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 31, 2010
Period covered: April 1, 2010 – June 30, 2010 (Budget Period 2 – 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 fossil fuel-fired power plants. These novel solvents are neutral molecules which react with CO_2 to form an ionic liquid, which then dissolves additional CO_2 by a physi-sorption 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 creating, 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 will develop a process for commodity-scale production of our solvents.

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

- The completed characterization for both the molecular and ionic liquid forms of 6 silyl-amine based RevILs is reported herein: (3-aminopropyl)trimethoxysilane, (3-aminopropyl)triethoxysilane, (3-aminopropyl)triethylsilane, (3-aminopropyl) tripropylsilane, (3-aminopropyl)trihexylsilane and (3-aminopropyl)diisopropyl (1H,1H,2H,2H-perfluoropentyl)silane. ***Preliminary results have lead the identification of 4 more candidates currently being synthesized and characterized, bringing the total to 01 compounds.*** (**<u>TASK 2 and TASK 5</u>**)
- We have completed the FT-IR data collection examining the chemical and physical absorption of CO_2 in the 6 silyl-amine based RevILs: (3-aminopropyl) trimethoxysilane, (3-aminopropyl)triethoxysilane, (3-aminopropyl)triethylsilane, (3-aminopropyl)tripropylsilane, (3-aminopropyl)trihexylsilane and (3-aminopropyl) diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane. Operating pressures up to 1000 psi and temperatures of 35, 50, 75, and 100°C were examined using attenuated total

reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy and our Generation 3 custom made high pressure reaction vessel. (**TASK 4**)
- We have proceeded with the analysis of the ATR FT-IR data, utilizing a novel analytical technique, in order to quantify the CO_2 captured through both chemical and physical mechanisms for the 6 sily-amine RevILs discussed above. Refractive indices have been measured as a function of temperature for both molecular and ionic liquids. (**TASK 4**)
- The viscosity data for the 6 silyl-amine RevILs has been completed for both molecular and ionic liquids as a function of temperature. (**TASK 5**)

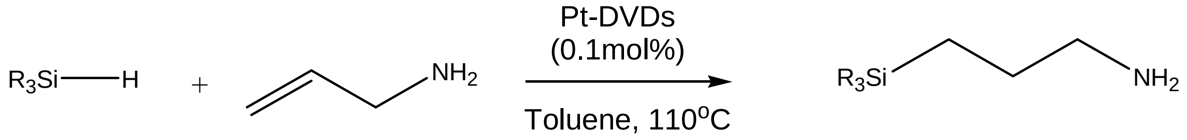
Our goal remains to minimize the cost and energy requirements of CO_2 capture to help DOE meet its goal – 90% CO_2 capture with no more than a 30% increase in cost by 2020.

5. Results of Work

a. Approach

1- Synthesis and Characterization of Custom Reversible ILs

We proposed to investigate the use of a variety of amine and guanidine based materials for the capture and subsequent controlled release of CO_2. The general reaction scheme for the synthesis of silyl-amine based RevILs is shown (Figure 1).



1 : **2**

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

The synthetic scheme being employed affords two main benefits for the production of RevILs for CO_2 capture from flue gas: (1) the synthesis is simple and efficient and (2) the molecular architecture of the RevILs can be easily tuned by using silanes with different substitution. This allows for the development of a plethora of compounds to be tested for application to CO_2 capture, as well as ensuring that the optimal candidate will be capable of scaling to synthesis on an industrial level. Additionally, as progress is made on existing compounds, we can identify molecular structures for improved absorption capacities and processing properties and alter the current synthetic techniques by simple substitution of silanes. ***The progression on molecular structure that will allow for the development of an optimal CO_2 capture solvent resulting in a drastic reduction in operating costs (relative to monoethanolamine absorption) and lower capital cost (through increasing capacity).***

After synthesis and isolation, we first characterize each compound to ensure the candidate is viable for use as a reversible ionic liquid solvent for the removal of CO_2 from power plant flue gas. The first study conducted is the confirmation of reaction with CO_2 (confirmed by both ^1H and ^{13}C NMR) to produce an ionic liquid capable of further physi-sorption (Figure 2).

Figure 2. Reaction of custom-made amine with CO_2 to form reversible ionic liquids.

As synthesized, each of these candidates will be tested for CO_2 capture as illustrated by the general reaction scheme in Figure 2. The resulting reversible ionic liquids will be fully characterized (NMR, elemental analysis, FT-IR, and solvatochromic polarity measurements). The solvatochromic polarity measurements will be performed using an HP 8453 UV-Vis Spectrophotometer and the polarity probe Nile Red. The wavelength of maximum absorption (λ_{max}) for the probe in a given solvent is a good measure of the polarity of the solvent. The λ_{max} of Nile Red has been found and reported for hundreds of solvents, making this an efficient approach for determination of solvent polarity.

The loss of CO_2 upon heating and thermal stability of the amines will be explored using NMR and differential scanning calorimetry (DSC). The DSC experiments are performed on a Q20 TA Instruments machine, with a temperature profile of 5°C/min from an initial temperature of -40°C to a final temperature of 400°C. The first endotherm was taken to represent the loss of CO_2 with the second endotherm representing the decomposition of the molecular liquid.

Although stability tests confirmed that the trialkyl-substituted precursors were stable over a period of two months in both water- and oxygen-containing environments, we shall still perform the experiment on the precursors that show promising thermodynamic properties or absorption capacities to ensure industrial viability of our new solvents. Stability will be monitored using ^1H NMR.

Additionally, we shall capture ^{13}C labeled CO_2 to differentiate and quantified the chemisorbed (single or multiple reactions) and physisorbed CO_2 present in the reversible ionic liquid. We anticipate capacities to exceed the 1:2 CO_2 to solvent ratio achieved by single reaction stoichiometry. Quantitative ^{13}C NMR will be used to perform the analysis and the results will be compared with FT-IR data. Candidates that exhibit favorable properties for use as CO_2 capture agents (such as usable liquid range, stability, capability to release CO_2, etc.) will then be tested for determination of thermodynamic properties, viscosity, and capacity.

2- Thermodynamics of CO_2 Capture

We proposed to exploit our knowledge of molecular design to understand and optimize the chemistry – for example using linear free energy relationships to account for electron donation or withdrawal and related effects (such as neighboring group effects) to increase capacity and modify the thermodynamics. Once promising candidates are identified after undergoing the characterization experiments (as describing in the previous section) we will then start to look at their thermodynamic properties and CO_2 capture capacities. The equilibrium constant (K) representative of the capture (and release) of CO_2 can be found by measuring the conversion of the precursor molecule to ionic liquid at a given temperature and CO_2 concentration, and compensation for the non-ideal behavior of the ionic species.

We are using attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectroscopy to determine the conversion under a broad range of conditions. ***This measurement technique allows for the simultaneous measurement of chemical and physical absorption CO_2 capacity, both used for the determination of the thermodynamic properties of the solvent***. The ATR FT-IR optics bench used for data collection will be the Heated Golden Gate ATR sample accessory supplied by Specac, with a working temperature range up to 300°C and pressure rating for the tungsten carbide embedded diamond being 15,000psi.

Equilibrium measurements are currently being performed by using a custom-designed and -built ATR FT-IR high pressure reactor. Although the scrubbing will be carried out at our near atmospheric pressure, the pressure range of the instrument permits us to acertain 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. To quantify the chemical absorption capacity measured with ATR FT-IR, simultaneous ^{1}H NMR and FT-IR measurements will be collected for each compound at an intermediate conversion (a mixture of molecular and ionic liquids). The NMR used is a Bruker AMX 400 located in the School of Chemistry and Biochemistry at Georgia Tech.

The purpose of collecting simultaneous spectra on both the NMR and IR will be to confirm the experimental technique using the molecular liquid and ionic liquid IR spectra to calculate the molar absorptivities. Changes in penetration depth will be accounted for by examining the refractive indices of the samples in both molecular and ionic forms. Density changes in the samples arising from conversion to ionic liquid and swelling of the liquid due to physical absorption will be corrected by examining the C-H stretch vibrational frequencies (<3000 cm^{-1}) in the samples. We will first analyze five different conversions for the same sample to verify that the carbonyl peak intensity is linearly proportional to the conversion determined by ^{1}H NMR. Previous experiments performed on the reversible ionic liquid N-butyl-N,N,N,N-tetramethylguanidinium methylcarbonate indicated that linearity between conversion and carbonyl intensity holds true.

In addition, we can gather information on the amount of CO_2 that is physically absorbed into the ionic liquids using the FT-IR data that is collected for the conversion measurements. The CO_2 that is in solution and not chemically bound to the amine (referred to as “free CO_2”) has a very distinct absorption band in the mid-infrared region (the 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. A calibration curve relating the absorbance of CO_2 and the concentration was obtained for a methanol/CO_2 system using VLE data found in literature to calculate the concentration of CO_2 at various temperatures and pressures. For the analysis, density and molar absorptivity of the ionic liquid is required. Density measurements will be conducted in our laboratory using an Anton Paar DMA 38 Laboratory Density Meter. Molar absorptivities will be calculated for the samples by examining the IR spectra of both the molecular and ionic liquids, and using the corresponding density and path length information. The simultaneous ^1H NMR and FT-IR measurements will be used to confirm this approach. The refractive index information, which will be used to calculate path length, is measured with an Arias 500 Refractometer.

Initial experiments use pure CO_2 feed streams. As we determine the equilibrium constants at multiple temperatures, we shall be able to determine the heat of reaction for the specific molecular structures. The molecular structures will be systematically altered to allow for the use of structure-property relationships where we can determine the optimal molecular configuration to give us desired capacities and enthalpies for reversing our solvents and expelling the CO_2. For example, the compound (3-aminopropyl)diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane will allow for us to determine the effect of fluorinated side chains on the enthalpic properties of the CO_2 capture candidates. The custom reversible ionic liquids that show promising pure CO_2 capacities and reaction enthalpies will be investigated with altered feed streams to examine the effects of mixed N_2/CO_2 streams, water, SO_x, NO_x, and carryover from the scrubbers. This will give us insight into how the solvents behave under "real world" operating conditions. We can then further modify the structures to overcome any problems that arise.

For the evaluation of the equilibrium constants, we must examine the noonideality of our ionic liquids solutions. We are measureing concentrations, but in fact the equilibrium constant is a ratio of activities, so some measure or estimate of activity coeefiecients is required. We have begun looking at available data and models, and this work is described below. Such information will be useful to develop accurate expression for the equilibrium constants and offer insight into how specific molecular structures can advantageously deviate from ideality for the purpose of CO_2 capture and, more importantly, release.

3- Viscosity Studies as a Function of CO_2 capture

The change in viscosity as a function of CO_2 capture will be investigated. Previous rheological results indicate that there is a three order of magnitude change in viscosity as they are completely converted from the molecular liquid to the ionic form. Laboratory observations indicate that the change in viscosity is non-linear, with viscosity increasing sharply at high conversions.

The viscosity as a function of conversion for each candidate is being measured using a Rheosys Merlin II Viscometer, located in our laboratory. Measurements are currently being done to identify a proper method to evaluate the isothermal viscosities of both molecular and ionic liquids. Once complete, the viscosities will be measured for the all candidates that have been successfully characterized. To ascertain the affect of conversion on viscosity, we will examine the viscosities of (3-aminopropyl)tripropylsilane at various conversions. The conversion of the samples will be measured using ^1H NMR.

4- Scrubber Process Design

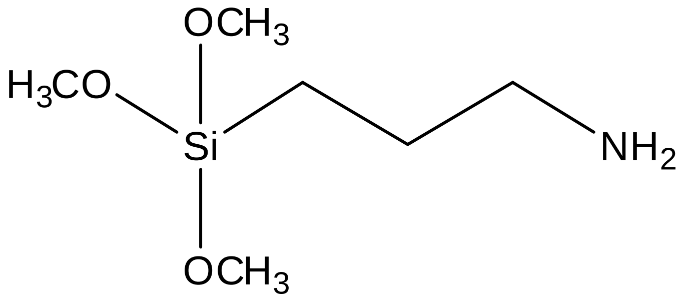
An ASPEN simulation to treat a ***model coal-fired power plant flue gas stream has been developed and validation with existing literature data is underway***. Initially, the model will be used to evaluate targets for our CO_2 capture agents to meet the goal of 90% CO_2 capture with no more than a 30% increase in cost. We are using the monoethanolamine (MEA) process as a basis for comparison, and are altering the operating conditions to give us targets for the development of one component reversible ionic liquids. The parameters we look to optimize are the enthalpy of capture and release, the capture and release temperatures, CO_2 capacities of the solvent, and viscosity of the solvent. The data acquired in the laboratory for the custom-made reversible ionic liquids will be put into the model and evaluated as it is collected, giving us real-time analysis of the economic viability and performance of our solvents. This information will be used to direct the modifications to molecular structure in order for us to meet the goals set forth by DOE and our previous models.

Additional design issues that we plan to consider in the future are the effects of the presence of SO_2, NO_2, and carryover gypsum particles from the scrubber in the gas. We do know 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

We have currently synthesized and ***fully characterized*** five reversible ionic liquid candidates (the fluorinated compound is incomplete due to a shortage of starting material). In compliance with Milestone E, the following lists the detailed characterization of all reversible ionic compounds:



Compound 1. Structure of **(3-aminopropyl)trimethoxysilane** (TMSA).

NMR Data:

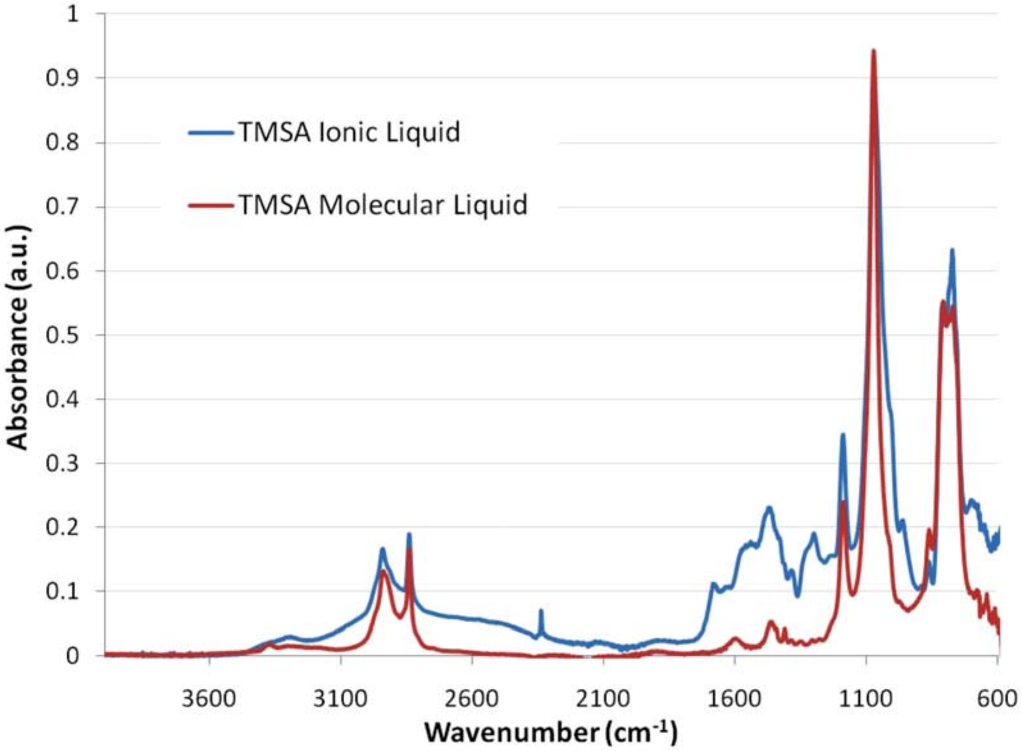
TMSA Molecular Liquid ^{1}H: 3.9(s,9);2.9(t,2); 1.8(m,2); 0.9(t,2)
TMSA Molecular Liquid ^{13}C: 49.7, 45.0, 27.1, 6.1
TMSA Ionic Liquid ^{1}H: 6.0(br,3); 4.5(br,1); 3.5(br,18); 3.0(br,2); 1.6(br,2); 0.2(br,4)
TMSA Ionic Liquid ^{13}C: 162.6, 50.0, 43.9, 42.8, 23.8, 23.2, 5.8

Elemental Analysis:

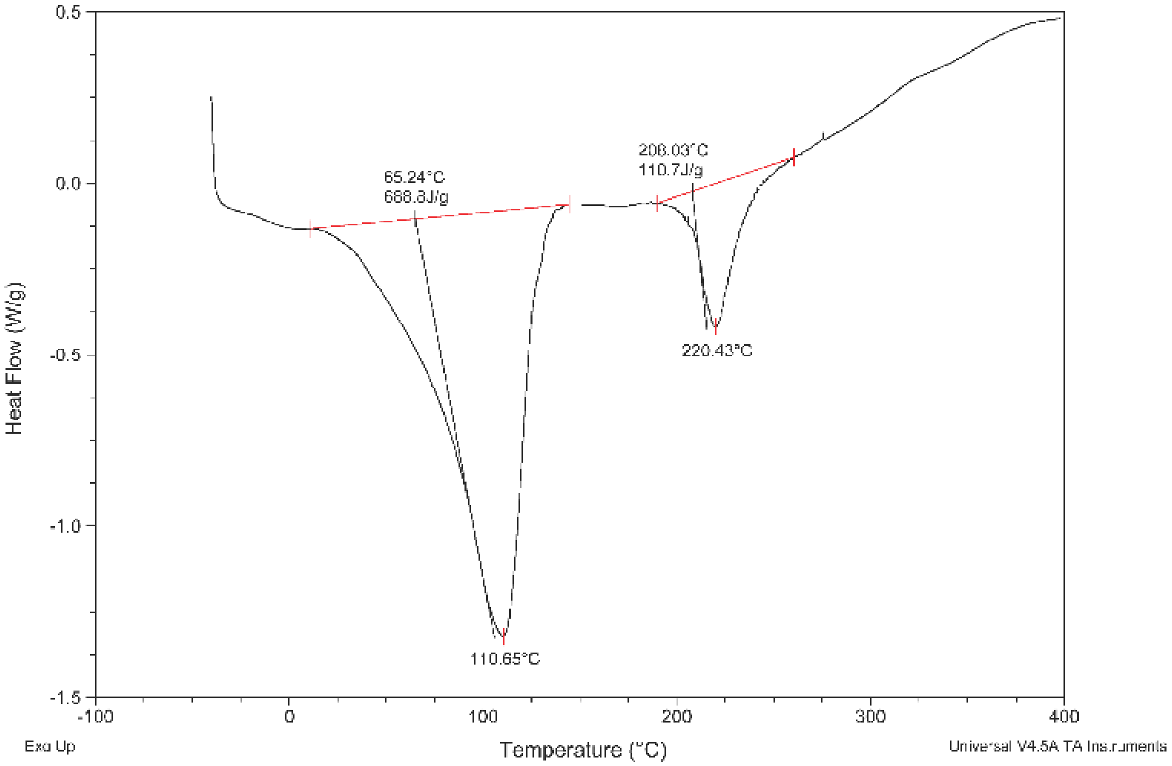
TMSA Molecular Liquid:	Expected: C(40.19), H(9.56), N(7.81)
	Actual: C(40.19), H(9.56), N(7.81)
TMSA Ionic Liquid:	Expected: C(38.78), H(8.51), N(6.96)
	Actual: C(38.34), H(8.57), N(6.95)

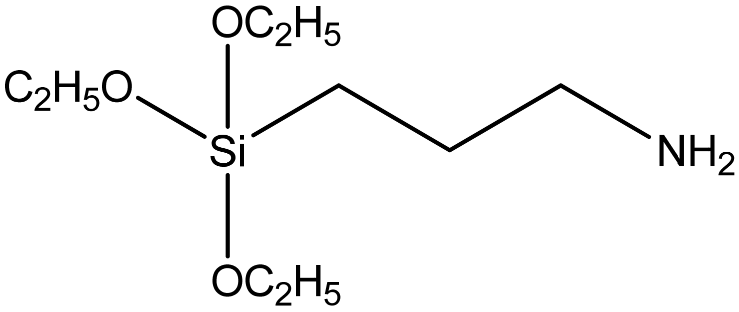
Distillation Temperature: Used as received

Infrared Spectra:



DSC Thermogram:





Compound 2. Structure of (3-aminopropyl)triethoxysilane (TESA).

NMR Data:

TESA Molecular Liquid ^{1}H: 4.1(m,6); 2.9(t,2); 1.8(m,2); 1.5(t,9); 0.9(t,2)

TESA Molecular Liquid ^{13}C: 51.2, 45.5, 18.9, 17.9, 8.8

TESA Ionic Liquid ^{1}H: 9.6(br,3); 6.0(br,1); 4.0(br,12); 3.2(br,2); 3.0(br,2); 1.9(br,2); 1.7(br,2); 1.4(br,18); 0.8(br,4)

TESA Ionic Liquid ^{13}C: 162.5, 57.7, 44.1, 41.5, 23.7, 21.3, 17.9, 7.6, 7.4

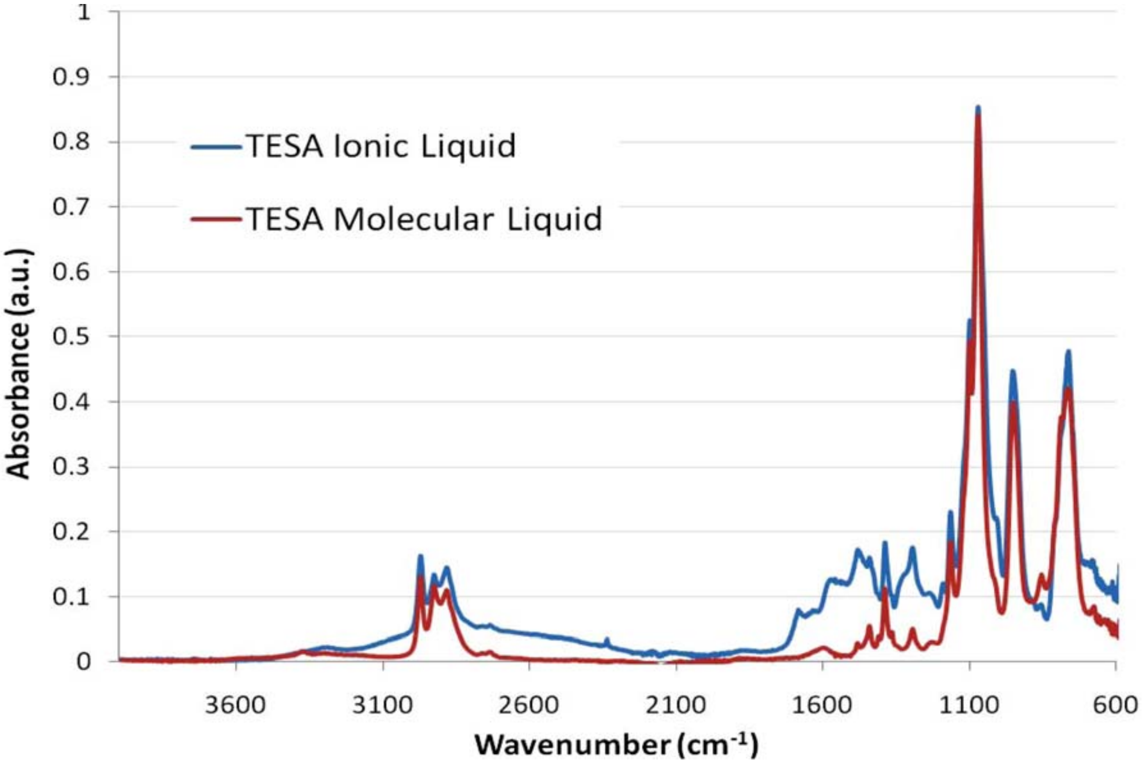
Elemental Analysis:

TESA Molecular Liquid: Expected: C(48.83), H(10.47), N(6.33)
Actual: C(48.29), H(10.56), N(6.05)

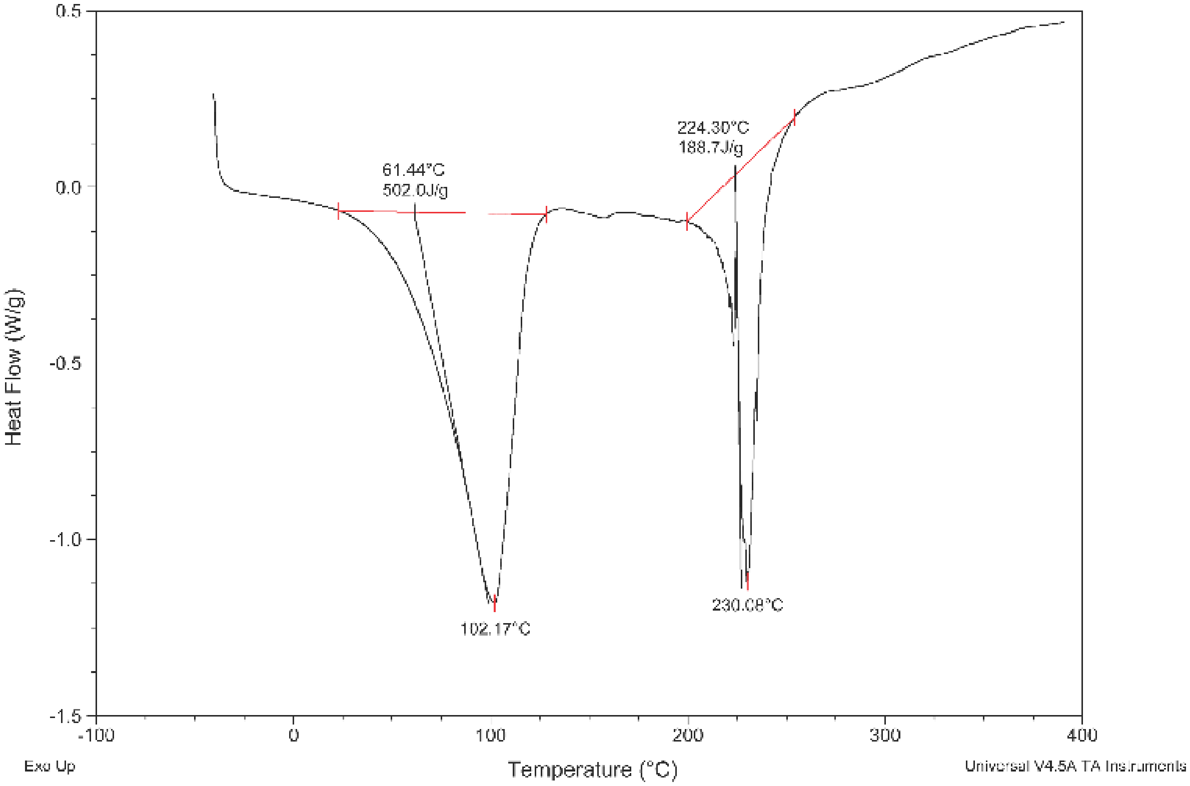
TESA Ionic Liquid: Expected: C(46.88), H(9.53), N(5.76)
Actual: C(46.66), H(9.49), N(5.77)

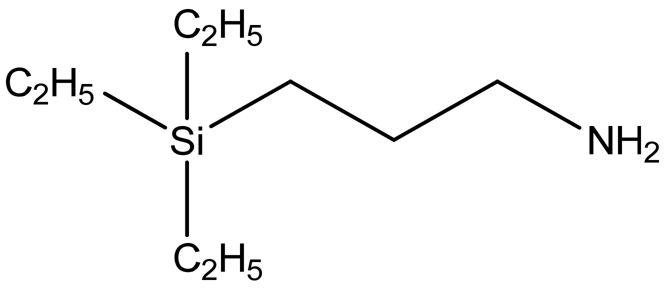
Distillation Temperature: Used as received

Infrared Spectra:



DSC Thermogram:





Compound 3. Structure of (3-aminopropyl)triethylsilane (TEtSA).

NMR Data:

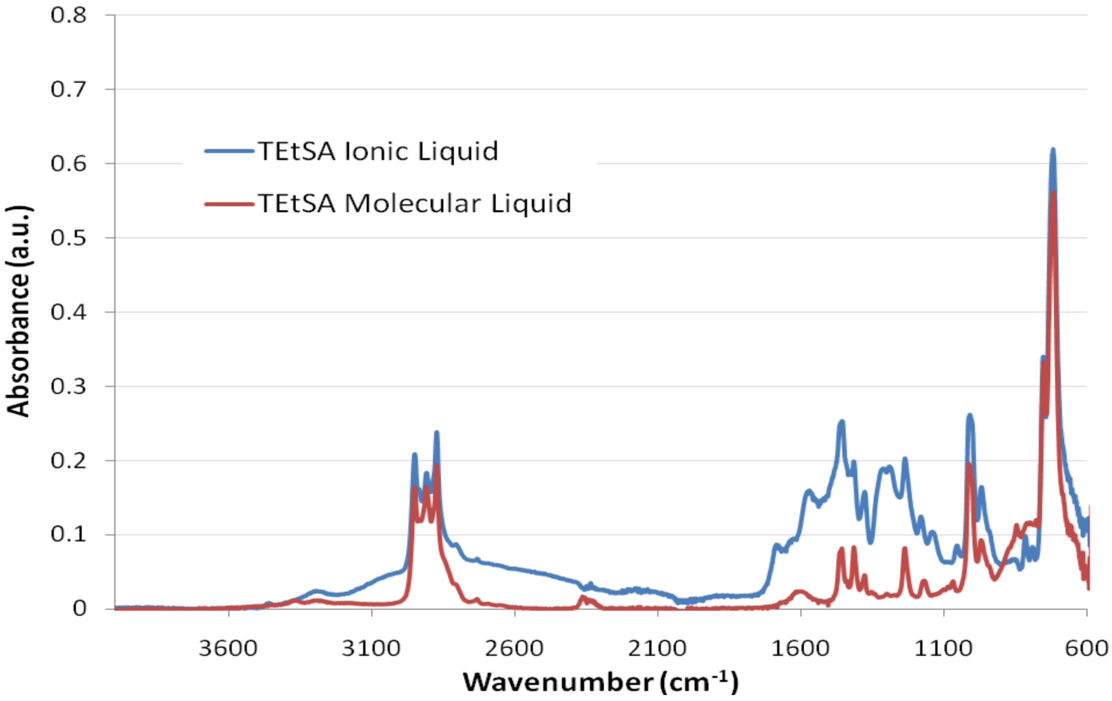
TEtSA Molecular Liquid ^{1}H: 2.59(t,2); 1.38(p,2); 1.02(s,2); 0.86(t,9); 0.45(q,8)
TEtSA Molecular Liquid ^{13}C: 45.68, 28.08, 8.10, 7.15, 3.07
TEtSA Ionic Liquid ^{1}H: 9.22(br,3); 5.84(br,1); 3.09(br,4); 1.58, 1.05, 0.64(3br,38)
TEtSA Ionic Liquid ^{13}C: 163.01, 45.52, 43.06, 25.23, 22.56, 9.07, 7.65, 7.61, 3.71

Elemental Analysis:

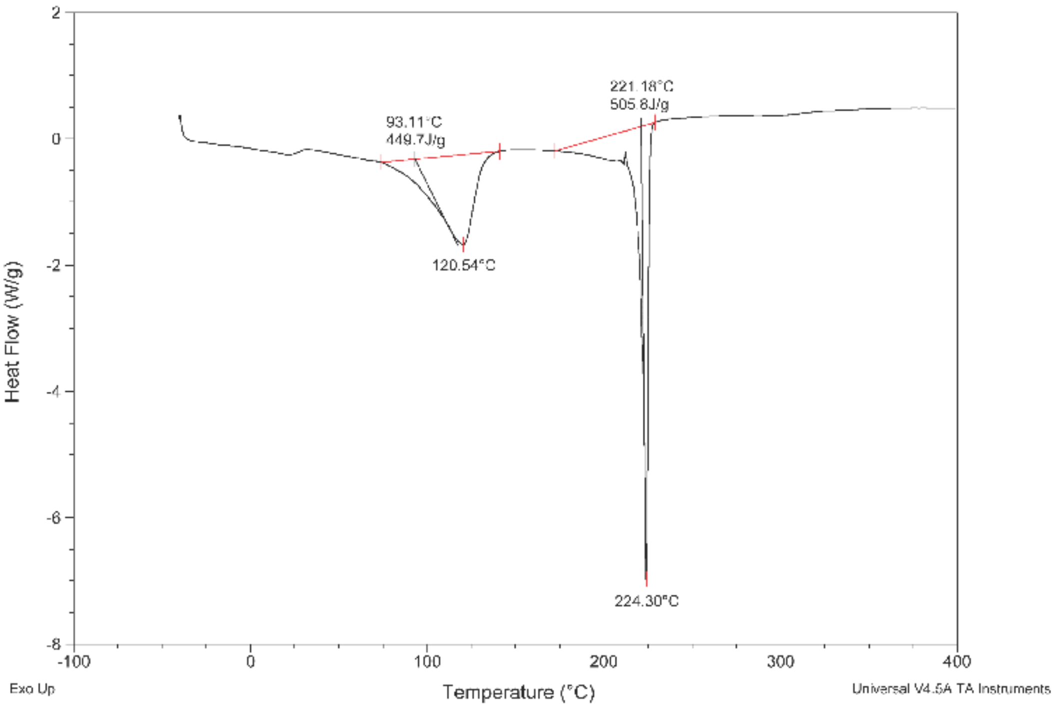
TEtSA Molecular Liquid:	Expected: C(62.35), H(13.37), N(8.08)
	Actual: C(62.41), H(13.42), N(7.94)
TEtSA Ionic Liquid:	Expected: C(58.40), H(11.87), N(7.17)
	Actual: C(57.93), H(11.79), N(6.91)

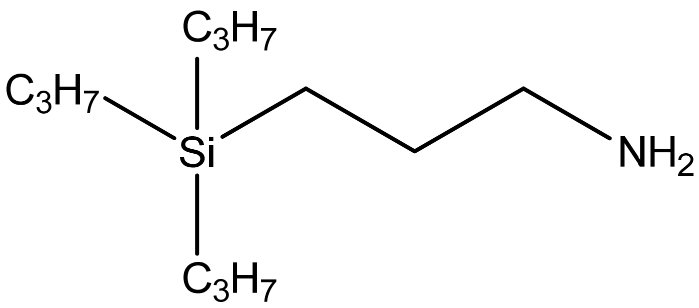
Distillation Temperature: 80-100°C

Infrared Spectra:



DSC Thermogram:





Compound 4. Structure of (3-aminopropyl)tripropylsilane (TPSA).

NMR Data:

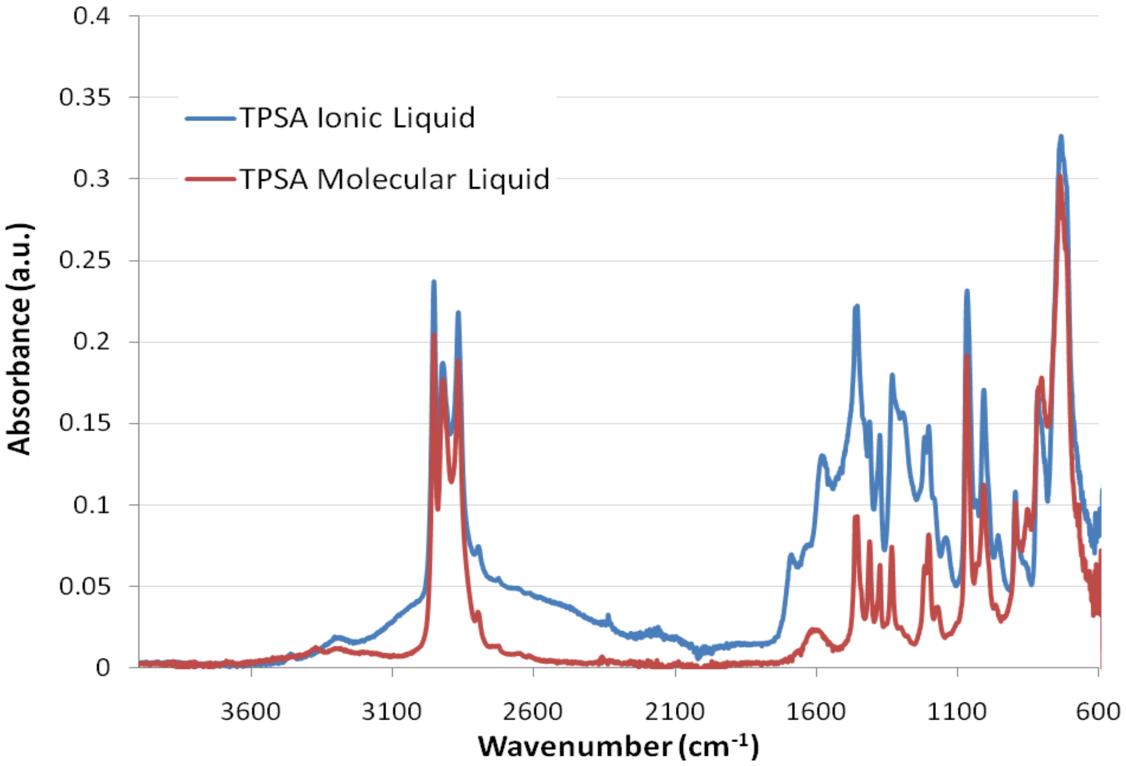
TPSA Molecular Liquid ^{1}H: 2.59(t,2); 1.38(p,2); 1.27(m,6); 1.17(s,2); 0.89(t,9); 0.43(q,8)
TPSA Molecular Liquid ^{13}C: 45.78, 28.27, 18.48, 17.35, 15.20, 9.47
TPSA Ionic Liquid ^{1}H: 9.54(br,3); 5.76(br,1); 3.14(br,4); 1.46, 1.07, 0.65(3br,74)
TPSA Ionic Liquid ^{13}C: 162.45, 44.9, 25.0, 21.5, 18.63, 17.59, 15.41, 15.26, 10.0

Elemental Analysis:

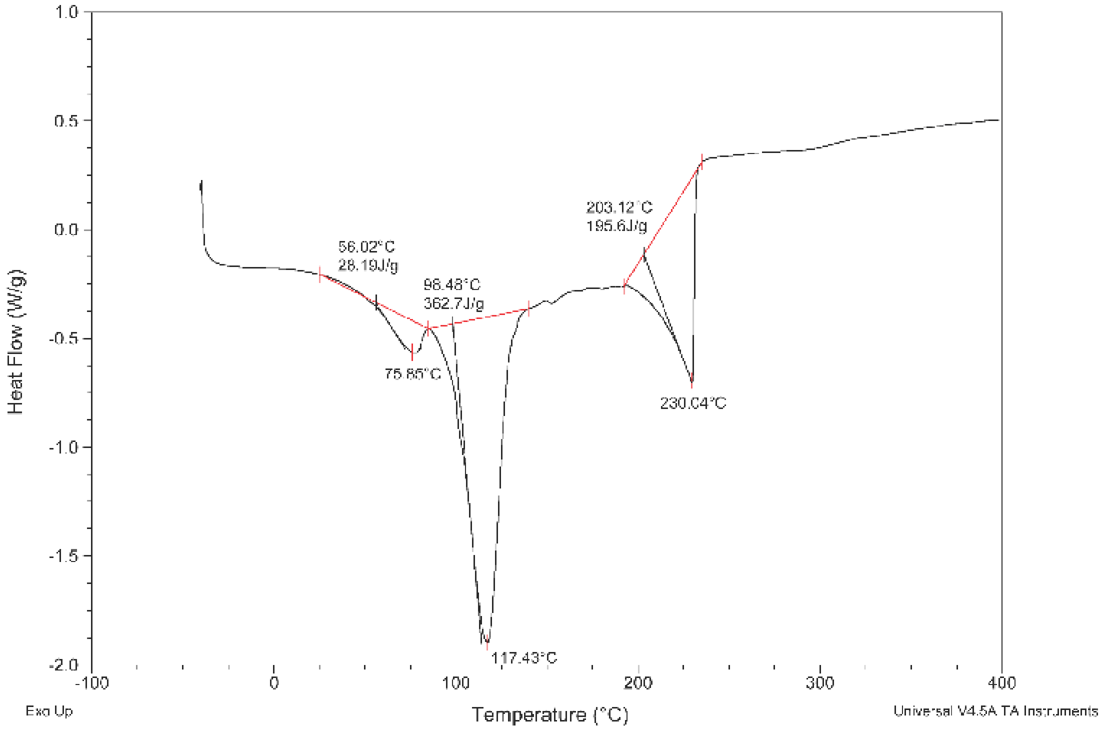
TPSA Molecular Liquid: Expected: C(66.90), H(13.57), N(6.50)
Actual: C(66.74), H(13.64), N(6.35)
TPSA Ionic Liquid: Expected: C(63.23), H(12.31), N(5.90)
Actual: C(62.78), H(12.31), N(5.72)

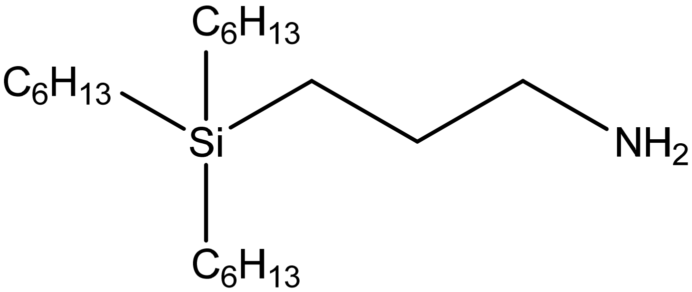
Distillation Temperature: 80-110°C

Infrared Spectra:



DSC Thermogram:





Compound 5. Structure of (3-aminopropyl)trihexylsilane (THSA).

NMR Data:

THSA Molecular Liquid ^{1}H: 2.63(t,2); 1.39(p,2); 1.25(s(br),26); 0.87(t,9); 0.47(m,8)

THSA Molecular Liquid ^{13}C: 45.73, 33.45, 31.40, 28.22, 23.71, 22.50, 13.95, 12.26, 9.30

THSA Ionic Liquid ^{1}H: 9.77(br,3); 5.59(br,1); 3.20(br,3); 1.46, 1.04, 0.70(3br,94)

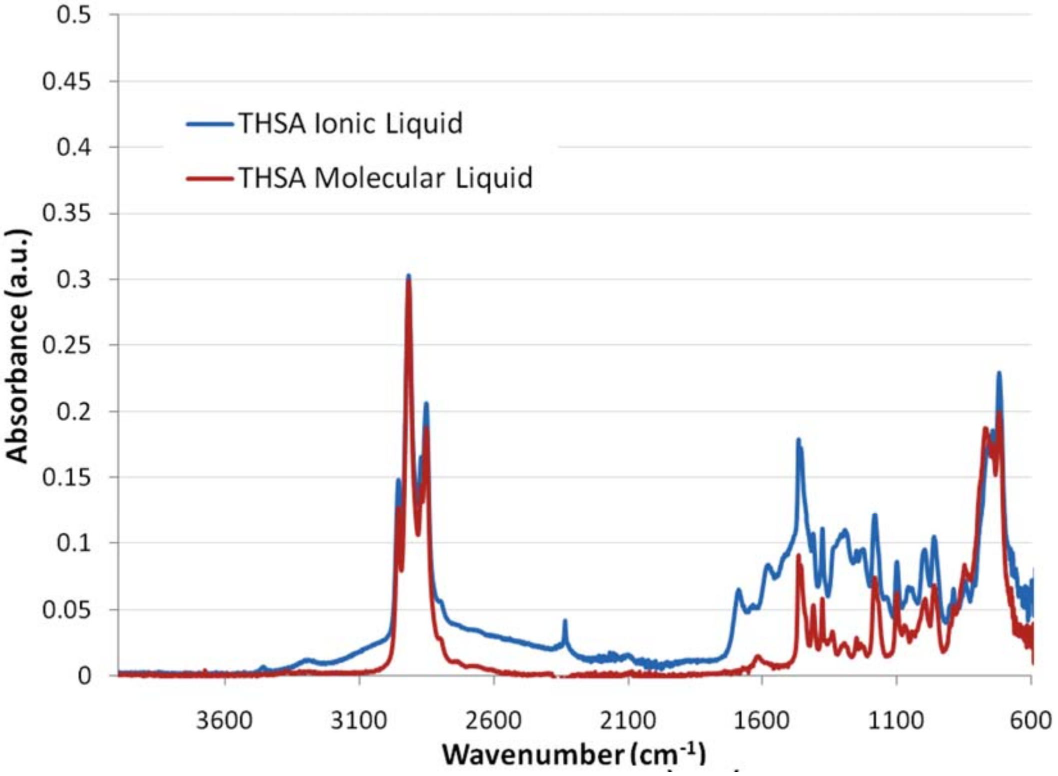
THSA Ionic Liquid ^{13}C: 162.34, 45.286, 33.76, 31.72, 25.03, 24.00, 22.80, 14.11, 12.52, 10.05

Elemental Analysis

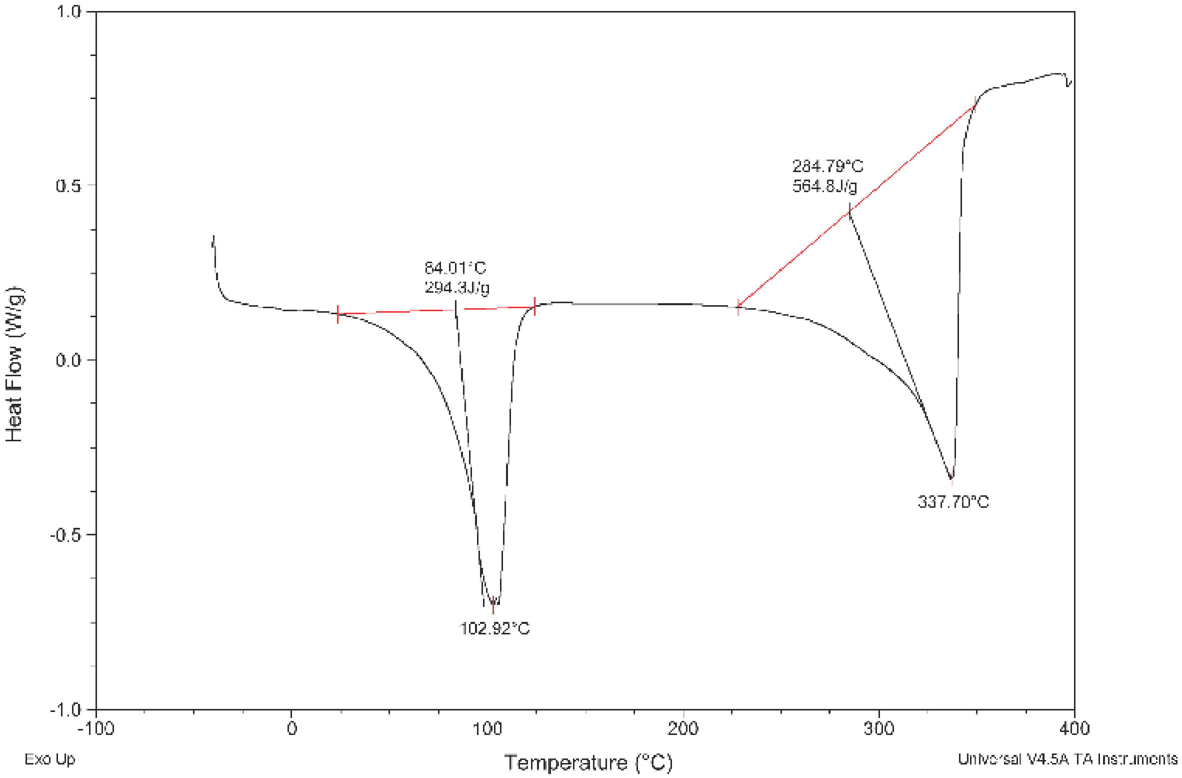
THSA Molecular Liquid: Expected: C(73.82), H(13.86), N(4.10)
Actual: C(72.87), H(13.59), N(4.07)
THSA Ionic Liquid: Expected: C(71.00), H(13.03), N(3.85)
Actual: C(70.92), H(13.12), N(3.74)

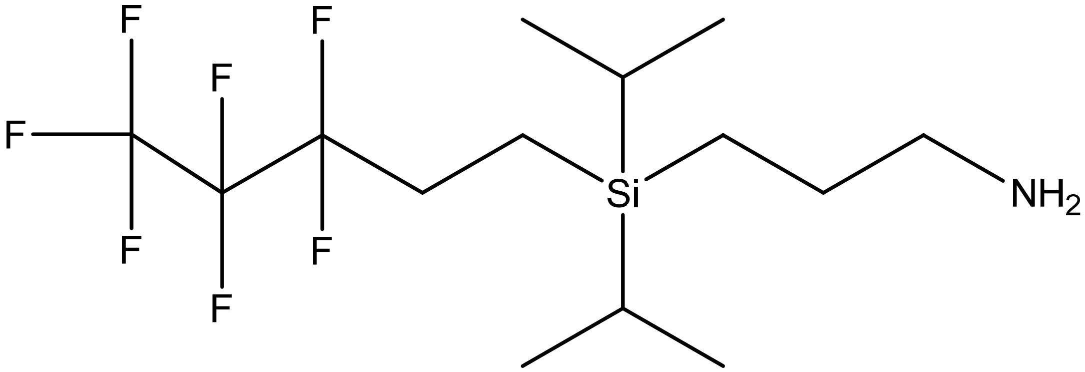
Distillation Temperature: 150-170°C

Infrared Spectra:



DSC Thermogram:





Compound 6. Structure of (3-aminopropyl)diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane (FSA).

NMR Data:

FSA Molecular Liquid ^{1}H: 2.68(t,2); 2.03(m(pent),2); 1.44(p,2); 1.013(s,16); 0.79(m,2); 0.58(m,2)

FSA Molecular Liquid ^{13}C: 45.9, 28.0, 25.9(trip), 18.1, 11.0, 6.4, -1.0

FSA Ionic Liquid ^{1}H: waiting on starting material

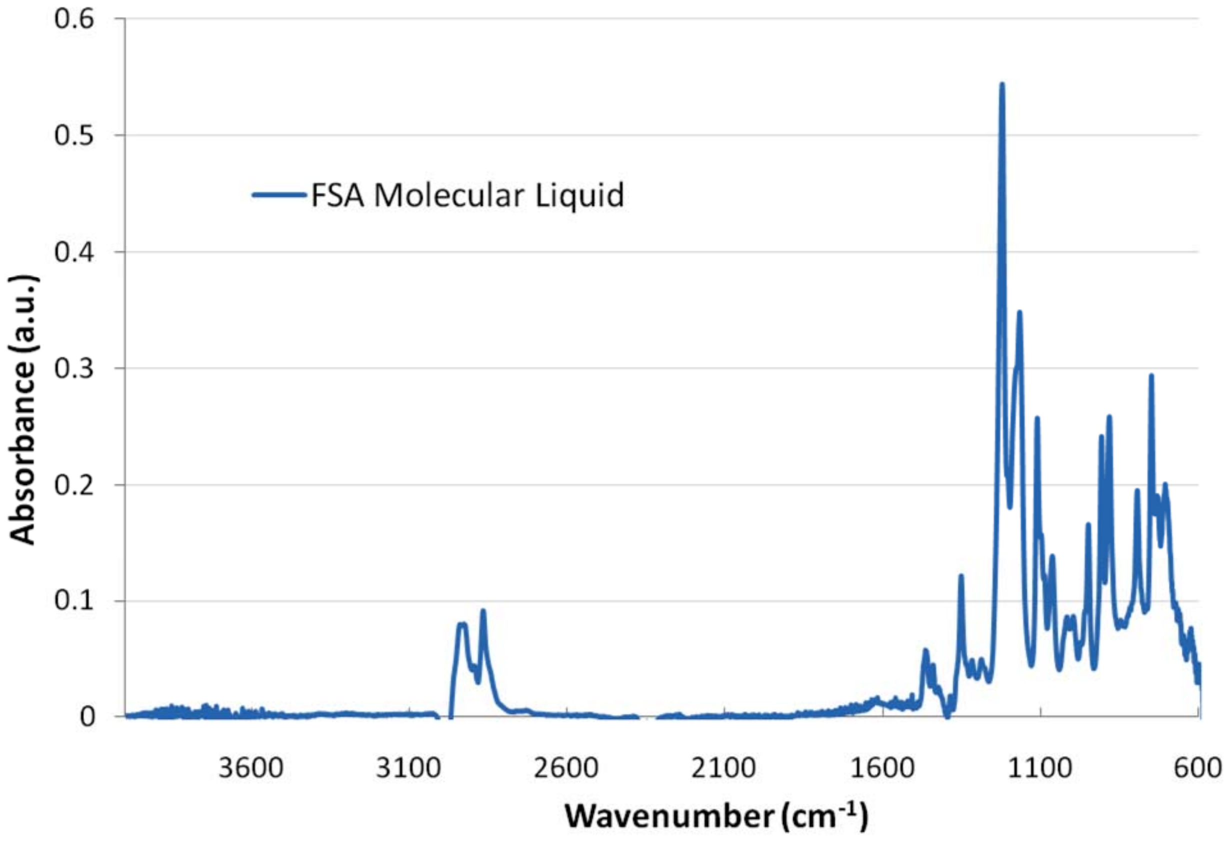
FSA Ionic Liquid ^{13}C: waiting on starting material

Elemental Analysis:

FSA Molecular Liquid:	Expected: C(45.52), H(7.09), N(3.79)
	Actual: C(45.29), H(7.12), N(3.84)
FSA Ionic Liquid:	Expected: C(44.49), H(6.69), N(3.58)
	Actual: C(44.42), H(6.69), N(3.58)

Distillation Temperature: 100-120°C

Infrared Spectra:



DSC Thermogram:

To be completed upon receipt of more starting material

The Nile Red values for the fully characterized CO_2 capture candidates are shown in Figure 3. The results indicate that as carbons are added to the branches on the silicon, the polarity of both molecular and ionic liquids decrease. Additionally, the difference in polarity for the switch from ionic liquid to molecular liquid also decreases as the length of the carbon chains increases. This information is useful for designing a solvent with a minimal water miscibility. As water will inherently be found in any combustion product stream, it typically accumulates in the solvent. Illustrated in Figure 3 is the ability to design a solvent with a low water solubility, allowing for simple separation of the water from the system.

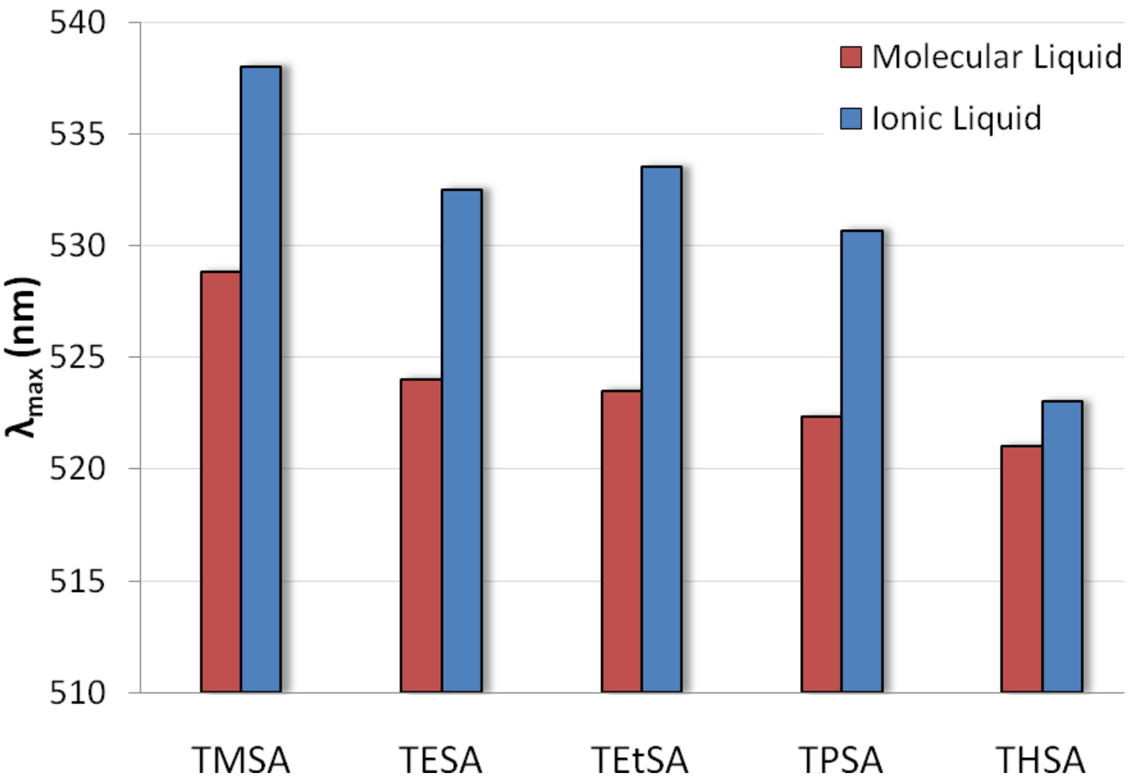


Figure 3. Nile Red results for both molecular and ionic forms of the RevILs.

As previously reported, we have shifted our focus from silyl-guanidine compounds to silyl-amine compounds, and plan to explore the effects of asymmetry and branching on the properties of the next generation CO_2 capture solvents (Figure 4).

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

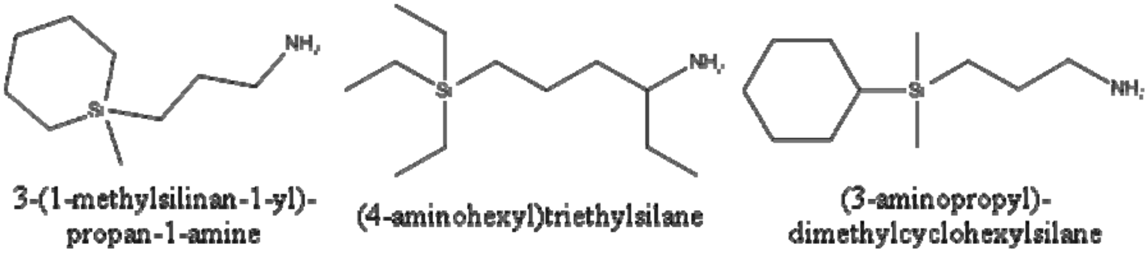


Figure 4. Structures of asymmetric silyl-amine based RevILs.

In an attempt to decrease the viscosities of the ionic liquids (enabling facile processing) and to increase capacity by lowering the molecular weight of the amine, we propose to examine the isomers of (3-amino-1-propenyl)triethylsilane (**Error! Reference source not found.**):

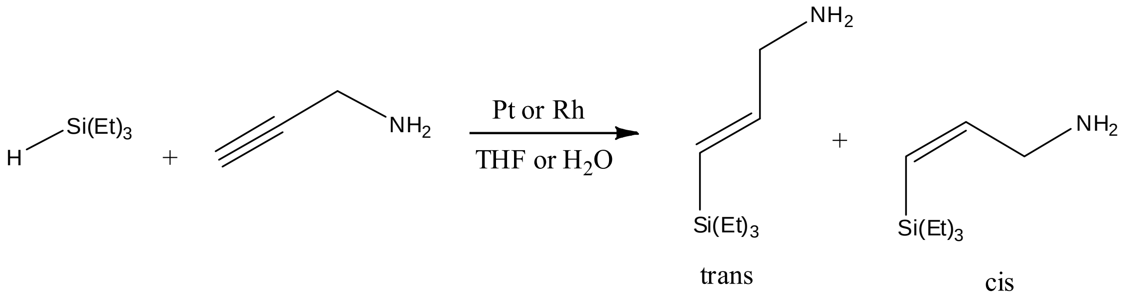


Figure 5. Synthetic scheme for *cis*- and *trans*- (3-amino-1-propenyl)triethylsilane.

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

2- Thermodynamics of CO_2 Capture

The ATR FT-IR measurements for TMSA, TESA, TEtSA, TPSA, THSA, and FSA have been ***completed***. Operating pressures up to 1000 psi and temperatures of 35, 50, 75, and 100°C were examined using attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy and our Generation 3 custom made high pressure reaction vessel. ***We are now measuring the CO_2 capacities in the preformed ionic liquids in order to ascertain the Henry's Law constants for CO_2 in the RevILs***.

We are currently processing the data that has been completed for the first and second generation RevILs. The amount of CO_2 captured through physical absorption can easily be quantified through application of the methanol/CO_2 calibration curve, as discussed in the "Approach" section of this report. However, we must know the molar absorptivity of the sample. This information will be calculated from the IR spectra for the molecular and ionic liquids.

In order to properly analyze the FT-IR data, we need the density of the molecular form of the RevILs and the penetration depth of the ATR (which is dependent on refractive index). As of this report, we have received the Anton Paar DMA 38 Laboratory Density Meter and a Reichert Arias 500 Refractometer. The density measurements are under way and the refractive indices have been recorded at temperatures up to 75°C (Figure 6). The values from 75-115°C have been extrapolated from linear fits of the 25-75°C data. Once quantification of physical and chemical absorption is complete for the first and second generation RevILs, the information will be used with the appropriate model to determine the thermodynamic properties of CO_2 capture.

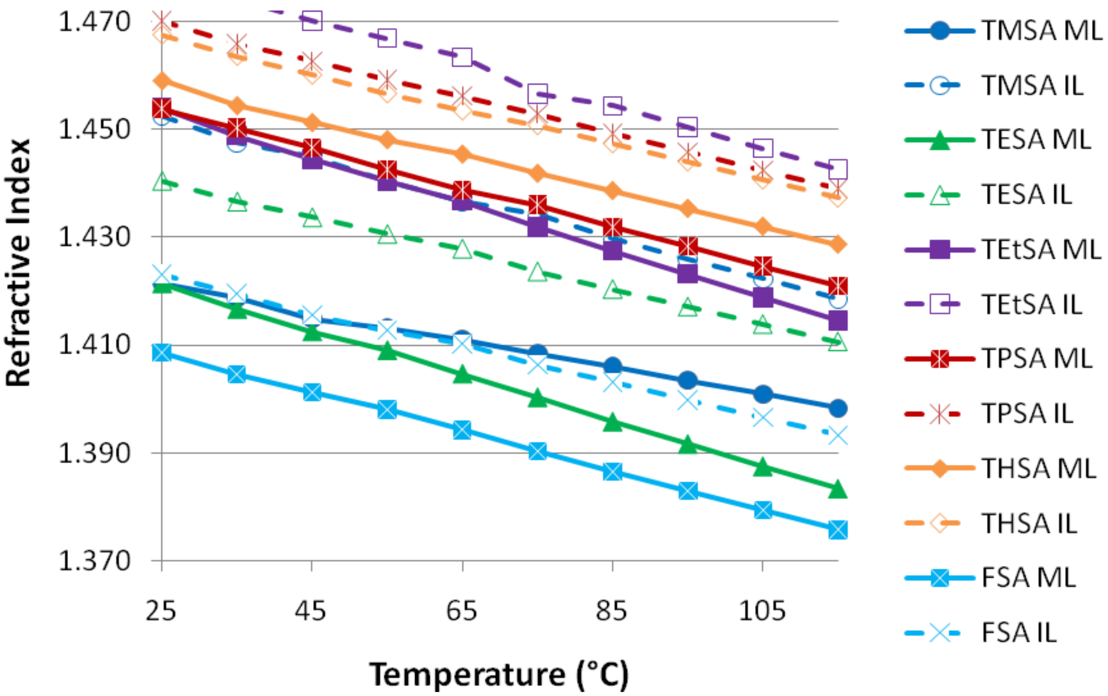


Figure 6. Refractive indices of molecular and ionic liquids.

In evaluating the equilibrium constant (K), we are going to 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 will evaluate the equilibrium constant with an activity based approach to account for the non-ideality of the mixture. We expect the system to exhibit a non-ideal behavior because of 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).

The evaluation of the equilibrium constant involves the estimation of the activity coefficient (γ) with excess Gibbs energy models. Conventionally, these models contain one or more adjustable parameters that are optimized to best fit the experimental data. In ternary systems, the binary interaction parameters are first obtained from experimental Vapor-Liquid Equilibria (VLE) data for each pair of system components and are used to estimate the γ for ternary systems. However, since our reversible ionic liquids are synthesized in house (no previous experimental data available) and due to the nature of the system (the reversible ionic liquid is only formed in the presence of the molecular liquid and CO_2), we are developing a unique approach to estimate the ternary system activity coefficients for the experimental data directly. We are currently reviewing published data and thermodynamic models for ionic liquids-CO_2, organics-ionic liquids, electrolyte solutions, and ternary systems including variations of these components. We are considering various thermodynamic models that represent mixtures containing polar and non-polar components such as the Universal Quasichemical (UNIQUAC) and Statistical Associating Fluid Theory (SAFT).

UNIQUAC is used to thermodynamically model phase equilibria of binary and ternary systems containing ionic liquids, hydrocarbons, and CO_2 [1]. UNIQUAC utilizes the volume and surface area of molecules, which can be calculated through variety of theoretical methods, and a binary interaction energy parameter fitted to experimental data. A similar method, Universal Functional Activity Coefficient (UNIFAC), has also been reported for systems containing ionic liquids however, the method relies on infinite dilution data which might not capture physical and chemical interactions present in our systems. Another method that could be used is the group contribution (GC) method, which represents the physical properties of the molecule by the summation of the interactions between specific functional groups within the molecule. A molecule is broken down into its functional groups (CH_2, C=O, etc.) and reported or calculated values are used to estimate interaction values for each functional group [2]. The principle of group contribution can be implemented into other thermodynamic models such as linear salvation energy relationships [3].

SAFT assumes that molecules consist of freely joint spherical segments and it has been widely used to represent complex mixtures. It is reported for vapor-liquid equilibria of binary and ternary mixtures of polymers-solvents-gases [4] and ionic liquids-CO_2 [5] systems. For nonpolar non-associating fluids, the method requires three parameters: the molecule's segment diameter (σ), the number of segments representing each molecule (m), and the segment energy parameter (ε). The pure component parameters are obtained from vapor pressure data and liquid densities for volatile liquids. For relatively non-volatile molecules (polymers and ionic liquids), the parameters are obtained by simultaneously fitting liquid densities and binary phase equilibrium data. Additional parameters are required for associating systems (hydrogen bonding) and polar interactions (dipole and quadrupole). The two main advantages of this method: 1) its wide applicability and acceptance and 2) semi-predictive power. On the negative side, method requires accurate and available experimental data, which is not optimal for newly synthesized molecules screening.

The evaluation of the activity coefficients will lead to constructing the structure-property relationships. We will examine the behavior of the different reversible ionic liquids – in terms of CO_2 capture and release - and how it relates to physical properties such as polarity or molecular volume/surface area. This analysis will provide insight into the molecular behavior of these liquids and allows for the design of an optimum solvent for CO_2 capture.

In addition to examining thermodynamic models for computing γ, we are considering Raoutl's law as an alternative approach. Raoult's law assumes an ideal mixture with a γ value of unity. This approach can be applied at the extremes – around minimal and around complete conversion of the ionic liquid – where the concentrations of two of the systems components are finite. We are gathering published data of infinite dilution activity coefficients for ionic liquids in organics and for organics in ionic liquids as well as Henry's constants for CO_2. These values will be used as guidelines for the optimization of the equilibrium constants of our Reversible Ionic Liquids.

References:

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4. (a) Gross, J.; Sadowski, G., Modeling polymer systems using the perturbed-chain statistical associating fluid theory equation of state. *Industrial & Engineering Chemistry Research* **2002,** *41* (5), 1084-1093; (b) Tumakaka, F.; Gross, J.; Sadowski, G., Thermodynamic modeling of complex systems using PC-SAFT. *Fluid Phase Equilibria* **2005,** *228*, 89-98.

5. (a) Andreu, J. S.; Vega, L. F., Capturing the solubility Behavior of CO2 in ionic liquids by a simple model. *Journal of Physical Chemistry C* **2007,** *111* (43), 16028-16034; (b) Andreu, J. S.; Vega, L. F., Modeling the Solubility Behavior of CO2, H-2, and Xe in C-n-mim Tf2N Ionic Liquids. *Journal of Physical Chemistry B* **2008,** *112* (48), 15398-15406.

3- Viscosity Studies

For the molecular liquid samples, 12 measurements were taken for each liquid using three different samples at 4 different temperatures (25, 34, 45, 55°C), Figure 7. Two samples were run with increasing temperatures, and one sample was run with decreasing temperature. The sample size was approximately 0.3 mL. The sample was left on the viscometer for the 4 different temperatures. For all of the molecular liquids run, the viscosity increased with the temperature, contrary to the standard negative correlation between viscosity and temperature. It is assumed that the reaction of the primary amines with the water in the air caused this increase, as the reaction occurs more at higher temperatures, as the temperature provides energy to overcome the activation energy of the reaction. For several of the molecular liquids, some bubbling was observed at 55°C, supporting the assumption of a reaction, as the amines do not boil at that low a temperature. The highest viscosities at 55°C were triethoxysilylamine (TESA) with 71.9 cP and trimethoxysilylamine (TMSA) with 52.2 cP. The alkoxy compounds readily react with water to cleave the Si-O bond, and have been shown to self-polymerize in wet and hot environments.

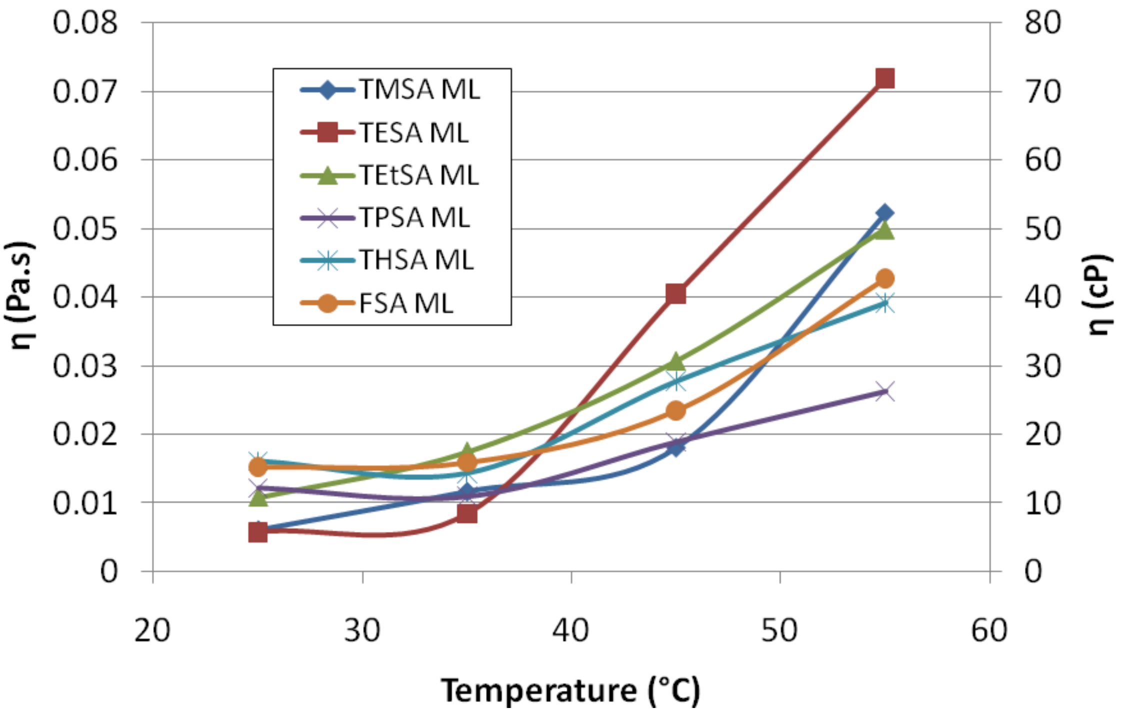

Figure 7. Viscosity of molecular liquids as a function of temperature.

For the ionic liquid samples, 12 measurements were taken for each liquid using twelve different samples at 4 different temperatures (25, 35, 45, 55°C), Figure 8. Each sample was only used for one test because the ionic liquids can reverse (desorption of CO_2), especially at higher temperatures. For all the ionic liquids, the viscosity decreased with temperature. At higher temperatures, there is some reversing of the liquids, causing the viscosity to decrease. If the sample was left on the viscometer long enough at 55°C, the viscosity would eventually drop to that of the molecular liquid, due to complete reversal, induced both by the high temperature and shear from the viscometer. The highest viscosity was for the FSA, which was over 25000 cP at 25°C. At lower temperatures, the viscosities of the alkyl amines followed a trend of the size of the side groups. Therefore THSA was less viscous than TPSA, which was less viscous than TEtSA.

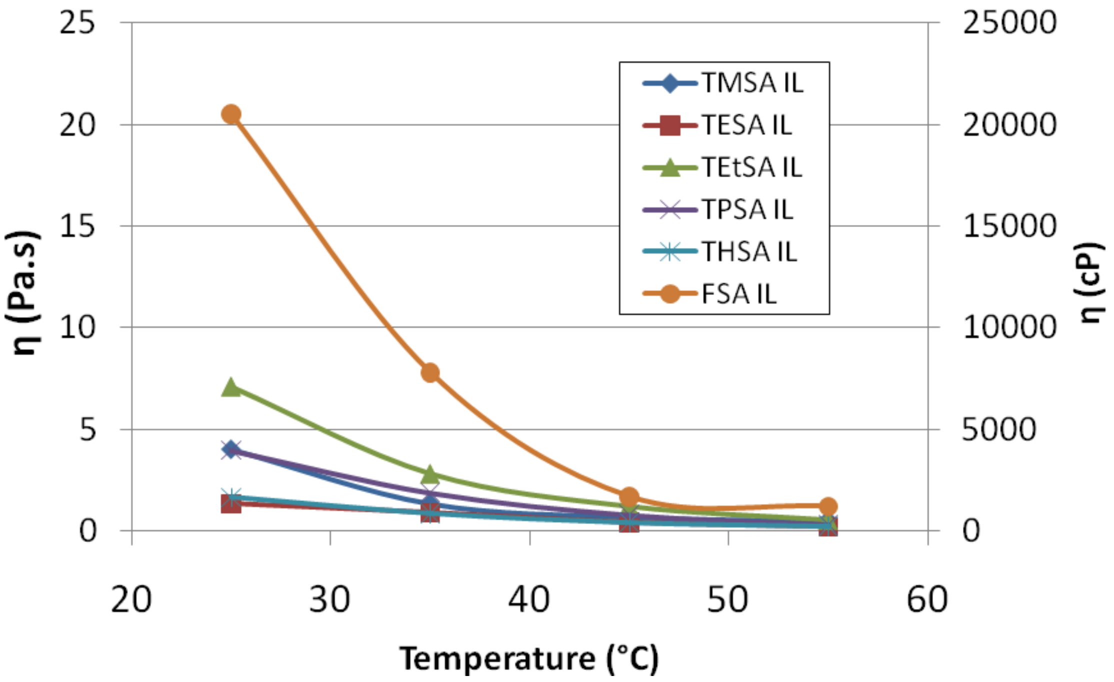

Figure 8. Viscosity of ionic liquids as a function of temperature.

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.

Significant accomplishments were made during the 7th Quarter of the project by identifying and establishing synthetic procedures for four additional silyl-amine based RevILs that we believe could reduce operating and capital costs of a CO_2 capture process by offering favorable chemical and physical properties. We continue to stay ahead of schedule on the thermodynamic analysis (**TASK 4**), and have used the measurement technique to simultaneously investigate conversion of the molecular liquids and absorption capacity in the ionic liquids for six CO_2 capture solvent candidates. The viscosities of both molecular and ionic liquids have been measured as a function of temperature for all six compounds (**TASK 2**), and we are getting the required information for the structure-property relationship analysis (**TASK 5**). And importantly, the information being collected is giving insight into compounds with enhanced properties for the application to CO_2 capture from fossil fuel-fired power plants. The information gathered thus far leads us to hypothesize that the silyl-amine reversible ionic liquid candidates are far superior to the one component guanidine reversible ionic liquids, which has been supported by the published findings of our collaborators. (**TASK 3**)

6. Cost Status

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

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

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 in fact that the guanidine based RevILs are unsuitable for CO_2 capture because 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 we have discovered that the silyl amine-based reversible ionic liquids are much superior to the guanidine-based reversible ionic liquids in terms of both properties and capacity – this was discussed in detail in the progress report for Quarter 6. Therefore we have focused on the silyl amine-based reversible ionic liquids only. For milestone D, we reported the complete laboratory synthesis and characterization of 3 more (7 total) new single-component silyl amine-based reversible ionic liquids in the Progress Report for Quarter 6, and we are currently developing 4 more (bringing the total to 11 total compounds!) for milestone E. Finally we are well on the way to completing Milestone F - Complete laboratory measurement of the thermodynamics of formation of multiple new single-component silyl amine-based reversible ionic liquids, and we shall have those results in the next few months, to be presented in the Progress Report for Quarter 8.

2. Summary of Significant Accomplishments

The significant accomplishments are:

- Prepare, isolate, purify and fully characterize six (6) total silyl-amine based reversible ionic liquids for CO_2 capture.
- Complete ATR FT-IR studies on six candidates to get information for thermodynamic analysis and directly measure both the chemical and physical absorption capacities.
- Successfully measure viscosities for molecular and ionic forms of all six candidates.
- Identify and synthesize promising target molecules for future synthesis and characterization based on evidence collected during the first 6 Quarters of the project.
- Completed stability tests that showed our custom-made compounds had superior degradation resistance than the commercially available compounds.
- Recent advancements have resulted in a submittal for publications in scientific journals and presentations at scientific conferences.

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*, in press, 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, 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, MI, 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 CO_2 Capture,” AIChE Spring National Meeting, Tampa, FL, April 2009

- Philip G. Jessop, Michael Cunningham, Charles A. Eckert, and Charles L. Liotta "CO_2 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.

c. Website

Webpages have been prepared and posted within the Eckert/Liotta group website http://www.chbe.gatech.edu/eckert/projects.html.

d. Intellectual Property

One invention disclosure based on the work of this project has been filed. It is Eckert, C.A., Liotta, C.L., Huttenhower, H.; Mestre-Llopes, V.; Blasucci, V.; Pollet, P.; "Reversible Ionic Liquids as Double Action Solventsfor Efficient CO2 Capture", Invention disclosure 9/29/2008.

e. 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:

Students Graduated

Vittoria Blasucci – PhD in Chemical Engineering, 2009 – Now at ExxonMobil
Hillary Huttenhower – PhD in Chemistry, 2010 – Now at Pratt & Whitney

Students Continuing

Dr. Pamela Pollet (Chemistry, Senior Research Scientist)
Dr. Ryan Adams (Chemical Engineering Postdoctoral)
Dr. Manish Talreja (Chemical Engineering Postdoctoral)
Dr. Elizabeth Biddinger (Chemical Engineering Postdoctoral)
Dr. Manjusha Verma, (Chemistry, Postdoctoral)
Ryan Hart (PhD Candidate, Chemical Engineering)
Olga Dzenis (PhD Candidate, Chemical Engineering)
Kyle Flack (PhD Candidate, Chemistry)
Amy Rohan (PhD Candidate, Chemical Engineering)
Greg Marus (PhD Candidate, Chemical Engineering)
Melissa Burlager (Senior, Chemical Engineering)
Paul Nielsen (Senior, Chemical Engineering)
Sean Faltermeier (Junior, Chemical Engineering)
Poomrapee Jewanarom (Sophomore, Chemical Engineering)

Note: Dr. Ryan Adams and Ryan Hart have accepted jobs and will be departing shortly. They will be replaced by two new postdoctoral chemical engineers, Manish Talreja and Elizabeth Biddinger.

f. 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.