CONCEPT

Relevance and Outcomes/Impacts: This effort has the potential to develop a whole new class of solvent systems capable of vastly increased capacity because of the dual action of stoichiometric reaction plus physical absorption of CO_2. Moreover, we shall develop a paradigm for optimizing the economics through structural changes in the solvents. The applicability of this would include not only coal-fired power generation, but removal of CO_2 from virtually any combustion effluent – gas, oil, or even biofuels.

Reversible Ionic Liquids for CO_2 Capture – Double Action

Our amine-based, one-component precursors actually capture more than stoichiometric CO_2 by dual mechanism. The solubility of gases, especially CO_2, in ILs is well documented. Our ILs function as both chemical and physical absorbents for CO_2. Two moles of solvent react with one mole of CO_2 to form the IL, which then acts as a solvent to physically absorb additional CO_2. Further, the 1:2 ratio of CO_2 to solvent can be improved to a 1:1 ratio with the addition of water, which already exists in the process.

The reversibility of the ionic liquid by heating will allow the recovery of CO_2 and regeneration of the CO_2-capturing agent. The structure-oriented tunability of these molecules allow us modify them to reach the desired properties for CO_2 capture such as high absorption capacity, low energy use for CO_2 desorption, low viscosity, low corrosion and low cost. It is desirable to absorb CO_2 at 30-80°C and desorb at 100-150°C. We shall exploit our extensive knowledge and experience in molecular design and structure-property relationships to modify the ionic liquid precursor structures and to achieve the desired physical and thermodynamic properties for CO_2 capture.

Synthesis and Characterization of Custom Reversible ILs

We have shown that basic nitrogen organic molecules can reversibly capture CO_2 to form an ionic liquid and that the reactions are rapid and quantitative.

We propose to investigate the use of a variety of amine and guanidine based materials for the capture and subsequent release of CO_2.

The importance of the use of amines and guanidines relies on the facile alteration of their substitution pattern, which allows easy modification to fine-tune their physical properties. We shall design the molecular architecture to tune the rapid and efficient capture and release of carbon dioxide within narrow temperature ranges.

We can obtain control over a range of selected properties by designing molecules with modest changes to their substitution groups. The release of carbon dioxide can be facilitated by

the presence of a weak Lewis acid such as silyl or silyloxy substituent. Also the designed molecules have to be low in viscosity to facilitate mass transfer of the CO_2. Low viscosity is also crucial in after-capture processing of ionic liquids such as transportation of the ionic liquids, recovery of CO_2, and recycle and regeneration of the ionic liquid precursors. Not only does silyl substitution produce a less viscous liquid, but also silyl groups are CO_2-philic and can enhance the CO_2 absorption capacity of the ionic liquid. This yields the double-action effect that increases the CO_2 capture capacity of this unique solvent.

We propose to alter the substitution pattern of the amine and guanidine based materials with the objective of optimizing the absorption-desorption of CO_2 in these compounds.
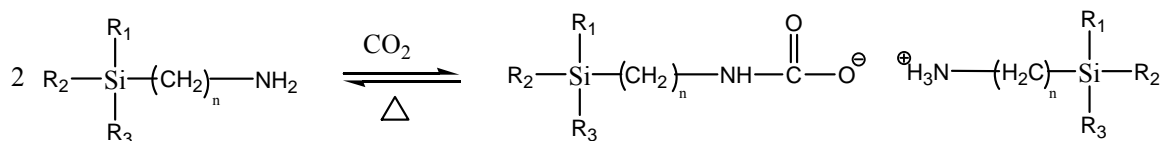
1. Amine based reversible ionic liquids

Primary and secondary amines are efficient functionalities for capturing CO_2 compared to tertiary amines. In fact, we have shown that CO_2 can be reversibly captured by a suitable primary or secondary amine to form a reversible ionic liquid at room temperature and one atmosphere (Scheme 4). In this case, the amine acts both as a base (to form an ammonium cation) and as a nucleophile (to form an alkyl carbamate anion).
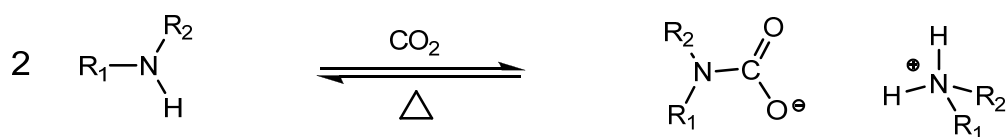
Scheme 4: Reversible capture of CO_2 by primary or secondary amines, R_2 = alkyl chain or H

Desorption of the absorbed CO_2 can be easily carried out by gentle heating of the ionic liquid. *We propose to study the use of amine based materials for the capture and subsequent release of CO_2.* Nevertheless, release of carbon dioxide by amine based reversible ionic liquids can be improved by using silyl derivatives of primary and secondary amines. *We propose to design amines in combination with a weak Lewis acid to optimize the capture of carbon dioxide* (Scheme 5).

Scheme 5: Reversible absorption of CO_2 by a silylated amine, where $R_1 = R_2 = R_3 = CH_3$-, $CH_3(CH_2)_n$-, CH_3O-, $CH_3(CH_2)_nO$- or $R_1 \neq R_2 \neq R_3$

In addition, the effective capture and release of CO_2 can be optimized by tuning the viscosity of the amine based reversible ionic liquid. For example, lower viscous amine reversible ionic liquids can be obtained by simply breaking the symmetry of the molecule.

Importantly, CO_2 capacities can increase in the presence of water. For example, a primary dry amine would first react with a CO_2 molecule, but then with another primary amine, as shown in Scheme 6 below, to give a CO_2:amine ratio of 1:2.
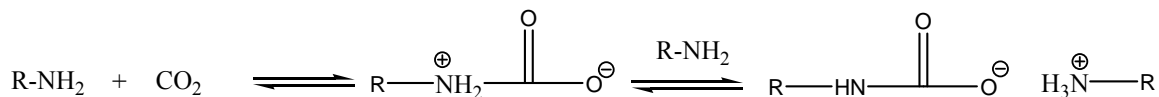
Scheme 6: Reaction of primary amine with CO_2 (dry). Intermediate is not stable in the presence of another amine

However, in the presence of water, as shown in Scheme 7, the product of the amine and CO_2 would react with a water molecule, and the ratio would be 1:1. This then doubles the capacity of the dry adsorption, and demonstrates an example of the presence of water actually being advantageous. In fact, there are numerous reports in the literature where CO_2 capacities increase in the presence of steam. In any real CO_2-capture process, water would of course be present.
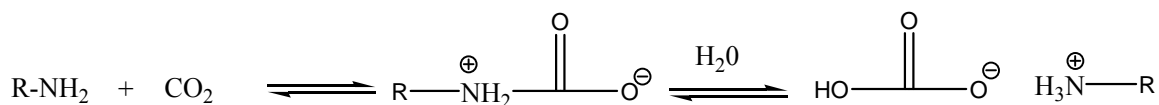
Scheme 7: Reaction products of a primary amine with CO_2 (wet)

Synthesis of silylated amines

Amine functional silicones can be prepared by a hydrosilation reaction using zero valent platinum catalyst. The synthesis involves readily available commercial starting materials and proceeds under mild conditions in high yield. Commercially available alkyl hydrosilicones are hydrosilated with allyl amine or other alkenyl amine in the presence of platinum (0) divinyltetramethyldisiloxane (Scheme 8).
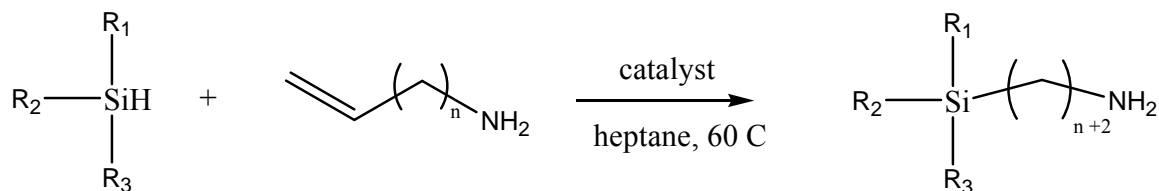

Scheme 8: Synthesis of amine functional silicones

A variety of aminofunctional silicones can be synthesized in this manner by modification of the alkyl functionality of the silicone (R_1, R_2 and R_3 may be the same or different functional or non-functional alkyl groups of same or different length) and the chain length of the amine.

The starting materials for the synthesis of the amines are commercially available at laboratory scales, and they are synthesized from inexpensive and readily available chemicals. As part of this work we shall develop and optimize the methods of large-scale bulk synthesis and production of solvents successful for capture and release of CO_2.

Guanidine based reversible ionic liquids

We have also shown that guanidines can absorb CO_2 at room temperature and one atmosphere resulting in the formation of guanidine based reversible ionic liquids. This absorption of CO_2 can be reversed by simply heating the ionic liquid under mild conditions (Scheme 9).
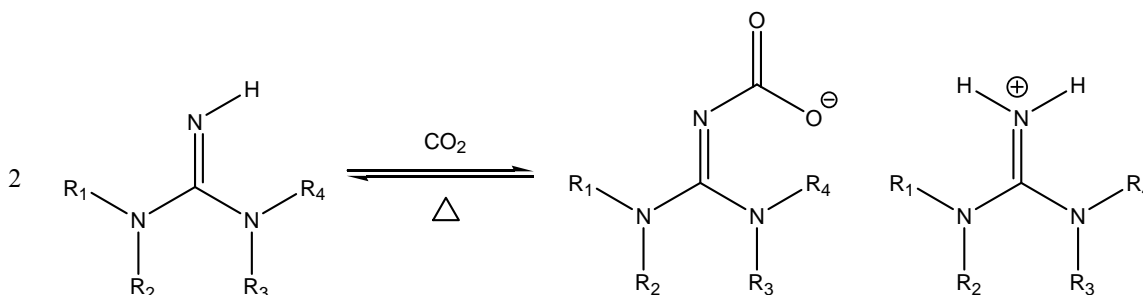
Scheme 9: Reversible absorption of CO_2 by guanidines, where R_1, R_2, R_3,and R_4 may be the same or different alkyl groups
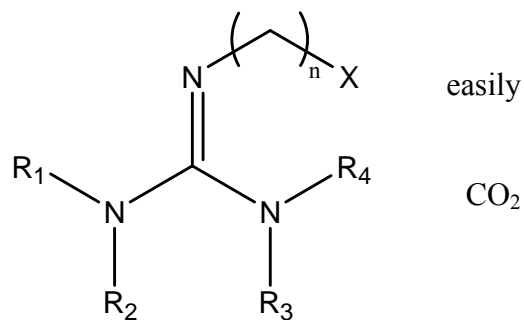
We propose to explore the use of guanidine based materials for the capture and subsequent release of CO_2.

In addition to guanidines reacting readily and reversibly with CO_2, their substitution pattern can be altered and modified to fine-tune the physical properties of the guanidine and the subsequent ionic liquid. Thus, optimization of the reversible capture of by guanidines can be accomplished by fine-tuning the substitution pattern around the nitrogen atoms of the guanidines.
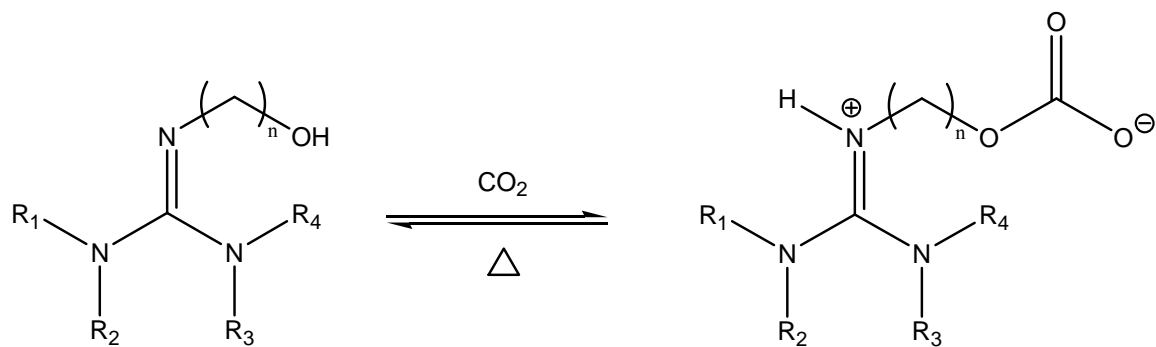
We propose to study the absorption-desorption behavior of CO_2 in different substituted guanidinium based reversible ionic liquids.

easily

CO_2

Scheme 10: Substitution pattern of guanidine based materials, X= OH- or NH_2-

We shall investigate the effect on the absorption-desorption of CO_2 when introducing functional groups such as alcohol or amines in the alkyl substitution pattern of the guanidine itself (group X-, Scheme 10).

Thus, a guanidine material with alcohol functionality will react with CO_2 to form a reversible ionic liquid that upon heating will release CO_2 (Scheme 11, below).
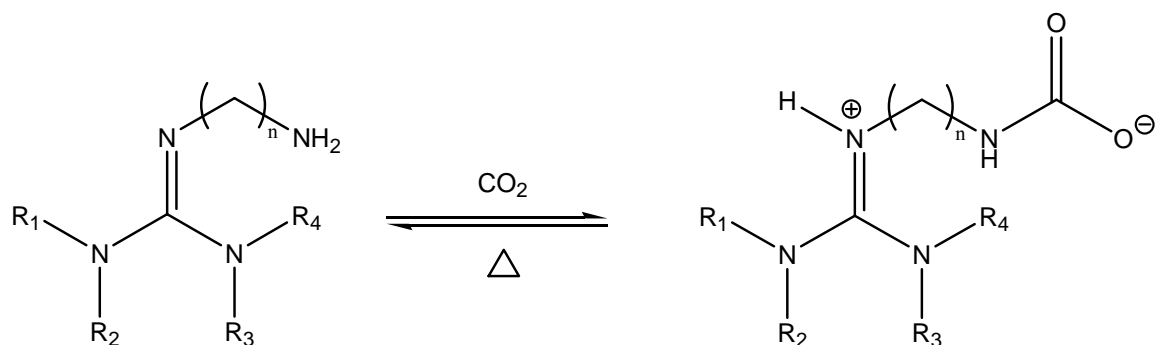
Scheme 11: Reversible capture of CO_2 by alcohol functional guanidine based materials

In the same manner, a guanidine material with amine functionality will reversibly capture CO_2 (Scheme 12).

Scheme 12: Reversible CO_2 capture by amine functional guanidine based materials

Instead of introducing functional groups in the alkyl substitution pattern of the guanidine itself to capture CO_2, alcohol or amine functionality can be introduced at the substitution pattern of the nitrogen atoms around the guanidine (groups R_1, R_2, R_3 or R_4). Such changes could be achieved by synthesizing unsymmetrical ureas, followed by reaction with different amines to form the desired guanidines (Scheme 13).
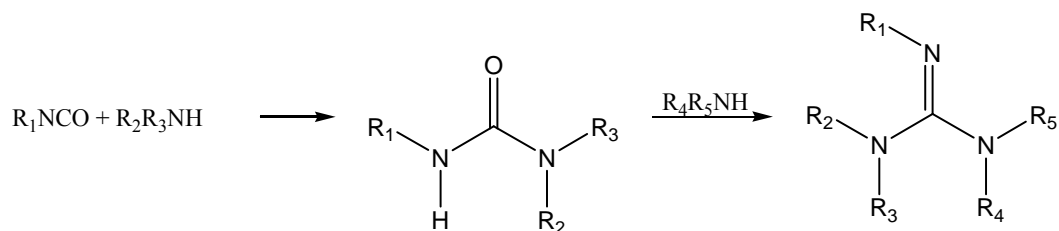

Scheme 13: Synthesis of different alkyl substituted guanidines, where R_1, R_2, R_3 or R_4 can have amino or alcohol functionality

Importantly, changing the substitution pattern of the guanidine itself or the nitrogen atoms around can provide dramatic changes of the viscosity due to breaking the symmetry of the molecule. In particular, the addition of silane groups in the substitution pattern of the nitrogen atoms around the guanidine (groups R_1, R_2, R_3 or R_4) to produce silicone-substituted guanidines can lower the viscosity of the liquid. This is because silicon has lower electronegativity than carbon and silicon-carbon single bond lengths are substantially longer than the analogous carbon-carbon single bonds. Thus, silicone substituted materials have a more flexible structure leading to a lower viscosity.

Again, the dual action of the solvent is an asset: silicone substitution can also enhance the physical CO_2 absorption by the guanidine based ionic liquid. Silicone functionality is well known to be CO_2-philic and enhances the molecular interactions with CO_2. In addition, the reversibility of the guanidine-based reversible ILs by release of carbon dioxide will be favored by silation of the guanidine. *We propose to investigate the effect of using silyl substituted guanidines based materials for reversible capture of CO_2.* Such changes can be achieved by synthesizing unsymmetrical ureas, followed by reaction with different amines to form the desired guanidines (Scheme 13).

Synthesis of substituted guanidines

The covalent guanidine with the "built-in" alcohol or amine can be simply synthesized from tetramethylurea by modification of our actual procedure (**Scheme 14**).
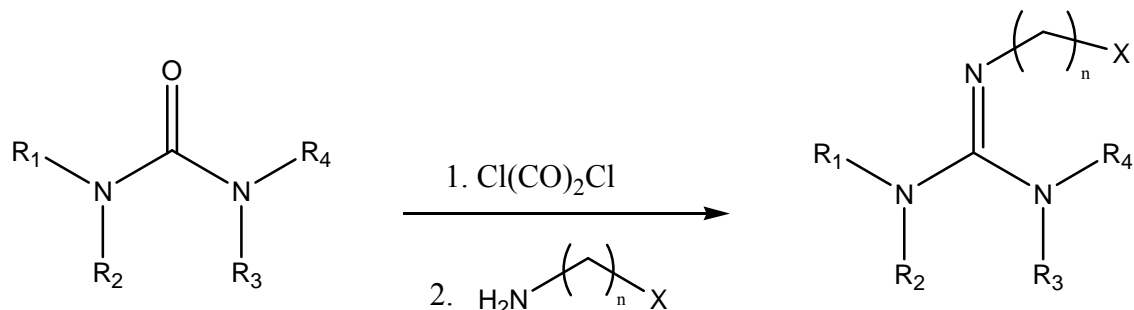
Scheme 14: Synthesis of functional guanidines based materials, X = NH$_2$- or OH- or SiO(CH$_3$)$_2$Si(CH$_3$)$_3$

Characterization of Custom Reversible ILs

Viscosity

The viscosities of our one-component trimethoxysilylpropylamine and triethoxysilylpropylamine ionic liquids were measured in a cup and bob rotary viscometer (Figure 2). The results demonstrate that this ionic liquid is a Newtonian fluid; the viscosity does not change with shear rate. Further, the change in substitution from methyl to ethyl changes the viscosity by more than a factor of two. Although the viscosity of many pure ionic liquids would be higher than desirable for the proposed application, many methods exist to easily reduce the viscosity of these materials. ***We propose to use a combination of structural changes, gas absorption, and co-solvent effects to lower viscosity.***
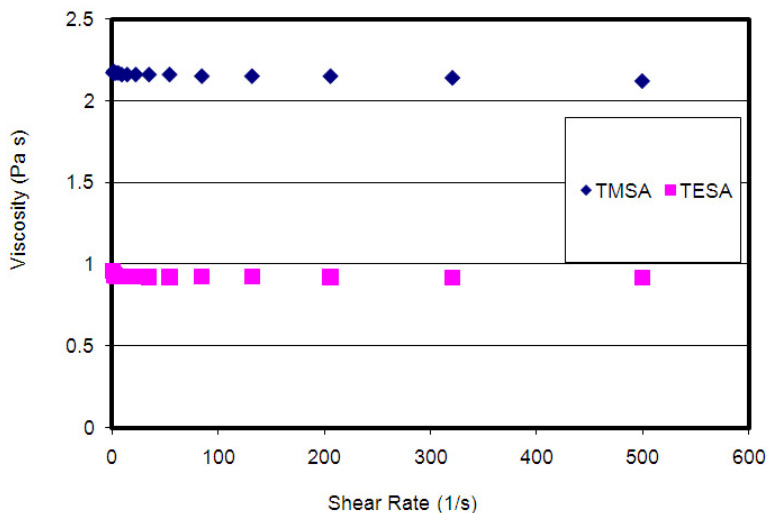

Figure 2. Viscosity of trimethoxylsilylpropylamine (TMSA) and triethoxylsilylpropylamine (TESA) ionic liquids

The addition of small amounts of co-solvent drastically reduces the viscosity of ionic liquids. Most relevant to this application, water can be added to decrease the viscosity of ionic liquids as has been demonstrated for the imidazolium based ionic liquids which showed a 2/3 viscosity reduction with 20 mol% water. The viscosity dependence on water concentration follows the equation, $\eta = \eta_s e^{-x/a}$, where η_s is the viscosity of the pure ionic liquid at 20 °C, x the mole fraction of water and a is a constant dependent on ionic liquid used. Water will be present in the proposed process in the form of water vapor in the gas stream, so addition of water to the ionic liquid and/or ionic liquid precursor will not be necessary to achieve the desired result. In addition, ionic liquids are hygroscopic, and completely dry ionic liquids exposed to ambient conditions for three hours can absorb over 6 wt% water. As has been previously mentioned, the addition of water not only reduces the ionic liquid's viscosity, making it more applicable for this process, but it also increases carbon dioxide capture capacity.

The second method that will decrease the ionic liquid viscosity is gas absorption, particularly of CO_2. We have shown that CO_2 decreases the microviscosity of [bmim][PF$_6$], a commonly studied ionic liquid, by a factor of 4 at 35 °C and 50 bar. Also, the structural characteristics of the ionic liquid affect viscosity. Therefore, new, reversible, one-component ionic liquids that meet our desired viscosity will be developed through structural modifications of our current ionic liquid precursors. Asymmetric ions lower ionic liquid viscosities. Also, the addition of multiple silyl groups to the compound's structure will reduce viscosity due to the increased flexibility of a silicon-carbon bond over a carbon-carbon bond. The addition of one silicon atom to a side chain of an imidazolium cation decreased its viscosity by an order of magnitude.

TGA_DSC, NMR, and Elemental Analysis

The TGA thermogram (Figure 3) shows an initial mass loss of 7 % starting at approximately 40 ºC, which corresponds to the loss of CO_2 from the ionic liquid. This loss proves the reversibility of the ionic liquids. The DSC curve can be used to calculate the enthalpy required to remove carbon dioxide from the ionic liquid for reversal.
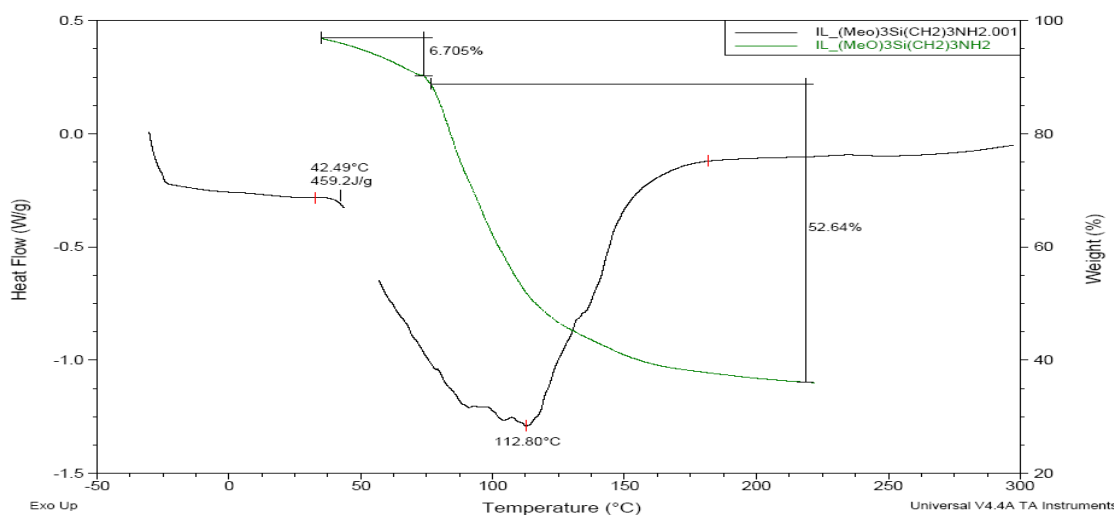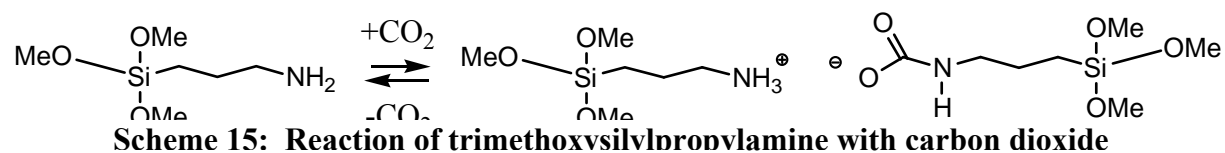

Figure 3.   TGA_DSC of trimethoxysilylpropylamine

The formation of the ionic species from the neutral silylamine precursor (Scheme 15) has been proven by both ^{13}C NMR as well as elemental analysis. Figure 4, on the next page, shows the ^{13}C NMR of the precursor, while Figure 5, on the next page, shows the ^{13}C NMR after reaction with CO_2. The appearance of a carbonate peak at 160 ppm in Figure 4 is consistent with formation of the ionic liquid.

Scheme 15: Reaction of trimethoxysilylpropylamine with carbon dioxide

The elemental analysis of the ionic liquid also confirmed its formation, with the experimental results being 96% in agreement with theoretical calculation.
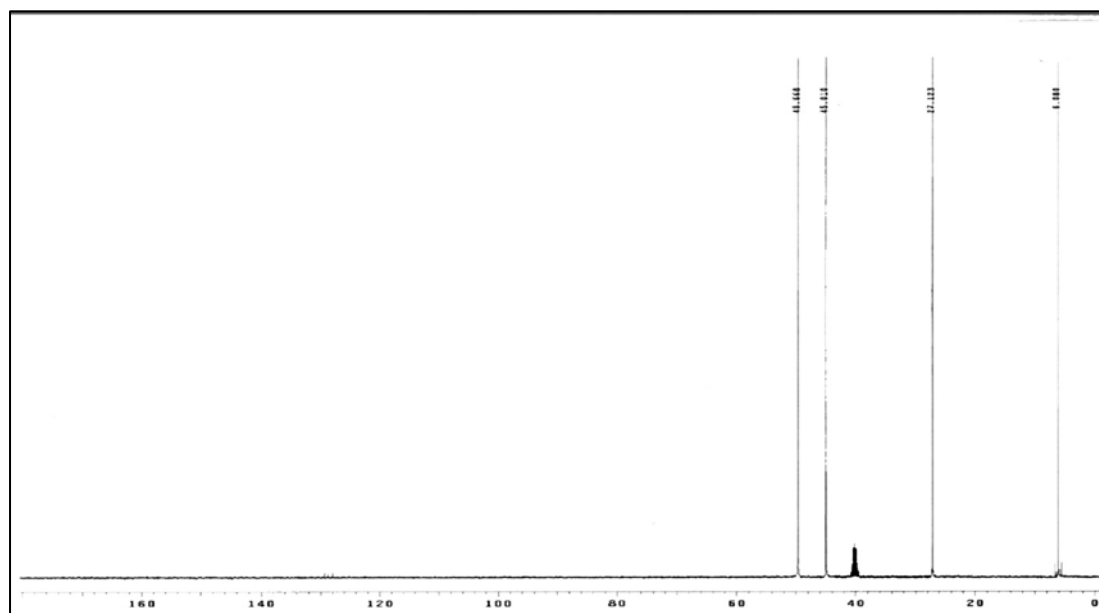
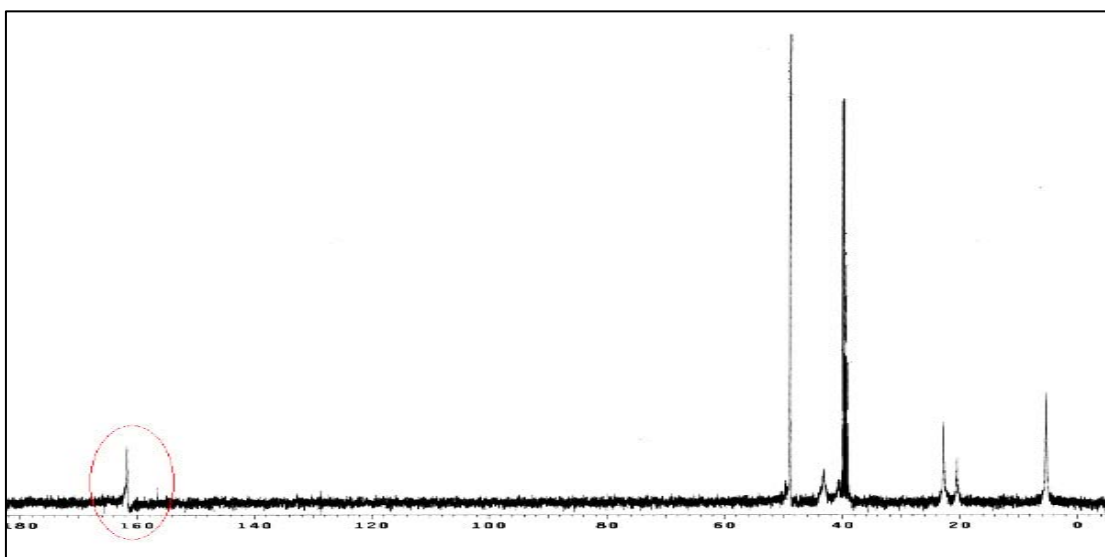Figure 4. ^{13}C NMR of trimethoxysilylpropylamine

Figure 5. ^{13}C NMR of trimethoxysilylpropylamine ionic liquid

Thermodynamics of CO₂ Capture

The thermodynamics of the absorption process will have a major effect on the energy use and thus economics. The process will involve absorption at a lower temperature, T_{low}, followed by heating to a higher temperature, T_{high}, for desorption of the CO_2 and regeneration of the solvent, followed by cooling back to T_{low} to repeat the cycle. Thus, there are three factors that affect the thermodynamics. These are the ΔH^{abs} (enthalpy of absorption, also desorption), the ΔG^{ads} (Gibbs energy of adsorption), and the energy required to change the bed temperature, $Q = mC_P(T_{high} - T_{low})$ where m is the mass and C_P the heat capacity of the bed.

Our goal is to absorb strongly at T_{low} (probably 30-80 ºC) and desorb strongly at T_{high}. (100-150 ºC). Thus, we seek an equilibrium constant for binding, K, which is K > 1 at T_{low} and K<1 at T_{high}. This K is related to ΔG^{ads} by the relationship:

$$K = \exp\left[\frac{-\Delta G^{ads}}{RT}\right]$$

ΔH^{ads} will determine the heat required for regeneration, but also the rate of change with temperature of ΔG^{ads}, as shown by the Gibbs-Helmholtz relationship, below. If ΔH^{ads} is low, very little heat will be required at T_{high} for desorption, but for $T_{high} >> T_{low}$, more energy will be required for the heating up process, Q, above.

$$\frac{d\left(\Delta G^{ads} / RT\right)}{dT} = -\frac{\Delta H^{ads}}{RT^2}$$

Thus the thermodynamics offer a suitable target for optimization. We can do mathematics to balance the ΔG^{ads} and the ΔH^{ads} to minimize the energy requirement, but better yet, we can chemically modify our solvents to achieve the desired values of G^{ads} and H^{ads}. In this regard, *we propose 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.

We are currently assaying the effect of solvent structure on K by FT-IR spectroscopy. FT-IR spectroscopy gives us the advantage of a non-invasive *in situ* assay of reaction equilibrium and kinetics. Additionally, spectroscopic techniques give us a molecular level insight so that we can better understand reaction progression on the most fundamental level. The K can be determined from the following expression:

$$K = \frac{x}{(1-x)^2 P_{CO2}}$$

By assuming that the solvent has a negligible vapor pressure, we can calculate K by from the conversion (x) and CO_2 pressure (P_{CO2}). The conversion to the IL as a function of CO_2

pressure is obtained through assay of the carbonyl peak (~1750 cm^{-1}) that is formed as the reaction proceeds. Application of the Beer-Lambert Law.

$$Absorbance(A) = absorptivity(\varepsilon) \times pathlength(l) \times concentration(c)$$

allows us to determine conversion as the absorbance of the characteristic IR frequency is proportional to concentration of ionic liquid formation.

These data are collected by use of a high pressure attenuated total reflectance (ATR) IR cell. Attenuated total reflectance gives us the opportunity to collect IR spectra for dense phases. The maximum intensity of absorbance is a limiting factor of spectroscopy, where signals above 3 A.U. completely saturate the detector. The Beer-Lambert Law governs that for molar densities of liquid phases, a path length would need to be on the order of microns. This is not feasible with conventional transmission spectroscopy. Our ATR-IR cell consists of a ZnSe optical element that enables the IR signal to reflect several microns past the element into the sample.

As the reaction proceeds, the density and absorptivity of the sample change. Our approach of understanding our solvents on a molecular level allows us to easily correct for this by taking ratios of the carbon-hydrogen stretch frequencies, located <3000 cm^{-1}. As there is no change in the number of C-H bonds in the sample, this technique gives us a built in standard that allows us to monitor the change in volume of the sample.

The ATR-IR cell also has excellent thermal control, which allows us to measure equilibrium constants as a function of temperature. By collecting equilibrium data at just several temperatures, we efficiently optimize the temperature for which our solvents will both absorb and desorb CO$_2$. Combined with our structure-property approach to determine K, *we can determine the best possible solvent structure for a given processing stream or set of processing criteria.*

As IL media have shown considerable physical absorption of CO$_2$, we aim to take advantage of a dual sorption process to more efficiently remove CO$_2$. The FT-IR measurement technique gives us the opportunity to simultaneously measure K and the amount of free CO$_2$ absorbed in our ionic solvent systems. CO$_2$ has a unique IR frequency, located ~2350 cm^{-1}. This CO$_2$ loading is determined in a similar fashion to the determination of ionic species conversion.

Scrubber Process Design

In conjunction with the optimization of the fundamental properties of our solvents, we propose to use chemical processing simulation software (such as ASPEN) to optimize the economics of our process. Simulation packages are a powerful tool that afford for efficient processing modifications and economic optimization. We can include experimental data collected for our CO$_2$ capture solvents in the laboratory, and quickly determine the effects of the solvent structure on the economics of our process.

The process flow diagram for typical solvent CO$_2$ scrubbing system (Figure 6) shows an absorber tower, a stripper column, and a heat exchanger to recover heat from the hot regenerated solvent. Flue gas enters the bottom of the absorber while cooled lean solvent is pumped in from

the top. The gas contacts the solvent and CO_2 and is absorbed; the remaining flue gas leaves out the top of the tower, and the CO_2-rich solvent leaves at the bottom. The solvent passes through
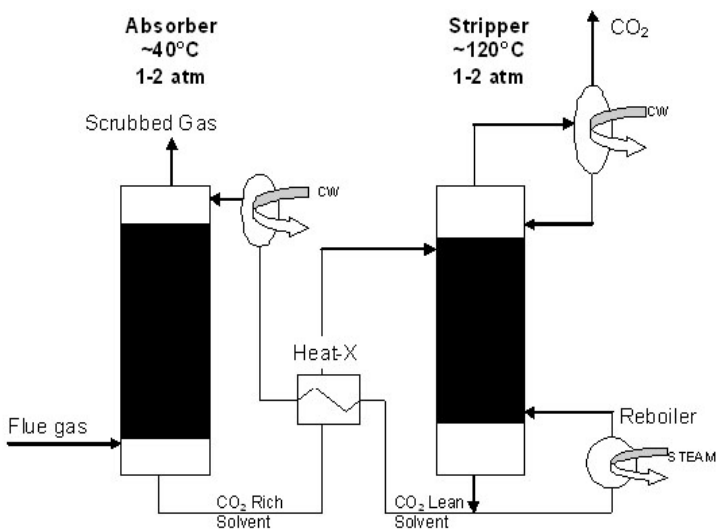

Figure 6: process flow diagram for typical solvent CO_2 scrubbing system

the heat exchanger, where it is heated slightly before entering the stripper column. A reboiler heats the solvent using steam to reverse the absorption reaction and regenerate the solvent. The hot lean solvent is recycled back through the heat exchanger and a cooler before it is pumped back to the top of the absorber. The CO_2 product stream from the top of the stripper column is saturated with water at nearly atmospheric pressure, and must be dehydrated and compressed before it is sent to a pipeline for transport to a consumer or sequestration site.

The thermodynamics of capture play the dominant role in the economic effectiveness for CO_2 capture techniques. Because of this, we shall optimize the process economics using structure-property relationships to optimize the thermodynamics of the solvent candidates, and then use the thermodynamic data to optimize the economics.

For a preliminary evaluation of the economic benefits of our one-component solvent systems for CO_2 capture, we choose to compare the relative energy requirements of our system to a common industrial solvent system, namely monoethanolamine (MEA). MEA processes are common due to the abundance of materials, the well-understood separation fundamentals, and familiarity with processing equipment. However, dilute solutions must be used to limit corrosivity issues, even with the addition of corrosion inhibitors. Also, there is an extremely high energy requirement for the regeneration of amine solvent systems. Much of the energy is not used to regenerate the amine, but rather to heat the solution that is ~70 % water.

It is, therefore, advantageous to operate solvent scrubbing systems with neat solutions, as dilution drastically increases the energy requirement. We assume a base case of a 30 %wt MEA solution for comparison, which is typical of most amine scrubbing systems. We start with the expression for the energy requirement to heat the regeneration tower, $Q = mC_P(T_{high} - T_{low})$. We assume that the heat capacity of the tower (C_p) for our process is equivalent to the typical amine system, and that we are operating our process at the same absorption and desorption temperatures. For an equivalent CO_2 removal efficiency and an equivalent energy input, ***our one-component solvents can effectively treat over 3 times the amount of CO_2 per cycle as the MEA process.***

We use simulation software regularly in moving our research from laboratory to practice. A demonstration of such a design follows with a detailed flow diagram used for the ASPEN
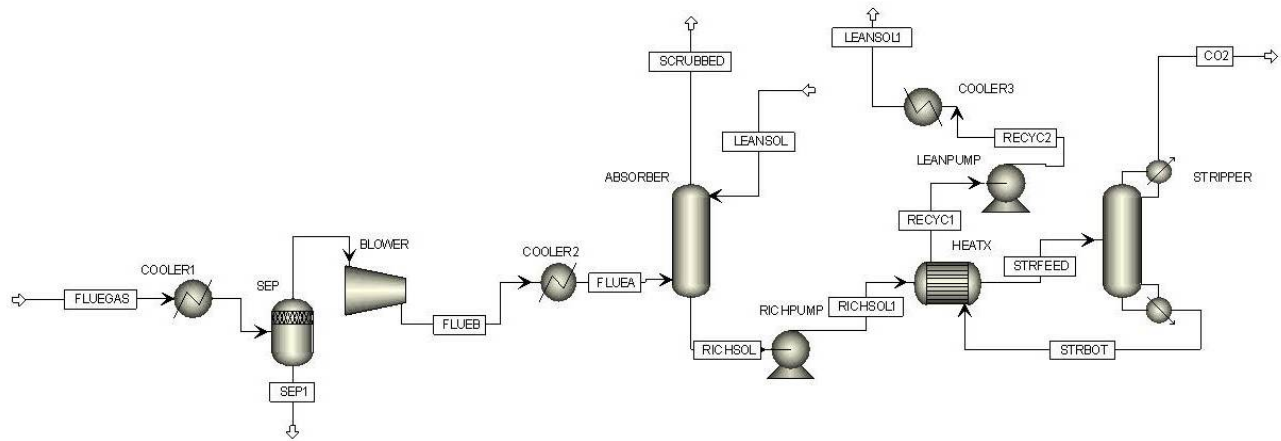
Figure 7. ASPEN flow diagram of novel solvent scrubbing process.

simulation, shown on the next page (Figure 7). To ameliorate the effects of the viscosity of the IL, we would recommend a trickle-bed column for the absorber.

The economic benefits of our methodology to explore one-component solvents in a structure-property relationship fashion not only decrease the solvent volume required, but also lead to the optimum temperatures for absorption and desorption. For the energy required to regenerate the solvents, a reduction in (T_{high} - T_{low}) by a mere 10°C will result in a **reduction in energy consumption by 12.5 %.**

STRUCTURE-PROPERTIES RELATIONSHIPS

The relationship between molecular structure and molecular properties has been a cornerstone of physical-organic chemistry for more than half a century. What it does is to establish a series of paradigms for predicting how various chemical structures will result in a plethora of physical properties, based on both enthalpic and entropic effects. Because our group thrives on the synergy of chemistry with chemical engineering, we have applied such techniques successfully to a great variety of situations in the past.

For example we have used these methods to characterize and modify a great many novel tunable solvents, such as supercritical fluids, nearcritical water, and gas-expanded liquids. Similarly we have exploited them to correlate, predict, and modify a variety of thermodynamic properties, as for example heats of solution and phase equilibria. We have used them to study and modify reaction processes. Finally we have even used them to design a solvent-free paint for aircraft.

REVERSIBLE IONIC LIQUIDS

Background on Ionic Liquids

Ionic liquids (ILs) are salts composed solely of ions, with melting points near or below ambient temperature. Some ionic liquids can exhibit unusual and advantageous properties like negligible vapor pressure, nonflammability, high thermal stability, wide liquid temperature range, high solvency, high thermal conductivity and immiscibility with many organic solvents. Their physical and solvent properties can be tailor-designed by tuning the pairing and structure of the cations and anions. The most common application of ionic liquids has been their use as chemical reaction solvents. ILs have also been used for electrochemical processes, removal of metal ions, purification of gases, generation of high conductivity materials, extraction solvents stationary phases in chromatography, thermal fluids, lubricants, and propellants.

Solvent properties of ILs are mainly determined by the ability of the salt to act as a hydrogen bond donor and/or acceptor and the degree of localization of the charges on the anions. For example, imidazolium-based ILs are highly ordered hydrogen-bonded solvents and they have strong effects on chemical reactions and processes. Charge distribution on the anions, H-bonding ability, polarity and dispersive interactions are the main factors that influence the physical properties of ILs. Even though some of the ILs such as $[EtNH_3][NO_3]$ were first described in 1914, the phenomenal growth has occurred in industrial and academic interest in the last decade due to their acceptation as a new green chemical with unique properties.

Recently solubilities of gases in ionic liquids have been investigated for purification processes. These experimental studies show that some gases, especially CO_2, are highly soluble in some ILs. The simulations performed explain that the anion of the IL is responsible for high gas solubility, and the relatively high solubility of CO_2 was explained as a result of its large quadrupole moment.
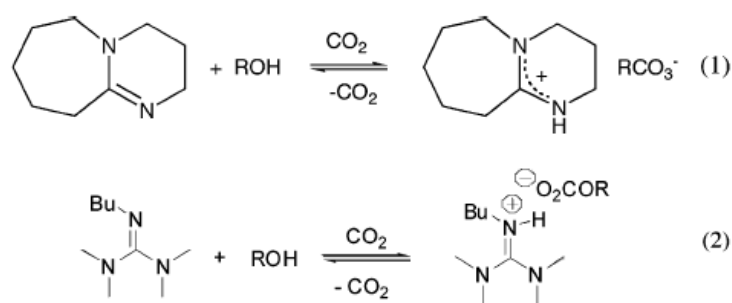
The green character of ILs has been usually related with their negligible vapor pressure; however the toxicity, biodegradation, bio-accumulation, safety, health, and environmental impact data of the conventional ionic liquids have been very limited until now, and are needed immediately. In recent studies it was shown that by pairing and structural tuning of anions and cations, it is possible to design non-toxic ionic liquids. One of the major concerns in applications of ionic liquids, such as imidazolium and ammonium ILs, is their high hydrophilic character, which can lead to decomposition, deactivation of catalysts, and degradation and contamination of solutes in ionic liquids. For example despite their wide spread usage, ILs containing PF_6- and BF_4- have been reported to decompose upon heating in the presence of water and emit HF. Also ILs containing halogen anions generally show poor stability in water, and give off toxic and corrosive species such as HF or HCl. Other challenges of conventional ionic liquids are extreme cost, separation issues, lack of estimated thermophysical and transport properties, and high viscosities. If recycling of an ionic liquid is possible, it generally requires extensive washing with water or organic solvents creating large amounts of wastes and VOCs.

However, the vast majority IL applications to date address only the reaction; they ignore product separation and purification. These are necessary for a full process and it is in the separation and reuse that the greatest problems occur – both in energy consumption and in losses and pollution.

Reversible Ionic Liquids: Facile separation and solvent recovery

We have developed sustainable, reversible ionic liquids in our labs to overcome the separation and purification problems of conventional ionic liquids, while taking the advantage of their beneficial properties. The built-in switch of these systems let us reversibly change the nature and the properties of these liquids from a molecular liquid to an ionic liquid on command, under mild conditions and preferably with mild reagents. This "on and off" chemistry has allowed us explore applications in which we can achieve a synergy of reaction and purification that are both green and economical.

We found that the exposure of a 1:1 mixture of the two neutral liquids 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) and 1-hexanol to gaseous CO_2 at 1 atm, causes an exothermic conversion of the molecular liquid phase to an ionic liquid (Scheme 1). This is akin to going from chloroform to dimethylformamide (DMF) in polarity. The ionic liquid can be converted back to a neutral liquid by bubbling an inert gas, i.e. N_2 or Ar, through the liquid at room temperature. Shown by the thermogravimetric studies, the ionic liquid can also be reversed by heating up to 50-60 °C, which yields higher reversal rates. We have then found many other switchable liquids, each of which can be converted to an ionic liquid upon exposure to an atmosphere of CO_2 gas and then converted back to a neutral organic liquid upon exposure to N_2 or Ar gas, or heat. We have reported another example based on the mixture of an alcohol with 2-butyl-1,1,3,3-tetramethylguanidine (TMBG) (Scheme 2). Our characterization studies of these switchable ionic liquids show that their physical properties such as melting point, viscosity and polarity, and thermodynamic properties such as ΔH and ΔG of reaction can be tuned with the alkyl-chain length of the alcohol and the attached group(s) on the amine base (see below).

Schemes 1 and 2 – New reversible ionic liquids

The switchable characteristic of the reversible ionic liquids allow facile separation, recovery and reuse of these solvents following a chemical synthesis or extraction, which can be repeated in many consecutive steps. The separation and recycle are viable due to the change in solvent properties change, as the non-ionic liquid is converted to ionic liquid. For example, the mixture of 1-hexanol and DBU under N_2 (neutral form) is miscible with the nonpolar solvent decane, whereas the ionic liquid form (under CO_2) is not. Also a TMBG/methanol equimolar mixture in its neutral form is miscible with the nonpolar solvents pentane, hexane, heptane, and octane, whereas the ionic liquid form is not. In both cases, the nonpolar solvents can be separated simply by decanting, and the ionic liquid can be recycled and reversed. Here therefore we use CO_2 and N_2 at 1 bar as triggers of miscibility and immiscibility,

which can be further tuned by the type of alcohol used and the attached groups on the amine based ionic liquid precursor.

We demonstrated the opportunity of the solvent switchability in chemical reactions by performing the polymerization of styrene in 1:2.5 molar ratio mixture of DBU and 1-propanol (Fig. 1). Styrene was polymerized with $K_2S_2O_8$ initiator in the neutral solvent at 50 °C. After polymerization, the solvent was switched to its ionic form, in which polystyrene has limited solubility. The precipitated polymer was collected by filtration, and the filtered solvent was reconverted to its neutral form and used again for another polymerization. The solvent was used for a total of four cycles with an overall yield of polystyrene of 97 %.

A single-component switchable ionic liquid could greatly simplify processing. In preliminary experiments we have shown that such ILs can be formed with CO_2 and silylated amines without the need of using an alcohol precursor (Scheme 3).
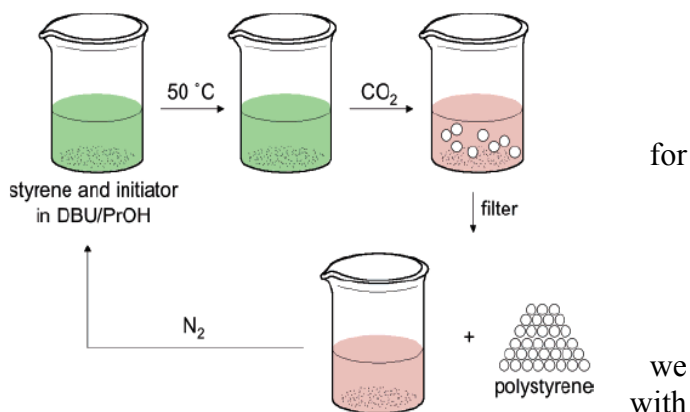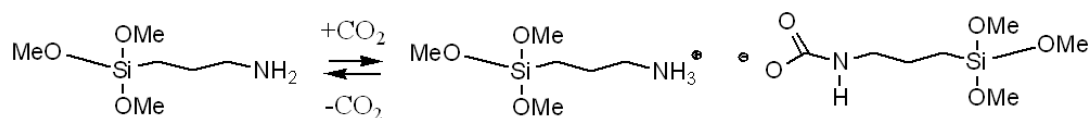

Figure 1: Styrene Polymerization in DBU/1-propanol-switchable IL precursor with recovery of polystyrene and solvent recycle.

Scheme 3

As we observed for the previous amidine or guanidine based ionic liquid systems, the silylated amine ionic liquids physical properties such as melting point, viscosity, and decomposition temperature, and thermodynamic properties such as ΔH and ΔG of reaction vary broadly with the structure of the ionic liquid precursor. A major thrust of this work is tailoring these properties for optimum use as a CO_2-capture solvent.