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:	April 30th 2011
Period covered:	January 1st, 2011 –March 31st, 2011 (Budget Period 3 – Q2)

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 are designing, testing, and optimizing 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 the tenth quarter include:

- We have performed characterization, and absorption and viscosity measurements for 4-(triethylsilyl) butan-2-amine (αM-TEtSA), thus establishing the effects of steric hindrance near the amine on the CO_2 capture behavior. **(TASK 2 and TASK 5)**
- We have studied absorption with a simulated flue gas mixture (CO_2+N_2) for (3-aminopropyl) tripropylsilane (TPSA). **(TASK 2 and TASK 5)**
- We have performed detailed analysis of recyclability of (3-aminopropyl) tripropylsilane (TPSA) to ascertain its applicability in the actual CO_2 capture process. (**TASK 5**)
- We have also analyzed the effects of kinetics and mass transfer on CO_2 absorption times. (**TASK 5**)
- Finally, we have studied the effect of water on our silyl-amines (**TASK 5**).

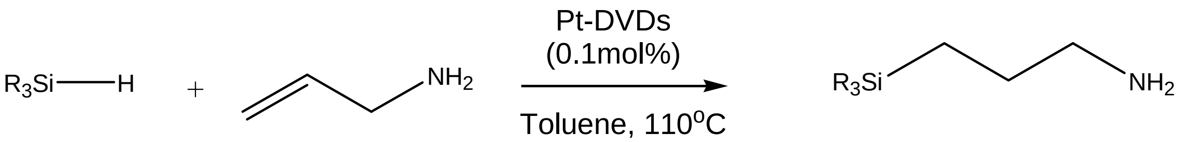
Our goal remains to minimize the cost and energy requirements of CO_2 capture to help DOE meet its goal – 90% CO_2 capture with no more than a 30% increase in cost by 2020.

5. Results of Work

a. Approach

1- Synthesis and Characterization of Custom Reversible ILs

One of the important requirements of a 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).



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 introduce changes systematically to the structure and to improve the properties for CO_2 capture application.

Through the knowledge gained from the compounds synthesized using Scheme I, we identified several other molecular structures that might offer improved properties for the CO_2 absorption process. In Scheme II (Figure 2) we introduced a methyl group at α C from NH_2 for steric hindrance. This requires a long synthetic route and we do not recommend this for the actual optimum CO_2 capture solvent. However, it does elucidate the effects of steric hindrance near the amine on the thermodynamics, capture capacities, and viscosities, which will help us in understanding the structure-property relationships better.

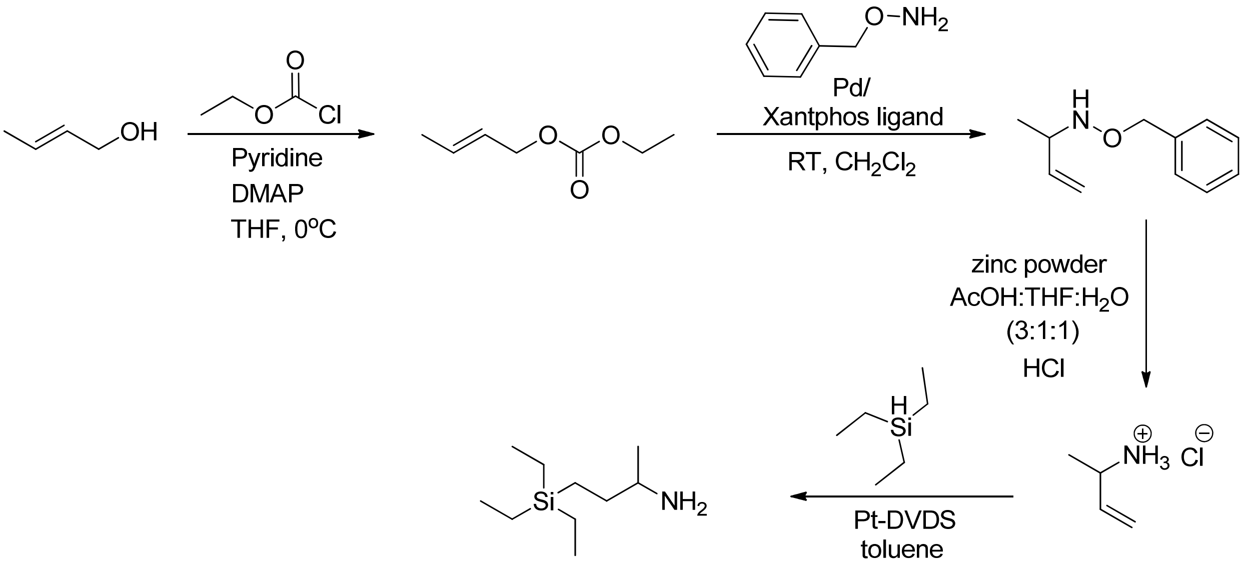


Figure 2: Scheme II for synthesis of silyl-amine based RevILs

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 3). The resulting ionic species (liquid or solid) was characterized by ^1H and ^{13}C NMR, melting point (if applicable), FT-IR, and solvatochromatic measurements.

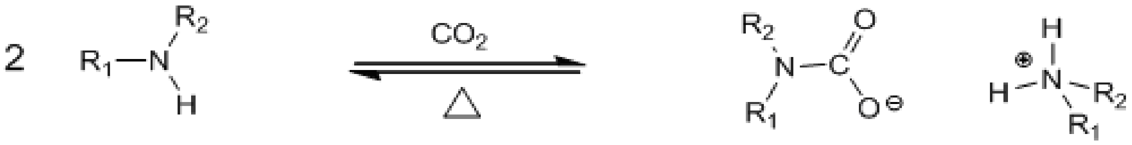


Figure 3: Reaction of custom-made amine with CO_2 to form reversible ionic liquids.

The loss 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

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

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},

$$Q = mC_p \, \Delta T \tag{2}$$

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.

$$K(T) = \frac{\gamma_{IL} x_{IL}}{(\gamma_{ML} x_{ML})^2 \gamma_{CO2} x_{CO2}} \tag{3}$$

where x_i is the mole fraction of the species and γ_i the activity coefficient. In evaluating K(T), we use the conversion of the molecular liquid to ionic liquid as well as the dissolved CO_2 concentration as measured by the FT-IR. We adapt standard methods of solution theory to these systems to account for the nonideality of the mixture (deviations from Raoult's Law) to reflect the highly polar nature of the liquid phase and the dissimilarity of the molecules in the system (CO_2, the amine precursor, and the highly polar and viscous ionic liquid).

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 CO_2 absorption capacity, both used for the determination of the thermodynamic properties of the solvent***.

The evaluation of the equilibrium constant involves the estimation of the activity coefficient (γ) with excess Gibbs energy models. Conventionally, one first uses the binary interaction parameters obtained from experimental Vapor-Liquid Equilibria (VLE) data for each pair of system components to estimate the γ for ternary systems. These models contain one or more adjustable parameters that are optimized to best fit the experimental data. However, such a method is not viable here, at least in part because reversible ionic liquid is formed only in the presence of the molecular liquid and CO_2. We are developing a unique approach to estimate the ternary system activity coefficients based on published data and thermodynamic models for ionic liquids-CO_2, organics-ionic liquids, electrolyte solutions, and ternary systems including variations of these components.

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 5C/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, ewith minimal increase in the process costs. The amount of CO_2 captured through chemisorption (reaction with the amine) is determined by 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.

Additionally, we shall react the molecular liquids with ^{13}C labeled CO_2 to differentiate and quantify the chemisorbed and physisorbed CO_2 present in the reversible ionic liquid using

NMR. Also, we are using attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectroscopy to determine ***simultaneous measurement of chemical and physical CO_2 absorption capacity***. Results from quantitative ^{13}C NMR experiments and FTIR experiment will be cross-examined.

The NMR used is a Bruker AMX 400 located in the School of Chemistry and Biochemistry at Georgia Tech. 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. Although the scrubbing will be carried out at near atmospheric pressure, the pressure range of the instrument permits us to ascertain better the effect of CO_2 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.

We have performed two types of measurements using our FT-IR. In the first set, we placed the molecular precursor in the ATR cell and pressurized it with CO_2 at different temperature and pressure conditions. This allows us to make simultaneous measurements of concentration of molecular liquid, ionic liquid, and CO_2. Data from these experiments will be presented in the subsequent quarterly progress reports.

In the second set, we put the preformed ionic liquids in the ATR cell and measured the solubility of free CO_2 as a function of CO_2 pressure; these results determine the Henry's law constants. 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 v_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. For the analysis, we also require density, refractive index, and molar absorptivity of the ionic liquid.

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 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 this quarter, we have performed extensive studies to systematically prove these findings. We have controlled conversion through the CO_2 bubbling time and measured it using gravimetric technique, and then related it to the refractive indices and viscosity.

Viscosity

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.

Refractive Index

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- Effect of Water

One of the major challenges in the ethanolamine based CO_2 capture solvent systems is the large quantities of water (70-80% by weight) used to bring down the viscosity and minimize amine degradation[1]. This results in a large parasitic energy requirement (165 KJ/mol of CO_2)[1] for heating water during regeneration as well as for separating CO_2 and steam in the exit stream of the stripper. However, some water will always be present because of water in the flue gas. In fact, in small quantities of water prove beneficial in improving the CO_2 capture capacity due to the formation of extra bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}). In addition, the presence

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[1] J.T. Yeh, H.W. Pennline, K.P. Resnik, Study of CO2 Absorption and Desorption in a Packed Column, Energy & Fuels, 15 (2001) 274-278.

of water also brings down the viscosity of the ionic liquid and hence the pumping costs. Upon reversal of the ionic liquid-water mixture, any excess water might phase-separate which can be decanted off and the water-saturated molecular liquid can be returned to the absorber for CO_2 capture. Identifying this, equilibrium water concentration in the molecular liquid-water and ionic liquid-water mixtures will be useful for further studying and modeling the CO_2 capture process.

Water content in the distilled molecular liquids and water solubility in the molecular liquids was analyzed using a Metrohm 852 Titrando Volumetric Karl Fischer Titration system. The Hydranal Composite 5 (Fluka) titer was determined using a 10.0 water standard (10.0 mg H_2O/g solution). The methanol working solution was buffered with salicylic acid for the presence of the amine-containing molecular liquids. Approximately 1g of synthesized molecular liquid was injected into the volumetric cell for a single analysis. Results were replicated, with a 10.0 water standard being run between samples to verify the result and the stability of the buffered system. For the water solubility analyses, 0.2-0.3 g of water-saturated molecular liquid was injected into the volumetric cell for single analysis and replicated with 10.0 water standards being run between samples. For the determining the water solubility in ionic liquid we plan to use D_2O in FT-IR. The concentration of ionic and molecular liquid in water rich phases will be determined using titration. The details of this will be discussed in subsequent quarters.

7- Scrubber Process Design

An ASPEN simulation to treat a ***model coal-fired power plant flue gas stream has been developed and validation with existing literature data is underway***. Initially, the model will be used to evaluate targets for our CO_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.

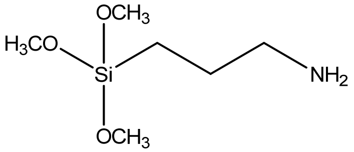
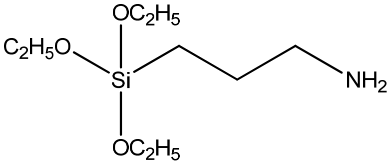
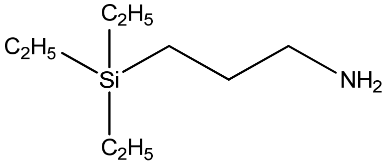
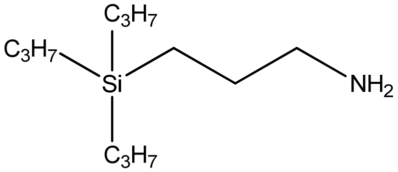
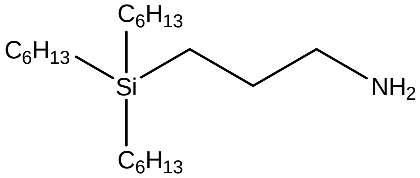
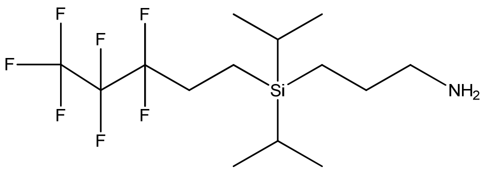
Additional design issues that we plan to consider in the future are the effects of the presence of SO_2, NO_2, and carryover gypsum particles from the scrubber in the gas. We believe that our reversible ionic liquids will also absorb SO_2, but the thermodynamics and kinetics have not yet been investigated. 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.

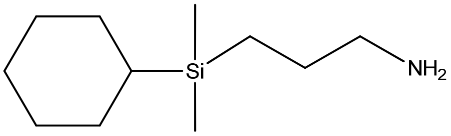
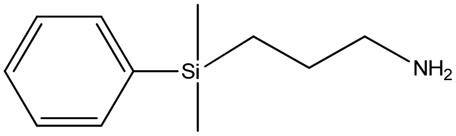
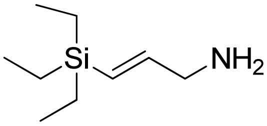
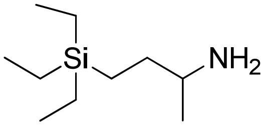
b. Results and Discussion

1- Synthesis and Characterization of Custom Reversible ILs

In quarter nine, we had reported successful synthesis of three new compounds, taking the number of compounds analyzed to ten. These have been listed in Table 1. In this quarter we have completed the characterization of 4-(triethylsilyl) butan-2-amine (compound 10), results for which are reported below.

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

Characterization: Compound 10. 4-(triethylsilyl) butan-2-amine (αM-TEtSA).

NMR Data:

αM-TEtSA Molecular Liquid ^{1}H: 2.77(sex, 1); 1.41(s,br, 2); 1.27(m,2); 1.03(d,3); 0.91(t,9); 0.48(q,8)

αM-TEtSA Molecular Liquid ^{13}C: 49.76, 34.21, 23.29, 7.53, 7.41, 3.18

Distillation Temperature: 45°C under vacuum

Elemental Analysis: Will be presented in the next quarterly report

Infrared Spectra:

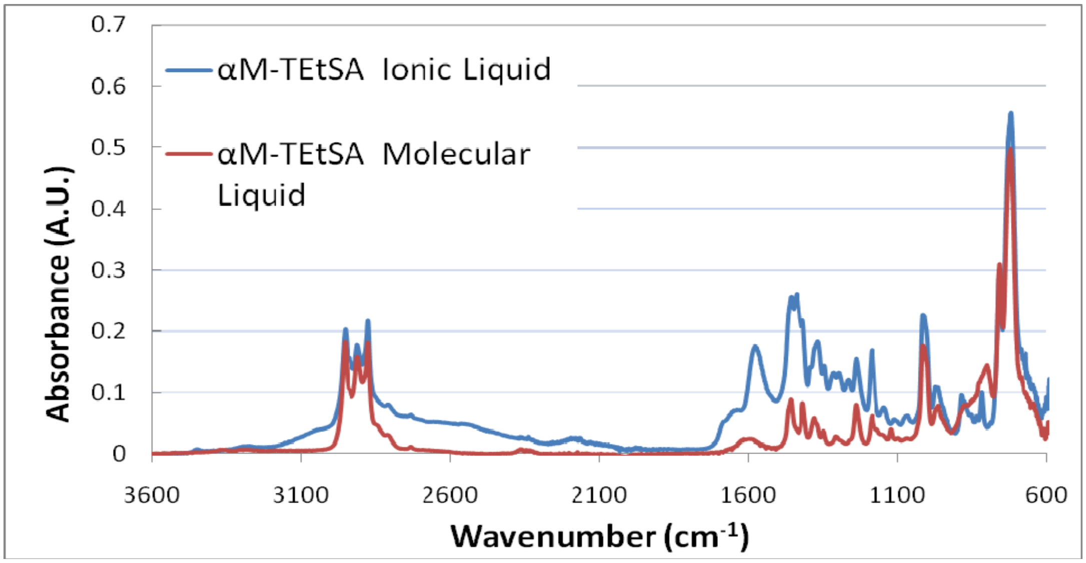


Figure 4: Infra-red spectra of the αM-TEtSA molecular liquid and ionic liquid

DSC Thermogram:

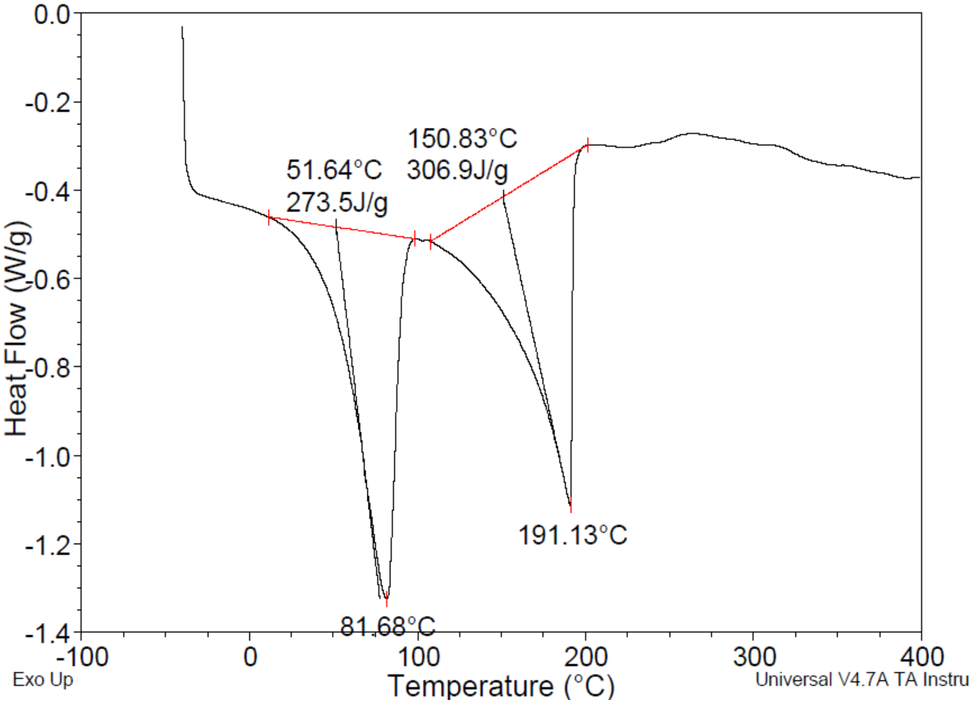


Figure 5: DSC thermogram of αM-TEtSA ionic liquid showing melting, reversal reaction and molecular liquid vaporization

2- CO$_2$ Capture Capacities

Overall Capacity:

The combined physisorption (at 1 bar) and chemisorption capacity was calculated as the net weight gained by sparging (bubbling) CO$_2$ at 1 bar through the molecular precursor at room temperature. In Figure 6, capture capacities of αM-TEtSA have been compared to those of TEtSA, TPSA, and THSA that were reported in previous quarterly reports. We have also compared these to the theoretical chemisorption capacities of the respective compounds. The difference between the experimental (total) capacity and the theoretical (chemisorption) capacity is the CO$_2$ physisorption at room temperature and 1 bar pressure. All four compounds can chemically absorb only 0.5 moles of CO$_2$ per mole. However, as we go from TEtSA to THSA the molecular weight increases from 173 to 342. Therefore the chemisorption capacity (in moles of CO2 per kg of solvent) decreases from 2.89 for TEtSA to 1.46 for THSA.

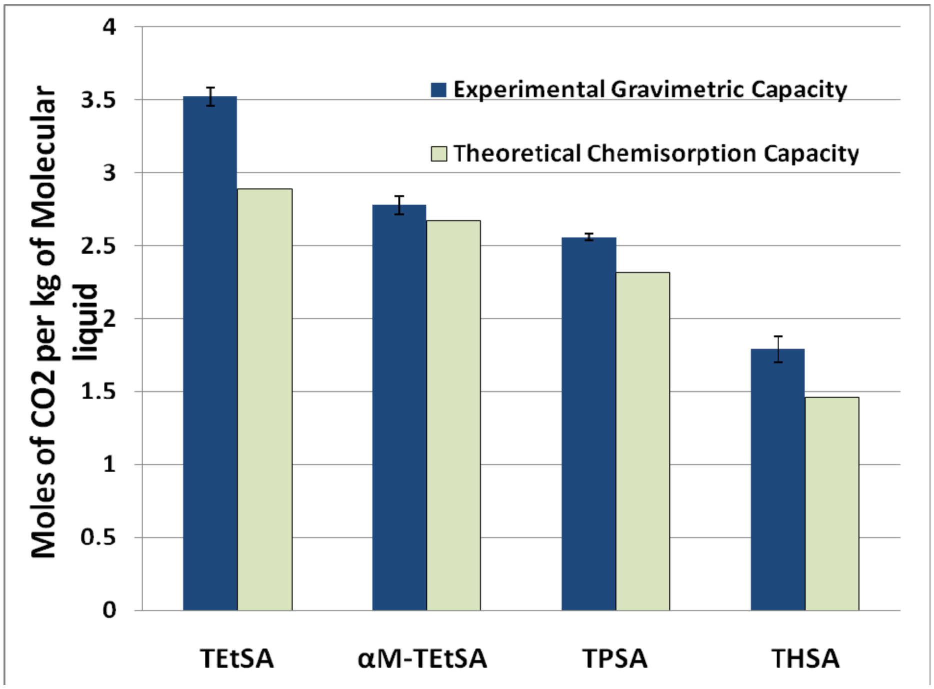


Figure 6: Overall CO$_2$ capture capacities found experimentally using gravimetric technique for silyl-amines

Physisorption and Henry's Law constants were discussed in detail in Q8 report. Physisorption in αM-TEtSA (~0.1 in moles of CO_2 per kg of solvent) is significantly less than the other compounds (0.25-0.6 in moles of CO_2 per kg of solvent).The probable reason for this is that presence of an extra methyl group that results in steric hindrance, hence the decrease in physisorption. It should also be noted that the distillation temperature of αM-TEtSA is significantly lower than the other compounds. This suggests that αM-TEtSA will have a higher vapor pressure (leading to losses) which might result in slight under-prediction of the capacity.

Sparging with N_2+CO_2 mixture:

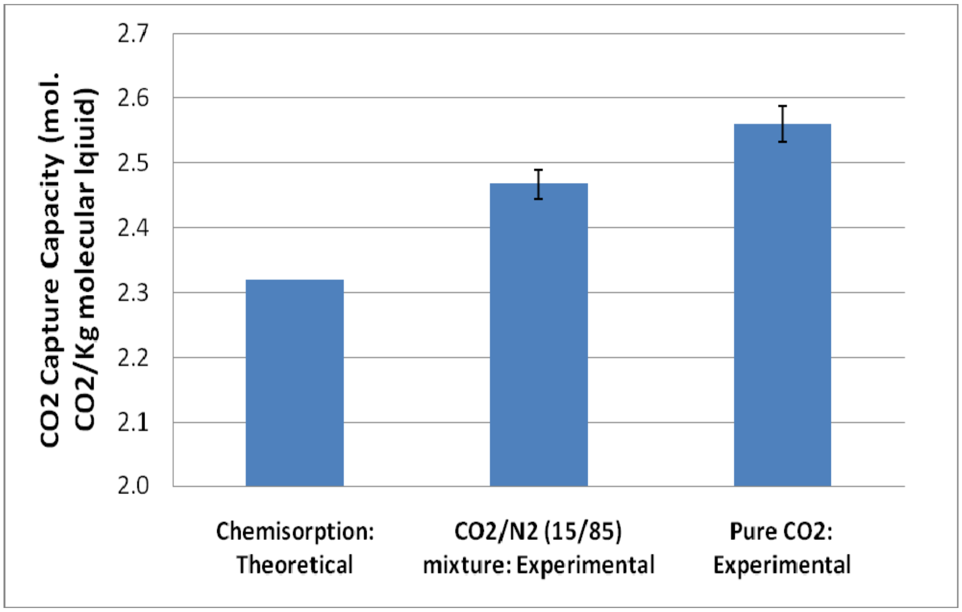


Figure 7: Comparison of CO_2 absorption capacity from pure CO_2 and CO_2+N_2 mixture (simulated flue gas) for TPSA.

To simulate actual flue gas we sparged a mixture of CO_2/N_2 (15/85) through our TPSA molecular liquid at room temperature and 1 bar total pressure. The chemisorption for this case remains the same as when pure CO_2 is sparged (2.32 moles CO_2/kg of TPSA), though the reaction times with the gas mixture are longer. The physisorption on the other hand, corresponds to 0.15 bar partial pressure of CO_2 and 0.85 bar partial pressure of N_2. As shown by Brennecke et al.[2] the solubility of CO_2 in ionic liquids is much higher than that of N_2. Hence, despite the same total pressure of 1 bar, the physisorption for the case of gas mixture is lower than that in pure CO_2 case. This is evident in Figure 7 where the CO_2 absorption capacity for the gas mixture (2.47 moles CO_2/kg of TPSA) is higher than chemisorption limit (2.32 moles CO_2/kg of TPSA) but lower than the pure CO_2 bubbling case (2.56 moles CO_2/kg of TPSA.)

Conversion and Refractive Index:

In quarter eight, we had reported that the viscosity of the ionic liquid was correlated to the refractive index. We had also conjectured that the dependence of refractive index on the extent of conversion followed non linear Lorentz-Lorenz rules. Here, we have experimentally studied the relationship between the RI and conversion measured using gravimetric technique. CO_2 was bubbled through the molecular liquid for short durations of times to allow incomplete conversion and the RI of corresponding samples was recorded.

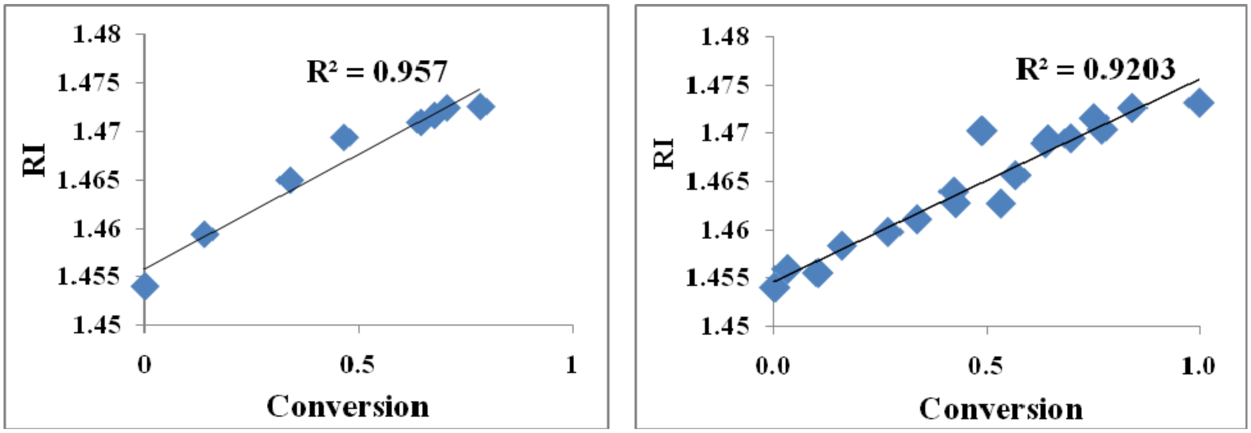


Figure 8: Relationship between refractive index and extent of conversion from molecular liquid to ionic liquid for (a) TEtSA (b) TPSA.

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[2] **Sudhir N. V. K. Aki, Berlyn R. Mellein, Eric M. Saurer, and Joan F. Brennecke** *J. Phys. Chem. B*, **2004**, *108* (52), pp 20355–20365

Figure 8 shows that the relationship between conversion and RI for TEtSA and TPSA is linear over the entire range, contrary to the concave down shape of the curve suggested by the Lorentz-Lorenz rules. This is a very useful result as it shows that we can easily establish the extent of reaction of a sample by its RI.

Recyclability:

In the last report we studied the recylability of THSA for five cycles. In this work we have extended the work to the recyclability of TPSA. CO_2 was bubbled through the molecular liquid and ionic liquid thus formed was reversed by heating at 100°C for 1-1.5 hours. Refractive index, which is considered the indicator of the extent of the reaction, was measured after every absorption and reversion step. We expect the refractive index of the pure molecular liquid to be 1.454 while that of the ionic liquid to be 1.473. Note that the reversal temperature of TPSA from DSC was 64°C, while the boiling point was 187°C. Therefore at 100°C we get faster reversion with minimal solvent loss.

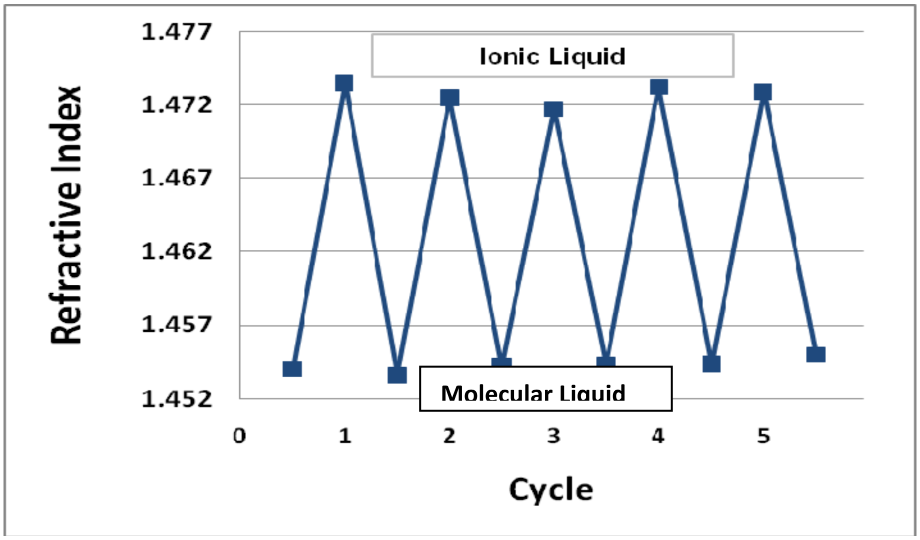

Figure 9: Recyclability of THSA explored using Refractive Index

Figure 9 shows the refractive indices over the five cycles. The molecular liquid at the end of the fifth cycle was analyzed using ^{1}H NMR and was found to be same as that at the beginning of the experiment. With almost negligible loss of activity over five cycles we expect that our silyl-amines (especially THSA and TPSA) can be effectively recycled over several more cycles.

3- Kinetics and Mass Transfer

During our experiments we found that the reaction of our amines with CO_2 was instantatneous. The reaction half lives are therefore less than a second (t_{rxn} ~ 1s). However, the total absorption time depends on three processes in series: (a) gas phase mass transfer from gas bulk to the solvent interface, (b) reaction kinetics and (c) CO_2 mass transfer through the ionic liquid skin into the bulk molecular liquid. The slowest of these dictates the absorption time. The three competing processes affecting the absorption times are depicted in Figure 10.

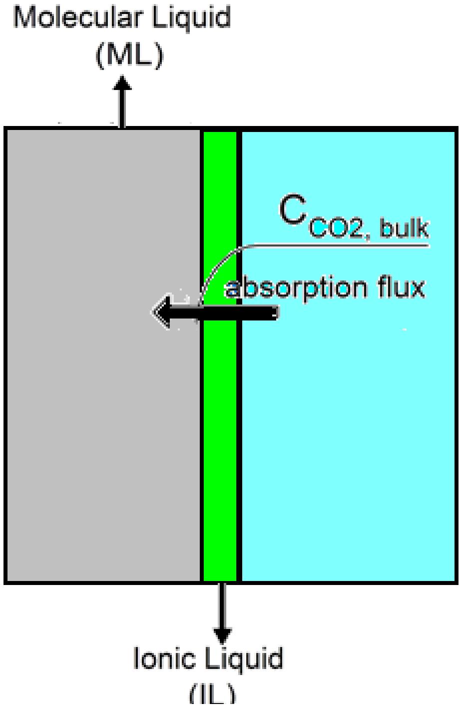

Figure 10: Competing processes affecting the overall absorption times

Here we will present a simple order of magnitude estimate of the dependence of absorption times on the three processes. For CO_2, the gas-phase diffusivity D_{gas} is *~16 mm²/s* at STP[3] while the diffusivity in the ionic liquid D_{IL} (estimated from Stokes-Einstein equation) is $\sim 3.1x10^{-6} mm^2/s$. The diffusion time scales can be related to diffusivity by ($t \sim \delta^2/D$), where δ is the characteristic

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[3] NIST Thermodynamics and Transport Database 23

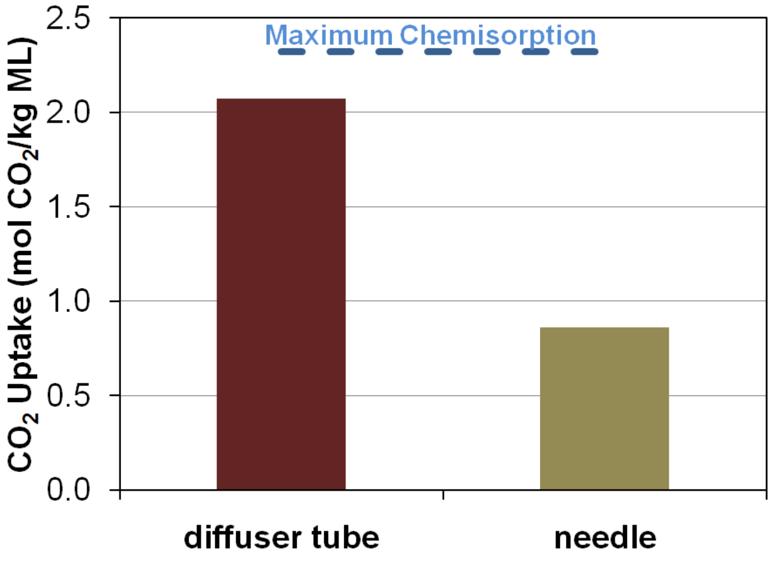

Figure 11: Effect of diffusion of CO_2 through solvent (mass transfer) on the absoption times.

diffusion path length. Typical diffusion length in gas phase is $\boldsymbol{\delta_{gas}}$~20μm [4], which gives $\boldsymbol{t_{diff,gas}}$ ~25μs (which is less than $\boldsymbol{t_{rxn}}$ ~ 1s.) Even if we consider a limiting case where the thickness of the ionic liquid layer is as small as $\boldsymbol{\delta_{IL}}$ = 1.8 μm, the diffusion time scale for CO_2 across ionic liquid layer will be $\boldsymbol{t_{diff,IL}} > 1$s. Typically $\boldsymbol{\delta_{IL}}$ is orders of magnitude larger than 1.8 μm, making the mass transfer of CO_2 in the IL the rate-limiting step.

Supporting experimental evidence for the dependence of absorption times on the mass transfer between the gas and liquid phase can be seen in Figure 11, which shows the extent of CO_2 capture for two modes of gas introduction into TPSA at room temperature for 1 minute with constant CO_2 flowrate of 200 ml/min . For the first case, the pure CO_2 is bubbled through a molecular liquid using an 18 gauge needle while for the second case CO_2 is introduced using a fritted glass tube providing much better mass transfer than a needle. It can be seen that the absorption was almost three times higher with better mass transfer.

4- Viscosity

Viscosity of the ionic liquids is one of the important parameters determining the processing costs for transporting the ionic liquid from the absorber to the stripper. We have

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[4] E.R.G. Eckert, R.M. Drake, Analysis of Heat and Mass Transfer, McGraw Hill, New York.

established that the viscosity can be decreased significantly by systematicstructural changes of our molecules. We had also shown that with the increasing size of the substituent chain, the viscosity decreases from 7600cP for TEtSA to 1650 for THSA at 25°C. We had also shown that the ionic liquid viscosity significantly decreases with temperature, in the seventh quarterly report. In Table 2 we compare the viscosity of αM-TEtSA with the other three ionic liquids at 25°C (room temperature) and 40°C (typical flue gas capture temperature.) The introduction of methyl group results in decrease in viscosity by nearly a factor of four (7600 cP for TEtSA to 2150 cp for αM-TEtSA.) The primary reason for this is the steric hindrance from the methyl group disrupts the packing of these molecules thus increasing its flowability. Similar to all trialkyl silyl-amines, an increase in temperature from 25°C to 40°C, decreases the viscosity of αM-TEtSA by nearly a factor of four.

Table 2: Comparison of viscosity of silyl-amine ionic liquid

Compound	Viscosity @ 25°C (cP)	Viscosity @ 40°C (cP)
TEtSA	7600	2000
TPSA	4000	1050
THSA	1650	500
αM-TEtSA	2150	500

5- Effect of Water

The solubility of water in the molecular liquids is important for multiple reasons as discussed in the approach section. To study the water solubility in the MLs, excess water beyond phase separation at 25°C was added to the ML and the solution was rapidly agitated, resulting in an emulsion. This emulsion was broken by centrifuging the ML-water system, again forming two separate phases. The top phase was identified as the water-saturated ML, based upon the density of the MLs. Analysis of this top phase with Karl Fischer titrations showed that water was more soluble in TEtSA than TPSA. The solubility of water in TPSA was found to be 9.8±0.2wt% and in TEtSA to be 17.2±0.6 wt%. The longer hydrocarbon chains in TPSA make the molecule more hydrocarbon-like in behavior, thus reducing the solubility of water.

We also analyzed water content in the distilled silyl-amine samples and found that to be less than 0.2% by weight.

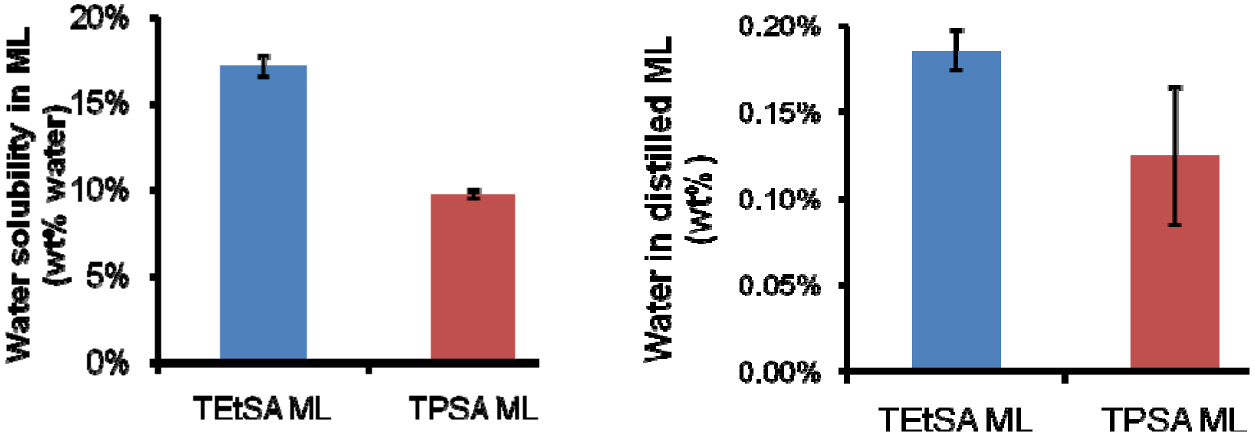

Figure 12: Water content (a) in saturated molecular liquid (solubility of water in molecular liquid) (b) in distilled molecular liquid (for determination of purity)

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 10^{th} Quarter of the project, we have continued to establish structure property relationships to find optimum solvent for CO_2 capture. In addition, we have focused on establishing our silyl-amines as suitable solvents for commercial scale CO_2 capture by performing absorption studies with simulated flue gas, determining the effect of water, and establishing the recyclability of our compounds. Finally, we have also studied the effects of kinetics and mass transfer on the absorption times in our silyl-amine solvents.

We have successfully performed the characterization and determined the capacity and viscosity of a new compound 4-(triethylsilyl) butan-2-amine (αM-TEtSA). This has helped us in determining the effects of steric hindrance near the amine on the CO_2 capture behavior. (**TASK 5.**) In our previous reports we had shown that (3-aminopropyl) tripropylsilane (TPSA) is one of the most promising CO_2 capture solvents. To find the suitability of TPSA for large scale CO_2 capture, we have determined its capture capacity in the presence of a simulated flue gas, its recyclability, and its interactions with water (**TASK 5.**) The CO_2 capture capacity decreased slightly in the presence of CO_2/N_2 mixture due to the decrease in the physisorption. Similar to the THSA silyl-amine TPSA showed excellent recyclability for the CO_2 capture application. The presence of water in a distilled silyl-amine was found to be negligible while the water solubility was found to be less than 20% by weight (17.2% for TEtSA, 9.8% for TPSA.) Finally, our experiments showed that the silyl-amine+CO_2 reaction is instantaneous and the mass transfer between CO_2 and the ionic liquid/molecular liquid mixture is the rate determining step in the CO_2 absorption (**TASK 5.**)

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 reversible ionic liquid and one new single-component silyl guanidine-based reversible ionic liquid.	9/30/10	Progress Report describing thermodynamics of formation of new single-component silyl 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). Finally in this quarter, we have 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.

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:

- Characterization of a new silyl-amine (αM-TEtSA) based reversible ionic liquid.
- Measurement of CO_2 capture capacity and viscosity of αM-TEtSA.
- Recyclability study of TPSA silyl-amine for CO_2 capture.
- Measurement of CO_2 capture capacity of TPSA in simulated flue gas.
- Analysis of interaction of water with TPSA.
- Study of effects of kinetics and mass transfer on absorption times.
- Identification and synthesis of promising target molecules for future synthesis and characterization based on evidence collected during the first 9 Quarters of the project.
- 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://eckert.chbe.gatech.edu/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

Dr. 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

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)

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)

Paul Nielsen (Senior, Chemical Engineering)

María González Miquel (Visiting Scholar, from Departamento de Ingeniería Química, Universidad Complutense de Madrid, 28040 Madrid, Spain)

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 will spend this summer in Bartlesville working on aspects of this problem with ConocoPhilips.