquids
G	1-Component Silyl Guanidine-Based ILs	02/28/11	Synthesis and Characterization results documented in Progress Report
H	Complete laboratory measurements of the rates of formation of one new single-component silyl amine-based reversible ionic liquid and one new single-component silyl guanidine-based reversible ionic liquid.	3/30/11	Progress Report describing rates of formation of new single-component silyl amine-based and single-component silyl guanidine-based reversible ionic liquids
I	Thermo & Rates of IL Formation	6/30/11	Test results documented in Progress Report

In year one, Milestone A was completed on schedule with the approval of the Project Management Plan. Milestone B was completed ahead of schedule, with the complete laboratory synthesis and characterization of four new single-component silyl-amine-based reversible ionic liquids. For Milestone C we proposed to synthesize and characterize a silyl-guanidine based reversible ionic liquid. However, before we achieved this goal, reports came from the Jessop group at Queen's University in Canada showed that the guanidine based RevILs are unsuitable for CO_2 capture because only very high MW compounds are in fact liquids – thereby offering extremely low capacities. We discussed this in our Quarter 6 Report, and are now focusing solely on the silyl-amine-based reversible ionic liquids.

In year two, for milestone D, we reported the complete laboratory synthesis and characterization of 3 more (6 total) new single-component silyl-amine-based reversible ionic liquids in the Progress Reports for Quarter 6 & 7. Subsequently, we realized that TEtSA, which is the compound with highest CO_2 capture capacity (moles of CO_2/kg solvent), is solid just below room temperature. In order to reduce the melting point of TEtSA, we introduced further changes in structure and synthesized four new compounds in Quarter 8 and Quarter 9, taking the tally to

ten silyl-amine solvents for milestone E. In Quarter 7, we had also reported the viscosities and refractive indices of six compounds both in molecular and ionic forms. In Quarter 8, we went ahead of our schedule (Milestone F) by measuring the physical absorption capacities of six silyl-amine compounds and other important thermodynamic properties (regeneration enthalpies and reversal temperature) for three alkyl substituted silyl-amines.

In Quarter 9 (year three), we presented the thermodynamics and capture capacities of Fluorinated silyl-amine (FSA) solvent along with further insights into the reversion temperature and recylcability of the solvent in CO_2 capture process (Milestone F). In Quarter 10, we completed Milestone H in time by showing the rate of formation of TPSA ionic liquid is dominated by the mass transfer between CO_2 and the ionic liquid/molecular liquid mixture. Finally, in this quarter we have successfully calculated the equilibrium constant of reaction of CO_2 with TPSA molecular liquid to give ionic liquid. This allows us to determine the extent of reaction at different temperatures and is an essential parameter for deciding the operating temperature of the stripping tower. We have also illustrated that faster and greater amount of CO_2 absorption using a diffuser tube. With these results, we have completely studied the thermodynamics, kinetics and mass transfer of CO_2 absorption (Milestone I).

As discussed in Quarter 6 progress report, we will not continue with Milestone G as it involves the guanidine based solvents. We have also started making progress towards Milestones K and L by studying the absorption capacities in simulated flue gas, recyclability, and interactions with water for our silyl-amines.

2. Summary of Significant Accomplishments

The significant accomplishments are:

- Measurement of equilibrium constants of CO_2 capture reaction at various temperatures.

- Refinement of physisorption results due to improved experimental technique.

- Validation of FT-IR methodology for CO_2 physisorption by comparison of our experimental results with the literature values for the Henry's Law constants of CO_2 in a conventional ionic liquid Bmim[PF$_6$].

- Study of effects of mass transfer on absorption times and capacity by diffuser tube and flowrate studies.

- Recent advances have resulted in submittals for publications in scientific journals and presentations at scientific conferences.

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

We do not anticipate any future problems or delays.

Products produced

a. Publications

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*, **89**, 1315–1319, 2010.

Vittoria M. Blasucci, Ryan Hart, Pamela Pollet, Charles L. Liotta, and Charles A. Eckert, "Reversible Ionic Liquids Designed for Facile Separations," *Fluid Phase Equilibria*, **294,** 1-6, 2010.

Ryan Hart, Pamela Pollet, Dominique J. Hahne, Ejae John, Veronica Llopis-Mestre, Vittoria Blasucci, Hillary Huttenhower, Walter Leitner, Charles A. Eckert, and Charles L. Liotta, "Benign Coupling of Reactions and Separations with Reversible Ionic Liquids," *Tetrahedron,* **66**, 1082-1090, 2010.

b.   Presentations

1- *Invited papers:*

Charles A. Eckert and Charles L. Liotta, "Reversible Ionic Liquids as Double-Action Solvents for CO_2 Capture," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, September 13, 2010.

Charles A. Eckert and Charles L. Liotta, "Reversible Ionic Liquids as Double-Action Solvents for CO2 Capture," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 24, 2009.

Ryan Hart, Charles L. Liotta and Charles A. Eckert, "Molecular Design of Liquid Sorbents for CO_2 Capture," Georgia Tech CO_2 Forum, September 2009

Charles A. Eckert, Ryan Hart, Vittoria Blasucci, Pamela Pollet, and Charles L. Liotta, "Smart" Solvents for Extractions and Purifications, Annual AIChE Meeting, Nashville, TN, November, 2009.

Charles A. Eckert and Charles L. Liotta, "Novel Solvents for Sustainable Technology," Basore Distinguished Lecture, Auburn University, January 2010

Charles L. Liotta and Charles A. Eckert, "Solvent Systems for Green and Sustainable Chemical Processes," BASF, Wyandotte, MI, March 18, 2010

Charles L. Liotta and Charles A. Eckert, "Solvent Systems for Green and Sustainable Chemical Processes," Virginia Commonwealth University, Richmond, VA, March 31, 2010

Charles L. Liotta and Charles A. Eckert, "Solvent Systems for Green and Sustainable Chemical Processes," Chemistry Department, U. Texas, Dallas, Wyandotte, TX, April 8, 2010.

Charles A. Eckert, Charles L. Liotta, Pamela Pollet, Ryan Hart, "Provoking Phase Changes for Extractive Separations," AIChE Annual Meeting, Salt Lake City, UT, November, 2010.

2- *Contributed Papers:*

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 CO_2 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.

Ryan Hart, Pamela Pollet, Dominique J. Hahne, Ejae John, Veronica Llopis-Mestre, Vittoria Blasucci, Hillary Huttenhower, Walter Leitner, Charles A. Eckert, Charles L. Liotta, "A Unique Class of Sustainable Solvents: Reversible Ionic Liquids," ACS Spring Meeting, March 21 – 25, 2010, San Francisco.

Cerag Dilek, Vittoria Blasucci, Ali Fadhel, Kyle Flack, Ryan Hart, Hillary Huttenhower, Kristen Kitagawa, Veronica Llopis-Mestre, Pamela Pollet, Manjusha Verma, Eduardo Vyhmeister, Charles L. Liotta, and Charles A. Eckert, "Reversible Ionic Liquids as Dual Functional Solvents for Post Combustion CO_2 Capture " 6th Chemical Engineering Conference for Collaborative Research in Eastern Mediterranean Countries (EMCC6), March 2010, Antalya-Turkey.

Rani Jha, Ali Fadhel, Vittoria Blasucci, Ryan Hart, Veronica Llopis-Mestre, Pamela Pollet, Charles L. Liotta, Charles A. Eckert, "Designer Reversible Ionic Liquids for CO_2 Capture," Fall National Meeting, ACS, Boston MA, August, 2010.

Ryan Hart, Kyle Flack, Jackson Switzer, Amy Rohan, Manjusha Verma, Charles L. Liotta, and Charles A. Eckert, "The Design of Reversible Ionic Liquids for Post-Combustion CO_2 Recovery," AIChE Annual Meeting, Salt Lake City, November 2010.

Amy Rohan, Swetha Sivaswamy, Ryan Hart, Pamela Pollet, Manish Talreja, Elizabeth Biddinger, Jackson Switzer, Kyle Flack, Manjusha Verma, Charles Liotta, and Charles Eckert, "Novel CO_2 Captue Solvent System," 2010 Strategic Energy Institute Energy Symposium, Atlanta, GA, December 6, 2010.

R. Hart, A. Fadhel, V. Blasucci, P. Pollet, C. A. Eckert, C. L. Liotta, "Design and development of one-component reversible ionic liquids for post-combustion CO2 capture." ACS PacifiChem, Honolulu, December, 2010.

Jackson R. Switzer, Amy L. Rohan, Ryan J. Hart, Pamela Pollet, Charles L. Liotta, Charles A. Eckert, "A Spectroscopic Technique for the Decoupled Measurement of Physical and Chemical Absorption in Reactive Solvent Systems," Pittcon, Atlanta, GA, March 13-18, 2011.

Swetha Sivaswamy, Ryan Hart, Kyle Flack, Amy Rohan, Jackson Switzer, Manjusha Verma, Elizabeth Biddinger, Manish Talreja, Pamela Pollet, Charles Liotta and Charles Eckert, " Reversible ionic liquids for carbon dioxide capture," ACS Meeting, Anaheim, CA, March 2011

Jackson Switzer, Kyle Flack, Ryan Hart, Amy Rohan, Swetha Sivaswamy, Elizabeth Biddinger, Manish Talreja, Manjusha Verma, Pamela Pollet, Charles Liotta, Charles Eckert, " Design of Dual-Capture CO_2 Solvents using Structure-Property Relationships," 2011 Georgia Tech Research and Innovation Conference (Poster).

Amy Rohan, Ryan Hart, Kyle Flack, Swetha Sivaswamy, Jackson Switzer, Elizabeth Biddinger, Manish Talreja, Pamela Pollet, Charles Liotta and Charles Eckert, " Advance of Reversible Silylamine-Based Ionic Liquids for Post-Combustion CO_2 Capture from Coal-Fired Power Plants," 2011 Georgia Tech Research and Innovation Conference (Poster).

Amy Rohan, Ryan Hart, Kyle Flack, Swetha Sivaswamy, Jackson Switzer, Elizabeth Biddinger, Manish Talreja, Pamela Pollet, Charles Liotta and Charles Eckert, " Use of Reversible Ionic

Liquids as Solvents for Post-Combustion Recovery of CO_2 from Coal-Fired Power Plants," AIChE National Meeting, Chicago, IL, March 2011.

Website

Webpages have been prepared and posted within the Eckert/Liotta group website

http://www.chbe.gatech.edu/eckert/projects.html.

c. Intellectual Property

Two invention disclosures based on the work of this project have been filed:

Eckert, C.A., Liotta, C.L., Huttenhower, H.; Mestre-Llopes, V.; Blasucci, V.; Pollet, P.; "Reversible Ionic Liquids as Double Action Solvents for Efficient CO_2 Capture", Invention disclosure 9/29/2008.

Hart, R.; Flack, K.; Switzer, J.; Pollet, P.; Eckert, C.; Liotta, C. "Substituted (Trialkylsilyl)-alkylpropylamine Reversible Ionic Liquids Systems." Invention Disclosure 4/14/2011

d. Education

A major thrust of this project is the education of our future scientists and engineers who will be working in the environmental area developing sustainable processes. We are pleased to report our contributions in this area:

Personnel/Students Graduated

Ryan Adams, (Chemical Engineering, Postdoctoral - Now at Algenol)

Vittoria Blasucci – PhD in Chemical Engineering, 2009 – Now at ExxonMobil

Olga Dzenis (MS in Chemical Engineering, 2011)

Ali Fahdel (PhD in Chemical Engineering, 2010 - Now at GE)

Ryan Hart (PhD in Chemical Engineering, 2010 – Now at Exponent)

Hillary Huttenhower – PhD in Chemistry, 2010 – Now at Pratt & Whitney

Paul Nielsen – BS in Chemical Engineering, 2011 – Now at University of Texas

Personnel/Students Continuing

Dr. Pamela Pollet (Chemistry, Research Scientist)

Dr. Elizabeth Biddinger, (Chemical Engineering, Postdoctoral)

Dr. Rani Jha, (Chemistry, Postdoctoral)

Dr. Manish Talreja, (Chemical Engineering, Postdoctoral)

Dr. Manjusha Verma, (Chemistry, Postdoctoral)

Kyle Flack (PhD Candidate, Chemistry)

Greg Marus (PhD Candidate, Chemical Engineering)

Farhana Momin (MS student, Chemical Engineering)

Emily Nixon (PhD Candidate, Chemistry)

Amy Rohan (PhD Candidate, Chemical Engineering)

Amber Rumple (PhD Student, Chemical Engineering)

Swetha Sivaswamy (PhD Candidate, Chemical Engineering)

Jackson Switzer (PhD Candidate, Chemical Engineering)

Melissa Burlager (Senior, Chemical Engineering)

Jordan Donaldson (Sophomore, Chemical Engineering)

Sean Faltermeier (Senior, Chemical Engineering)

Poomrapee Jewanarom (Sophomore, Chemical Engineering)

e. Industrial Collaboration

As a result of our work on this project we have generated an industrial collaboration with ConocoPhillips, who have agreed to partner with us for the next three years. This not only provides for facile technology transfer, but gives us enhanced access to real-world problems and opportunities. And of course, it provides a vehicle for future testing and implementation.

Third-year ChBE PhD student Swetha Sivaswamy is spending the summer semester in Bartlesville working on aspects of this problem with ConocoPhilips.

f. Academic Collaboration

We have collaborated with Francisco Rodríguez and Jose Palomar from Universidad Complutense de Madrid and Universidad Autónoma de Madrid, respectively. They specialize in using COSMO-RS for estimating the thermodynamic properties of the systems based on just the structural information of the components of the system. In this report we have shown how we have successfully integrated the COSMO-RS estimates with the FT-IR results for the calculation of equilibrium constants. The collaboration is *not part of the current DOE project* but complements the work in the project.