Design and Evaluation of Ionic Liquids as Novel CO_2 Absorbents

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Abstract

Progress from the first quarter of activity on the project “Design and Evaluation of Ionic Liquids as Novel CO_2 Absorbents” is provided. Major activities in three areas are reported: *assembling equipment and a research team*, *compound synthesis* and *molecular modeling*.

Nine new ionic liquid compounds have been made or acquired, and are in line for physical property testing to assess their potential for CO_2 sequestration. Quantum mechanical calculations between CO_2 and different ionic liquids have been conducted. The simulations have shed light on the nature of interactions between CO_2 and the ionic liquids, and are providing insight that will be used to suggest new compounds to be synthesized and tested.

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Introduction

Ionic liquids are a new and exciting class of compound that have the potential to overcome many of the problems associated with current CO_2-capture techniques. Ionic liquids (ILs) are organic salts that are liquid in their pure state near ambient conditions. ILs are regarded as potentially environmentally-benign solvents due to their immeasurably low vapor pressure, which essentially eliminates the opportunity for solvent release to the atmosphere.

Typical ILs usually have either imidazolium, quaternary ammonium, pyrrolidinium, pyridinium, or tetra alkylphosphonium as the base for the cation. Possible anions include hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$, bis(trifluoromethylsulfonyl) imide $[(CF_3SO_2)_2N]^-$, triflate $[CF_3SO_3]^-$, acetate $[CH_3CO_2]^-$, trifluoroacetate $[CF_3CO_2]^-$, nitrate $[NO_3]^-$, chloride $[Cl]^-$, bromide $[Br]^-$, or iodide $[I]^-$, among many others. Our group and others have shown that adjusting the structure of either the anion or the cation can have large effects on many properties including melting points, viscosities, densities, and gas and liquid solubilities (Bonhote, 1996; Seddon, 2000; Anthony, 2001; Anthony, 2002; Anthony, 2003). Due to the variety of possible cations and anions, there are virtually an infinite number of possible combinations, which means there should be ample opportunities to tailor and optimize the properties of these solvents for CO_2 sequestration.

The goal of this project is to obtain a fundamental understanding of the solubility of CO_2 and other components present in flue gas in ILs, with the practical objective of tailoring the properties of the liquid to maximize the engineering properties for this process. Our plan is to do this through a combination of *synthesis and experimental measurements*, *molecular simulation* and *applications development.*

The project is led by the PI, Prof. Edward Maginn. Other team members include the co-PI Prof. Joan Brennecke, postdoctoral researchers Dr. Mark Muldoon (synthesis), Dr. JaNeille Dixon (synthesis) and Dr. Haizhong Zhang (simulations), and Ms. Jessica Anderson (physical property measurement).

This first technical report describes the results of our work on this project since project initiation (7/16/04) through the end of the first quarter (9/30/04). This includes assembling the research team and initiating the project, selection of compounds for Phase I synthesis, characterization and evaluation of Phase I compounds, and performing quantum mechanical calculations on a range of different ILs to assist in the selection process. Details of each of these elements and well as results to date are discussed below.

Executive Summary

Ionic liquids (ILs) are organic salts that are liquid in their pure state near ambient conditions. They are a new and exciting class of compound that have the potential to overcome many of the problems associated with current CO_2-capture techniques. This project is concerned with developing a fundamental understanding of the solubility of flue gas species (mainly CO_2) in ionic liquids. Using this knowledge, we hope to develop new IL compounds that can be used in a cost effective manner for CO_2 capture. During the first quarter of the project, we have undertaken three major activities: *assembling equipment and a research team*, *compound synthesis* and *molecular modeling*.

Assembling Equipment and Research Team

We have collected the equipment and personnel necessary to initiate the project. The research team consists of Prof. Edward Maginn (PI), Prof. Joan Brennecke (co-PI), Dr. Mark Muldoon (synthesis), Dr. JaNeill Dixon (synthesis), Dr. Haizhong Zhang (molecular modeling) and Ms. Jessica Anderson (property measurement).

Synthesis

The plan is to synthesize a diverse set of compounds during Phase I of the project. These compounds will be subjected to screening tests to determine their efficacy in removing CO_2 from flue gas, as well as their thermal stability. A diverse set of compounds is desirable, so that the chemical and structural factors responsible for good CO_2 solubility can be identified, and then exploited in subsequent synthesis efforts. We have made excellent progress so far, synthesizing or acquiring nine new ionic liquid compounds for testing. These are:

- 1-n-butyl-3-methylimidazolium acetate
- 1-n-butyl-3-methylimidazolium trifluoroacetate
- 1-n-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide
- 1-n-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate
- 1-butyl-3-methyl imidazolium 2-(2-methoxyethoxy)ethylsulfate
- Tetrabutylammonium bis(2-ethylhexyl) sulfosuccinate
- 1-methyl-3-(nonafluorohexyl)-imidazolium bis[(trifluoromethyl)sulfonyl]imide
- 1-methyl-3-tetreadecylfluorooctylimidazolium bis[(trifluoromethyl)sulfonyl]imide
- 1-n-butyl-3-methylimidazolium perfluoroctonate.

These compounds will be subjected to screening tests to assess their potential for CO_2 removal from flue gas.

Molecular Modeling

We have initiated ab initio calculations at the Hartree-Fock level of theory to gain insight into the nature of CO_2 interaction with ionic liquids. We have performed calculations of CO_2 interacting with different cations as well as cation / anion pairs in the gas phase. We

find that the interactions are complex, and involve multiple interactions between positively charged and negatively charged regions of the cation and anion. We find that CO_2 can associate with the oxygen and fluorine atoms of the bis[(trifluoromethyl)sulfonyl]imide anion as well as positive hydrogens on the cation, which may explain why CO_2 tends to be more soluble in ionic liquids with this anion. We will use the results of these calculations to suggest new compounds for synthesis.

Experimental

Synthesis and Characterization

The first step in the project was the identification of a broad range of compounds to be synthesized for Phase I. The strategy was to come up with a diversity of compounds so that the dependence of different aspects of the cation and anion on CO_2 solubility could be determined. In developing the list of Phase I compounds to synthesize, we relied upon our experience from previous work, as well as theoretical calculations (discussed below). A list of the compounds synthesized to date is given in the Results and Discussion section, along with references where synthetic details may be found.

Synthetic procedures varied depending on the type of ionic liquid to be made. The following basic procedure was followed for many of the compounds. First, the appropriate cation base material is reacted with a halide salt containing a desired constituent group. For example, if an imidazolium ionic liquid is desired, the appropriate imidazole is reacted with a salt containing a substituent group such as alkyl, fluoroalkyl, or aminoalkyl halide to form the imidazolium halide salt. Ion exchange with a salt or an acid then yields the desired IL. Washing with water removes unreacted organic halide and byproducts from the water immiscible ILs. The resulting compound is flowed through a column of alumina and/or activated carbon to remove trace impurities. The compound is then analyzed by NMR spectroscopy and elemental analysis. Halide impurities are measured using a chloride or bromide specific electrode after dilution in water. All samples are dried under vacuum at 70°C for 48 hrs and the water content measured using Karl-Fisher titration (EM Science AQUASTAR V-200). Water content is typically less than 1500 ppm for all ILs.

Physical Property Measurement

We have assembled the necessary equipment to make the physical property measurements required for the project. The particular property to be measured, its relevance, and the apparatus to be used are listed below.

Gas solubilities in pure ILs – Low Pressure

We will measure the solubility of CO_2, N_2, O_2, NO, NO_2, N_2O, and SO_2 in the pure ILs using a gravimetric microbalance. By obtaining isotherms at various temperatures between 10 and 70 °C, we will obtain Henry's law constants, needed to evaluate carrying capacity and gas selectivities, and enthalpies of absorption, needed to evaluate feasibility and energy requirements for regeneration. The microbalance (Hiden, IGA03) consists of a sample pan and counterweight, which have been symmetrically configured to minimize buoyancy effects (See Figures 1 and 2). The measurement procedure is as follows. A small sample of IL is added to the sample pan and the chamber is sealed. The sample is dried and degassed by evacuating the chamber to about 10^{-9} bar and heating to 75°C. Once the mass remained constant for at least 30 min, the sample is assumed to be free of

volatile contaminants. Then the temperature-controlled chamber is pressurized with the gas of interest using the static gas mode on the apparatus; the sample mass subsequently increases as gas absorbs into the sample. The weight change is monitored until the mass does not change significantly for at least 15 min, after which the sample is deemed to have reached equilibrium, thus yielding a single point on the absorption isotherm. This process gets repeated in steps up to a pressure of 13 bar. Following this, the process is reversed; the gas pressure above the sample is gradually reduced in a series of small desorption steps, during which the decrease in sample mass is recorded. Upon completion of this process, a complete absorption/desorption isotherm is obtained. After the completion of an absorption/desorption loop, the sample is dried and degassed and the mass compared with the initial mass to confirm that the ionic liquid did not volatilize or decompose during the run. The isotherm will be fit to a quadratic function, and the Henry's law constant determined from the limiting slope (i.e. the low pressure limit).

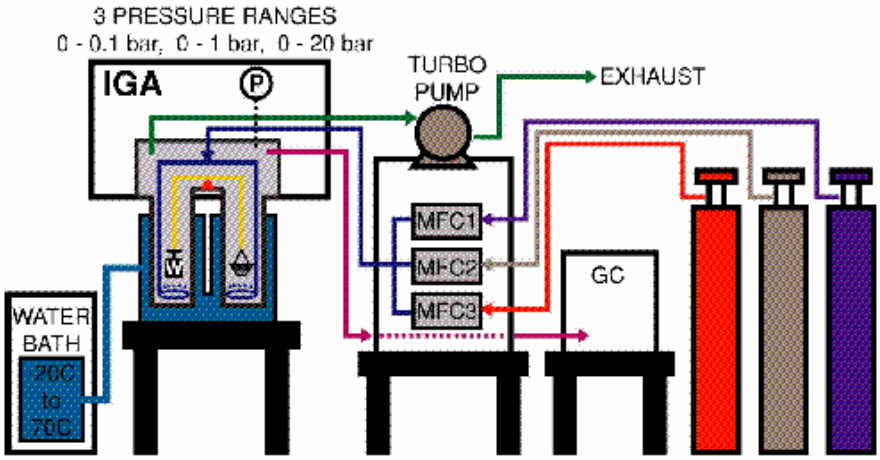


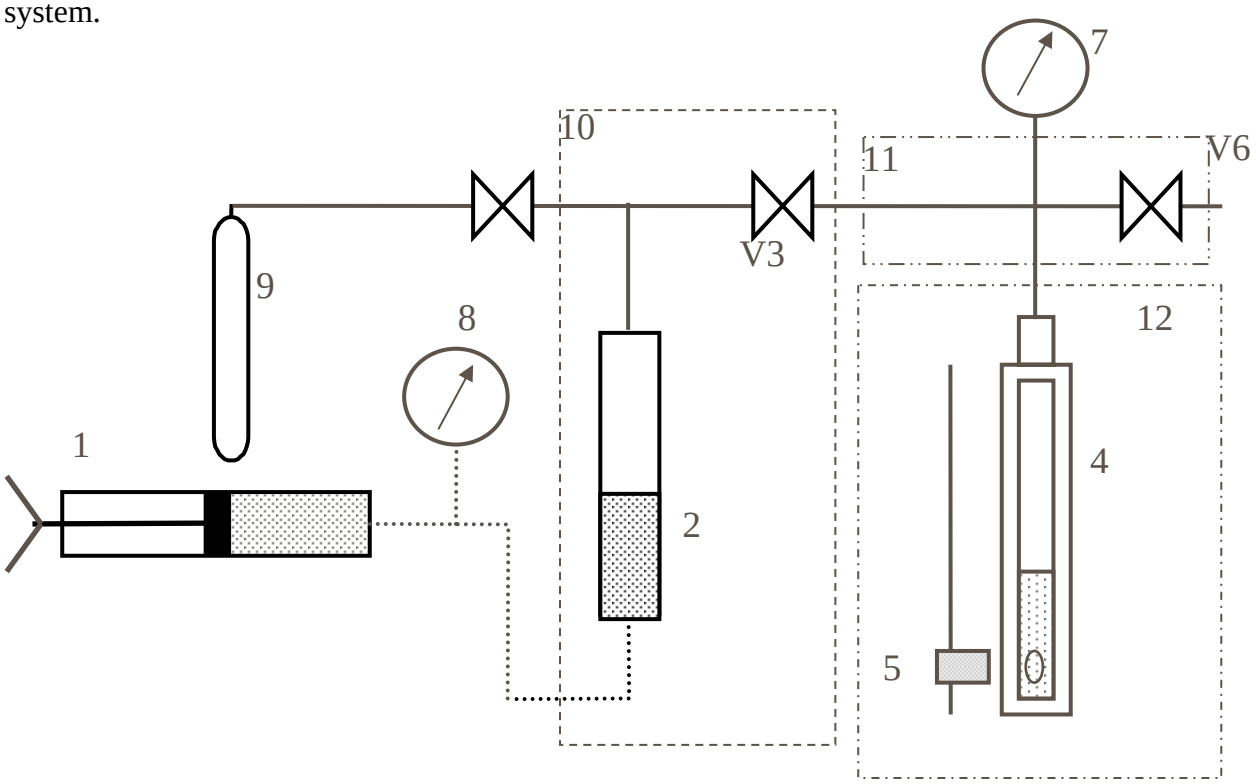
Figure 6: Schematic of the gravimetric microbalance to be used for low pressure gas solubility measurements.

Two factors are critical in performing these experiments. The first factor is to carefully account for buoyancy effects in the system. We will follow a procedure we developed in previous work with this microbalance (Macedonia et al., 2000). Proper buoyancy correction requires that accurate liquid densities be known. Thus, we will have to measure the density of each liquid we are interested in at each temperature. The second factor is to ensure that sufficient time is allowed for the system to reach equilibrium. We expect that many of the ionic liquid samples will be viscous, so the diffusion of gas into the liquid can be quite slow. A major advantage of using a microbalance for these measurements is that the weight change can be monitored as a function of time, which allows easy determination of the time necessary for equilibrium to be reached. The assurance of attaining equilibrium is important during the run as well as prior to the run to ensure the sample is sufficiently dried.

Figure 7: Picture of gravimetric microbalance.

CO_2 Solubility in ILs – High Pressure

We will also measure CO_2 solubility in the ILs at pressures above 13 bar using a high pressure apparatus, shown schematically in Figure 3. The apparatus consists of a feed system with a metering pump at a constant temperature and pressure and a sample chamber. In a typical experiment, a known amount of IL sample (~ 1.5 g) is loaded in a sapphire sample cell and the cell is connected to the sample chamber and brought to thermal equilibrium in a constant temperature water bath. A known amount of CO_2 is metered in to the sample cell and the sample is stirred until equilibrium is attained. The saturation pressure is measured using a Heise pressure gauge. The amount of gas dissolved is obtained by calculating the difference in the amount of gas delivered to the sample chamber and the gas present in the vapor phase using an equation of state. The solubility is measured as a function of pressure at a given temperature. Measurements to 100 bar are possible with this apparatus. We will only measure CO_2 solubility in this system.



1. Ruska Pump
2. Pressure Vessel
3. Main Valve
4. View Cell
5. Magnet
6. Vent Valve
7. Heise Transducer
8. Heise Gauge
9. CO_2 Reservoir
10. Air Bath
11. Heat Tape
12. Water Bath

Figure 3: Schematic of high pressure absorption apparatus.

Gas solubilities in IL/amine mixtures

We proposed to measure the solubility of CO_2 in actual mixtures of physical absorbent ILs and relatively low volatility amines. The goal of this strategy is to further increase the CO_2 carrying capacity of the sorbent, while retaining most of the favorable characteristics of the pure ILs. This may be an effective compromise between a physical absorbent, that is easily regenerated but doesn't have as a high a carrying capacity, and a chemical absorbent, that has high carrying capacity but requires tremendous amounts of energy for regeneration. These experiments will determine whether the solubility of CO_2 deviates from the expected linear combination of the CO_2 solubility in the IL and the amount of CO_2 that is known to complex with the amine. We cannot use the gravimetric microbalance for these measurements, since it requires full evacuation of the system (and subsequent evaporation of the amine) prior to the experimental run. Thus we plan to use the static, high pressure apparatus for these measurements.

Density Measurement

For accurate solubility measurements with the gravimetric system, we need the density to correct for buoyancy. These measurements will be made with a standard 1 ml pycnometer. By filling the pycnometer with the IL of interest and recording the mass, an accurate density may be obtained. The temperature of this system can be controlled to obtain density as a function of temperature.

Liquid-liquid equilibrium with water

Since ILs used for recovery of CO_2 from flue gases will become fully saturated with water, we plan to measure the liquid-liquid equilibrium of each of the ILs with water. Water content in the IL rich phase will be done by Karl-Fisher titration (EM Science AQUASTAR V-200) and IL present in the water rich phase will be done by UV-vis spectroscopy.

Heat capacities and decomposition temperatures

Constant pressure heat capacities (C_p) are needed to evaluate requirements for thermal regeneration of the absorbent. We will measure C_p of the pure and water-saturated ILs over the entire liquidus range, up to about 50 °C below the decomposition temperature in N_2, using a Mettler-Toledo (DSC822) differential scanning calorimeter. To provide limits for the C_p measurements and to gain an understanding of the usable operating range for each IL, we also plan to measure decomposition temperatures using a Mettler-Toledo (TGA/SDTA 851) thermal gravimetric analyzer. We will investigate stability in inert environments as well as in the presence of typical off gas mixtures. These instruments are assembled and ready for use.

Simulations

To gain an understanding of the way in which CO_2 associates with different ionic liquids, molecular simulations will be used. In the first part of the project, we have used first principles quantum mechanical calculations of gas phase cation / anions pairs with and without CO_2 to gain an understanding of the chemical interactions between these species.

Hartree-Fock calculations with a 6-31g(d) basis set were used in all the calculations. Partial charges were obtained using a CHELPG procedure (Morrow and Maginn, 2001). Later, we plan to develop classical condensed phase simulation techniques to directly compute gas solubilities in these systems. Most of our work in this area during the present reporting period has focused on the first principles calculations.

Results and Discussion

Synthesis

The following compounds have been made or acquired to date.

1-butyl-3-methylimidazolium acetate and trifluoroacetate (Figures 4 and 5) were synthesized by anion exchange of 1-butyl-3-methylimidazolium bromide with the appropriate silver salt following standard procedures (Aki et al., 2004, Bonhote et al., 1996).

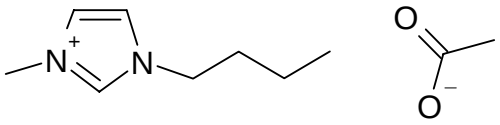


Figure 4: 1-n-butyl-3-methylimidazolium acetate.

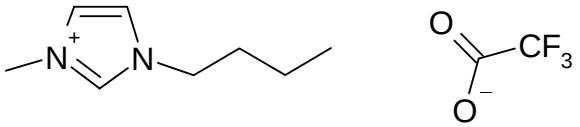


Figure 5: 1-n-butyl-3-methylimidazolium trifluoroacetate.

1-n-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (Figure 6) was made following literature procedures (Singh et al., 2002).

Figure 6: 1-n-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide.

1-n-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (Figure 7) was obtained from Merck KGaA (Germany).

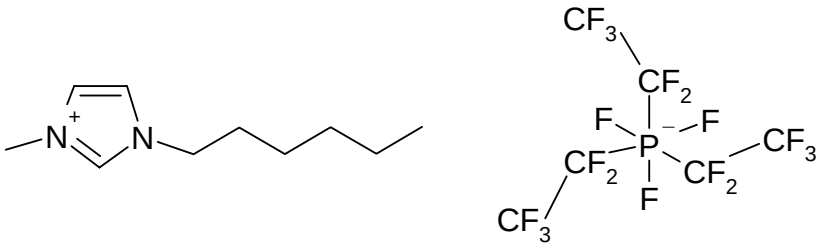


Figure 7: 1-n-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate.

1-n-butyl-3-methyl imidazolium 2-(2-methoxyethoxy)ethylsulfate) “Ecoeng 41 M” was obtained from Solvent Innovation GmbH (see Figure 8).

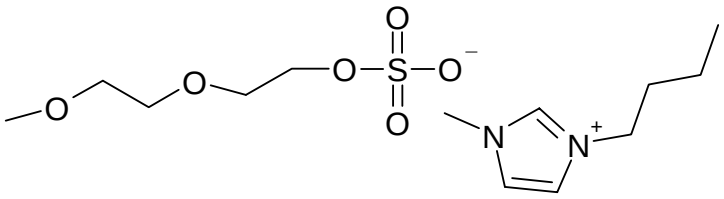


Figure 8: Ecoeng 41 (1-butyl-3-methyl imidazolium 2-(2-methoxyethoxy)ethylsulfate)).

Tetrabutylammonium bis(2-ethylhexyl) sulfosuccinate “docusate” was obtained from Sachem Inc (see Figure 9).

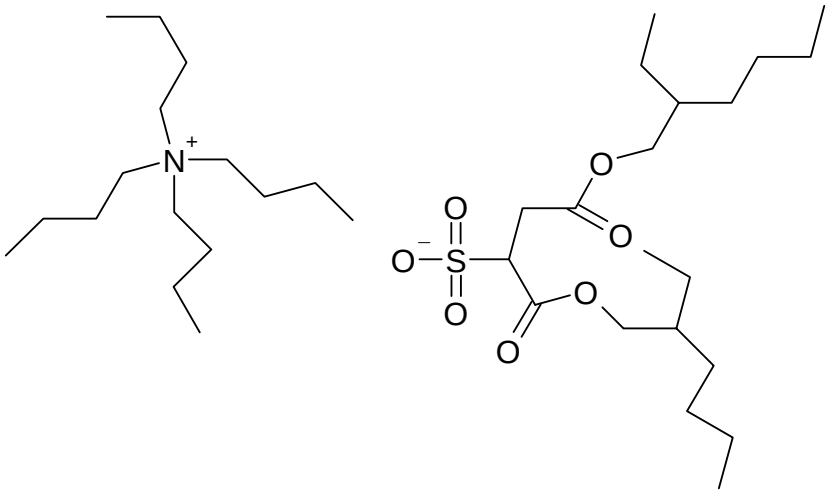


Figure 9: Tetrabutylammonium bis(2-ethylhexyl) sulfosuccinate.

1-methyl-3-(nonafluorohexyl)-imidazolium bis[(trifluoromethyl)sulfonyl]imide (Figure 10) was made following literature procedures (Singh et al., 2002).

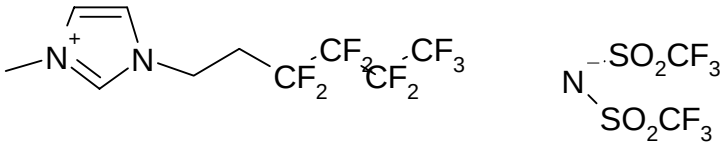


Figure 10: 1-methyl-3-(nonafluorohexyl)-imidazolium bis[(trifluoromethyl)sulfonyl]imide.

1-methyl-3-tetreadecylfluorooctylimidazolium bis[(trifluoromethyl)sulfonyl]imide and 1-n-butyl-3-methylimidazolium perfluoroctonate (Figures 11 and 12) were made following literature procedures (Singh et al., 2002).

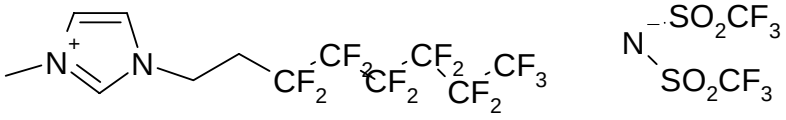


Figure 11: 1-methyl-3-tetreadecylfluorooctylimidazolium bis[(trifluoromethyl)sulfonyl]imide.

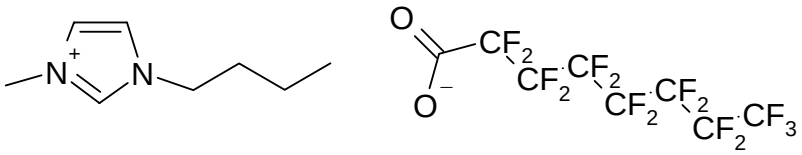


Figure 12:1-n-butyl-3-methylimidazolium perfluoroctonate.

Simulations

Quantum calculations were performed on CO_2 interacting with imidazolium, pyrollidinium, phosphonium and pyridinium-based cations. As an example, Figure 13 shows the lowest energy conformation of the 1-n-butyl-3-methylimidazolium with CO_2. Notice that the oxygen of CO_2 interacts strongly with the hydrogen on the 2-postion of the imidazolium ring. It is known that this hydrogen is the most acidic hydrogen, and the negative charge on the CO_2 oxygen is strongly attracted to it, as well as one of the hydrogens on the methyl group at the 3-position. When the alkyl group is fluorinated, we notice some subtle changes in the manner of association, as can be seen in Figure 14. Now the positively charged carbon atom of the CO_2 interacts with the electronegative fluorine atoms on the fluoroalkyl group.

The picture of association changes when the anion is present. Figure 15 shows the interaction of CO_2 with 1-n-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide. Now, the anion associates with the acidic hydrogen at the C2 position, mainly through the oxygen atoms on the anion. CO_2 positions itself to maximize favorable interactions between its negatively charged oxygen atoms and the positively charge hydrogens at the C4 and C5 positions on the imidazolium ring, and its

positively charged carbon with the free oxygens of the anion. This demonstrates that, in the condensed state, the interactions become a complex interplay among the different species. It suggests that one needs to consider the surface accessible to a cation – anion pair. An ideal IL would be one that offers CO_2 multiple binding sites, such as the bis[(trifluoromethyl)sulfonyl]imide does. This explains why this anion tends to show higher CO_2 solubility than small anions such as BF_4^-. We are using this insight in our efforts at coming up with new compounds to be synthesized and tested.

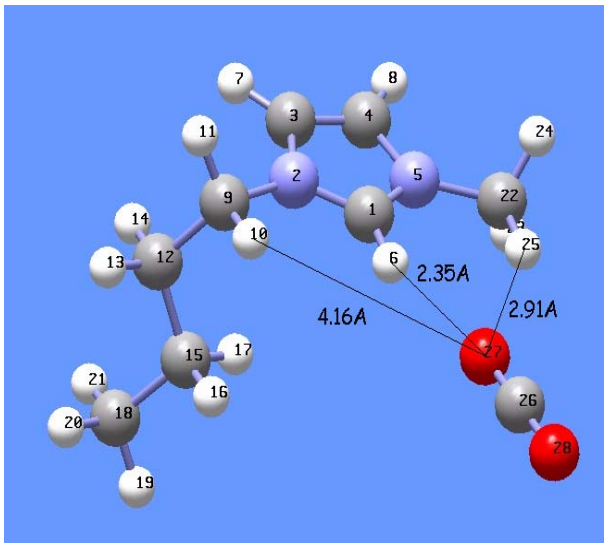


Figure 18: Interaction of CO_2 with 1-n-butyl-3-methylimidazolium cation.

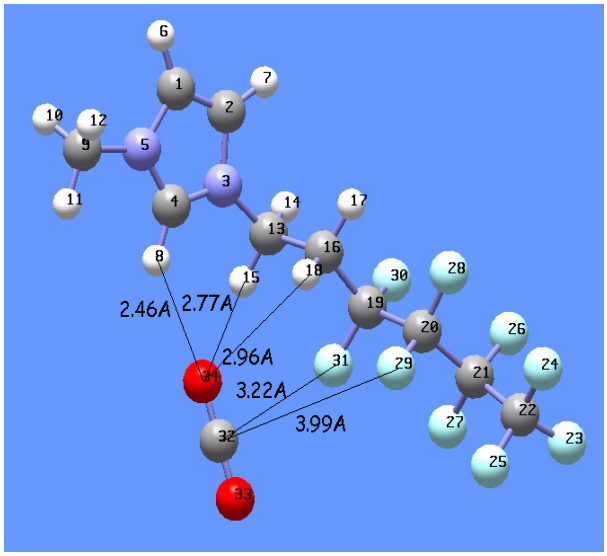


Figure 19: Interaction of CO_2 with 1-methyl-3-(nonafluorohexyl)-imidazolium cation.

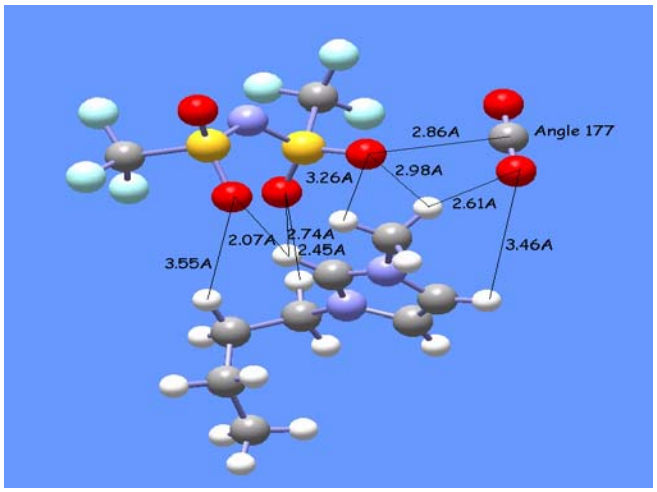


Figure 110: CO_2 interacting with 1-n-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide. Notice the multiple interactions between CO_2 and different sites on the cation and anion.

Conclusion

We have initiated a study aimed at developing an understanding of CO_2 solubility in ionic liquids. The project involves synthesis of new compounds, experimental measurement of physical properties relevant to application of these liquids in CO_2 sequestration efforts, and molecular modeling. The goal is to develop ionic liquids that can be more effective (technically and economically) than conventional absorbents such as amines. We have much of the equipment in place and have initiated synthesis efforts. Already, nine new ionic liquids have been synthesized or acquired. These compounds will be tested for CO_2 solubility, as well as thermal stability and other physical properties. Several other compounds will be made and tested in the initial phase of the project. Molecular modeling in conjunction with these experimental tests will be used to gain insight into the factors governing CO_2 solubility, and this insight will be used to guide future synthesis efforts.

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